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# EDITORIALS

## Righteous Victory

"FINDING no ground upon which the sale of enemy property to the defendant may be set aside, the bill of complaint must be dismissed." Thus reads the last paragraph in a twenty thousand word opinion dated January 3, 1924, signed by Hugh M. Morris, Jr., and handed down in the widely advertised case of the United States of America *vs.* the Chemical Foundation, Inc. The trial was held at Wilmington last summer and lasted thirty-three days.

It is doubtful whether there has ever been a case of such importance to chemistry, and we regret that the demands upon our space make it impossible to reprint this decision in full. Certainly there could be no decision clearer in its emphasis that the contentions of the Government have not been sustained, that the assertions of the defendant have been truthful, and that the acts of the Foundation have been performed in good faith and are fully justified. However, certain quotations from the decision will be given here, because there appears to have been some confusion in the minds of a few chemists as to whether, after all, they could give their support to the Foundation's cause without reservation.

The bill of complaint charges that the seizure and sales of the property in suit were induced, brought about, and accomplished by and through a combination, scheme, and conspiracy of certain representatives of the chemical and dye industries.***

At the opening of the trial the court announced that each party to the suit would be permitted, without regard to the usual rules of evidence, to take and put of record all evidence that, in the opinion of its counsel, would in any manner tend to prove or disprove any issue of the case. Notwithstanding the generality of the allegations and the unlimited opportunity afforded the plaintiff to support them by evidence, the charges of deception and conspiracy have failed utterly.

The opinion then recites as an illustration of this point a part of the testimony of the present Alien Property Custodian, wherein the contrast between the allegations and the proof is emphasized. With further reference to this matter, the court says, regarding the plaintiff: "Its allegations and evidence with respect to conspiracy and deception do not advance the plaintiff towards the goal for which it strives."

There has been much discussion as to whether Mr. Garvan, as the alien property custodian, sold the German patents to Mr. Garvan, president of the Chemical Foundation. This has been argued so frequently that we quote extensively from the opinion.

The plaintiff contends that the assignments made by Mr. Garvan as alien property custodian to the defendant are invalid for the further reason that at the time of making the assignments Mr. Garvan was its president. Prior to Mr. Palmer's resignation as alien property custodian he caused the organization of the defendant "for the purpose of diverting these German chemical patents into general public use for the benefit of this country." The terms and conditions of sale had been agreed upon. To make certain that all the purposes for the consummation of which the defendant was organized would be carried out not only in the letter but in the spirit in which they were conceived, Mr. Palmer made it a condition that the officers of the defendant should be persons named by him. Mr. Garvan who had been particularly and intimately associated with the work of investigating the German hold upon the chemical industry in America, and in evolving the plan to be carried out through the instrumentality of the defendant, and who "was more familiar with this situation than anybody in the country," was selected by Mr. Palmer to be the president of the defendant.

Mr. Garvan agreed to accept. Mr. Palmer was then appointed attorney general of the United States. Late in the afternoon of March 3, 1919, he called upon the President of the United States to present his resignation as alien property custodian and to urge the immediate appointment of his successor. The sale of the property to the defendant was discussed. The President was told the facts above narrated. Mr. Palmer stated to the President that he considered the actual consummation of the Americanization of the German chemical patents was the most important constructive work that "we had on hand."

Mr. Palmer urged Mr. Garvan's appointment as custodian, and said ***:

"My purpose in urging Mr. Garvan's appointment as alien property custodian was quite largely in view of the fact that he had undertaken to be the president of this corporation, and I knew he could be absolutely trusted to carry out its plans and purposes to the letter and in their full spirit. I would not have felt so safe in putting this plan over if I had not been able to pick out from my organization men of that kind who could and would operate it not only as we wanted it to be run, but with a patriotic desire to serve their country." Mr. Palmer had with him the commission in blank as alien property custodian, and after Mr. Palmer's statement the President took the commission and wrote in the name of Francis P. Garvan. Mr. Palmer delivered it to Mr. Garvan that evening. Mr. Garvan took the oath of office the next day. He became president of the defendant on March 8. With the exception of the two assignments executed by the present custodian, all the assignments to the defendant were executed by Mr. Garvan as custodian. Plaintiff's present contention rests upon section 41 of the criminal code of the United States, which provides: "No officer or agent of any corporation, joint stock company, or association, and no member or agent of any firm, or person directly or indirectly interested in the pecuniary profits or contracts of such corporations, joint stock company, association, or firm shall be employed or shall act as an officer or agent of the United States for the transaction of business with such corporation, joint stock company, association or firm. Whoever shall violate the provision of this section shall be fined not more than $2000 and imprisoned not more than two years." The first paragraph of section 7(e) of the Trading-with-the-Enemy Act provides, however, that "No person shall be held liable in any court for or in respect to anything done or omitted in pursuance of any order, rule or regulation made by the President under the authority of this Act."

On the question of whether the alien property custodian was a common law trustee, the court holds that the custodian acted, not in a capacity as a common law trustee, but under the extraordinary powers devolving upon him as the President's representative under the amendments to the Act to which reference has been made. The trust created "was constituted for the benefit of the nation and the public at large. It was a public, not a private trust." Congress having granted to the President, and through him to his representatives, powers as broad as those of an absolute owner:

The trustee is the judge and, in the absence of fraud, the sole and exclusive judge of the rank and priority to which each of the divers demands is entitled.*** If, in his judgment, the widespread use of the trust property would tend to advance the safety of the nation, the health of its citizens, or the permanence of peace, the property may, in its disposition, be devoted to the public use even though thereby its monetary value for purposes of sale would be substantially destroyed. Such powers are, in truth, broad. But they were granted in the public interest in time of war by Congress, in the exercise of its war powers, to him who, by virtue of his office, knows "the state of the Union" and is Commander-in-Chief of its Army and Navy.

With respect to the Government's contention that the sales were tantamount to confiscation in violation of the law of nations, Judge Morris quoted at length from Supreme Court decisions leading to the following conclusions:

Any property which the enemy can use or which the adherents of the enemy have the power of devoting to the enemy's use is a proper subject of confiscation. Yet while the right of the nation

to confiscate enemy property is absolute, the extent to which that right shall be exercised during any particular war is a matter of policy to be determined solely by Congress in the passage of its war measures. Courts may inquire whether an act passed by Congress is within the scope of its constitutional power. Beyond this they may not go. The scope of judicial inquiry does not extend to a review of legislative *policy*. Whether a legislative act is wise or unwise, whether it is based on sound theory or principle, are matters solely for the judgment of Congress. Such matters are not within the range of judicial cognizance.

In speaking of the value of the patents sold, Judge Morris held that, while Dr. Carl Holderman, a German, asserted the Haber patents were worth $17,000,000 to the Germans:

The evidence is overwhelming that the Haber process patents were and are without substantial affirmative value to American citizens. Had those patents been sold to American citizens at public sale instead of at private sale and only the net proceeds of such sale paid to their former enemy owners those owners would have suffered an almost total loss in the value of their property. ***
By the Treaty of Berlin, Germany gave to the United States and the United States accepted the benefits of the Treaty of Versailles. *** By *** the treaty, Germany undertook to compensate her nationals in respect of the sale or retention of their property, rights or interests in allied or associated States. Manifestly all claims of Germany and Germany's nationals to the property in suit are barred.

Another much discussed subject is whether the sale was made at a fair value, the plaintiff having argued that the transaction was in effect the granting of a subsidy to private industry, that the price paid was obviously unfair, and therefore that the sale should be set aside. On this the court states:

This challenge of the motives of the officers making the sale is supported, I think, neither by the facts nor by the law. *** Mr. Polk *** determined that "the public interest will be best served by a wide use of the inventions covered by said letters, patents and similar rights."*** If the property was sold under such terms and conditions as to assure its being devoted to the public use, it matters not what benefits or detriments may have flowed as incidents therefrom.
The property is in the keeping of men who have in its management no selfish interest to serve and whose devotion to the public interest has been established. No better plan for devoting the property to the public use has been suggested. The plan has stood the most severe of all tests—actual trial. The defendant has kept the faith. This it has done, not only by granting licenses in furtherance of the purpose for which defendant was chartered, but also, at its great expense, by the distribution of books and pamphlets showing the national necessity for the practical development of chemical science in America. If, perchance, those heretofore engaged in the chemical and allied industries have derived an incidental advantage from the plan, that incidental result cannot invalidate a transaction lawfully consummated in the public interest. The same charge would lie against the validity of every tariff act. *** The sale was, in effect, a sale to America and its citizens, not to persons then engaged in chemical and allied industries.

The decision of the court, namely, that Mr. Garvan acted by the direction of President Wilson and that his acts, supervised by the President under the wide war powers granted by Congress, could not be brought to court is one of the most important. It would seem clear that the courts cannot pass judgment on the wisdom or lack of wisdom of the acts of a President in time of war, it being reasonable to assume that in such emergencies he will have information as to the needs of the Nation not possessed by other individuals.

The *New York Times*, in its issue of January 5, begins its leading editorial with this statement:

No one can have been surprised by the decision of Judge Morris of the Federal Court at Wilmington, Del., in the case of the Government against the Chemical Foundation. The result was foregone in the mind of any one who had followed the trial. The Government's case broke down at nearly every point. Its charges of "conspiracy" had been so loosely framed, on a sort of drag-net theory, that several of them were withdrawn in the course of the trial. The rest of them are swept aside by the decision of Judge Morris, who holds that they had no foundation either in fact or law. The breakdown of this Government prosecution is, in fact, so complete that, although it is announced that an appeal will be taken, and the matter finally got before the Supreme Court of the United States, it is improbable that it can ever be pushed to a successful conclusion. Certainly it cannot along the original lines of indictment and argument. The case goes on the list—already too long—of the court failures of the Department of Justice under the present Attorney General.

The leading editorial in the *Journal of Commerce* of the same day begins as follows:

In handing down a decision adverse to the Government in the so-called "Chemical Foundation" case Judge Morris of the Federal District Court at Wilmington has administered a well-merited rebuke. The facts in the situation are complex and involve elaborate technical discussion, but the general issue is sufficiently clear for common understanding.

The editorial concludes an interesting discussion of the case and the actions of which it is typical with this statement:

Will President Coolidge rectify the conditions which now exist in Washington and absolutely forbid the use of our machinery of prosecution and investigation save in those cases where it is obviously appropriate?

It is always gratifying to be on the winning side, but it is far better to be on the right side. The AMERICAN CHEMICAL SOCIETY has much of which it can be proud in its uniform support of the Chemical Foundation from the very inception of the Foundation itself. There has been no hesitation on the part of the SOCIETY in standing squarely behind the Chemical Foundation and those gentlemen who have made this organization possible and who, fortunately, have been in position to make a defense which an organization less favorably placed could not have furnished. Indeed, chemistry in America owes a debt of gratitude to the group of men who have willingly and without hesitation given much of their time and personal fortune to the cause of chemistry in America. This assistance, apparently unobtainable from any other quarter, came at a time when without such support our industry might have been annihilated in its developmental stage. The thoroughness with which the attorneys for the defense prepared their case, the masterful way in which it was presented, and their alertness in cross-examination and the argument of points at law deserve high praise.

It must not be supposed that this is the end of the fight for an American chemical industry. Comments in the daily press indicate the hope of our former enemies that higher courts may reverse this decision. The progress made by our synthetic organic chemical industry is such as to make us a competitor in world business. This is highly distasteful to our erstwhile enemies, who will continue attempts to re-establish their former world monopoly. Announcements are made that an immediate appeal will be taken and time will pass while the case drags its way through the labyrinths leading to the Supreme Court. We are just as confident of ultimate victory as the Attorney General is reported to be. As taxpayers we are not so interested in this continual expense undertaken by the Attorney General. When one thinks what could be done merely with the income on the cost of the trial thus far to all parties concerned, it seems a pity that approximately $500,000 has thus been wasted. The Government having been given free opportunity to prove its contentions and having so completely failed, has the time not come when we, as taxpayers, can call upon the President to apply the administration's policy of economy, accept defeat, and allow the chemical industry to proceed without the degree of uncertainty which must continue until it is known that we are through with trials?

# Interdepartmental Patents Board

A FEW years ago a bill was introduced in Congress which sought to empower the Federal Trade Commission or some other organized group to develop patents resulting from work in Government laboratories so that they might be licensed and the waste in ideas which now results thereby avoided. There was a great deal of opposition to this plan and the bill failed to pass, but as a result of the discussions that ensued there was created an Interdepartmental Patents Board composed of representatives of the Departments of War, Commerce, Agriculture, Justice, and the Interior, to consider what might be done to remedy the situation. This board has thoroughly investigated all phases of the question, including the legal status, and has found several important questions which bear upon the accustomed procedure of assigning patents to the public. Thus a patent is really a form of property, and since Government property cannot be disposed of without the authority of Congress, it may be questioned whether the Government in the absence of legislative sanction has the right to dispose of a patent owned by it, either by license or by outright sale.

An improvement in the situation requires consideration of the fact that a Government employee, like the employee of any corporation, is entitled to his patents, even though they are developed on the time of his employer, unless there is a contract between the employer and himself which requires him to assign his patents to the employer. Some of the patents which might result from work in Government departments have no relation to national defense, do not involve the public interest to the extent which requires them to be kept secret, and may be those in which the Government desires merely a shop right. In rare instances patentable ideas, though not directly related to the work in hand, may be developed in the course of pure research. It seems reasonable, therefore, to create a board through which all questions pertaining to patents now owned by the Government or those which may be developed in future may be cleared and decisions reached as to whether they should be filed in a secret file for obvious reasons, taken over by the Government, or released to the inventor. There has never been a uniform departmental policy with respect to inventions, and there have been many misunderstandings and much embarrassment as a result. Frequently, valuable ideas have been lost because there has been no patent policy and the obstacles to the development of the inventor's idea have been so great as to discourage him completely. On the other hand, while the Government cannot be sued for infringing a patent, the patentee may file a claim against the United States in the Court of Claims, and it is estimated that such claims now pending against the United States in the various courts total approximately $1,000,000,000.

Two bills have been introduced which seek to correct the present unsatisfactory condition. One of these provides that:

The President, or such person or agency as he may designate, shall, whenever the publication of any invention by the granting of a patent would, in his opinion, or in the opinion of the said designated person or agent, be prejudicial to the national defense, order that the patent be sealed and kept in a secret file until released by order of the President or the said designated person or agency.

Suitable provision is made for handling cases where the patentee objects, and for other details.

The other bill would establish an Interdepartmental Patents Board, the duties of said board to be:

1—To act as sole agency through which all patents and patent rights hereafter conveyed to the Government shall be acquired, and to have custody of the records of, and to control and administer on behalf of the Government the right, title, and interest in and to all patents and patent rights owned by the Government,

provided that the title to any patent or patent right otherwise acquired by the United States shall not be invalid for that reason.

2—To issue nonexclusive licenses under patents owned by the United States to such individuals, firms or corporations, and on such terms, as may in the said Board's judgment be in the public interest. Any moneys received in respect of licenses granted hereunder shall be covered into the Treasury under the head of "Miscellaneous Receipts."

3—To keep a record of all patent applications and unexpired patents of government employees, and rights therein or incident thereto; and it shall be the duty of all government employees to register with the said Interdepartmental Patents Board, in such manner as the Board shall direct, all applications for patents they may make and all patents that may be granted to them, individually or collectively, on any invention discovered or developed during the period of their employment in the Government Service.

4—It is hereby expressly made a part of the terms of employment of any government employee, having the effect of a contract, that any patent application hereafter made or patent granted appertaining to any invention discovered or developed during the period of his government employment and incident to the line of his official duties which in the judgment of the said Board should in the interest of the national defense, or otherwise in the public interest, be controlled by the Government, shall upon demand by said Board be assigned by said employee to the Government.

Both these bills deserve careful consideration and a full expression of opinion. It is agreed that present conditions must be improved. Does the present procedure promise the relief desired?

# Easy Money

SCIENTISTS will have difficulty in appreciating the point of view of those who are enthusiastic over the award of the much advertised peace plan prize. Some enthusiasts for the League of Nations, state that merely causing the public again to engage in discussing the old issue is an accomplishment of such importance that the peace plan contest must be called a success. Others, equally zealous for the success of the League of Nations, interpret the plan as emasculating the League, killing any chance for the world court because it seeks to connect it with the League, and then urging the United States to enter what is left because it is perfectly harmless. One paragrapher offers this comment:

Mr. Bok discloses how the easiest $50,000 ever earned has been grabbed off by an anonymous genius who conceives the brilliant idea of sneaking into the League of Nations through the coal hole. It is, indeed, a satisfying thought that the peace plan promoters had to read 22,165 mss. before they found one written by a man who was asleep when the 1920 elections were held. As for safeguarding the Monroe Doctrine, we can continue to leave that to the Army and Navy—if we don't sell 'em to Mexico.

Chemists, who realize better than other folks that the manufacture of nearly any chemical could be interpreted under modern conditions as producing munitions of war, will be somewhat amazed to find that the prohibition of the manufacture of materials for munitions of war is demanded.

Whatever the view may be with regard to the League of Nations or the winning plan, it will occur to scientists that in their field the award of such a substantial and generous prize is always made for an outstanding discovery, for something new and unique, something which distinguishes the recipient from his fellows, for a brilliant conception, a piece of difficult research well conceived and carried out, or for a contribution to his science which can be interpreted in terms of promoting human welfare.

To have $50,000 (or will it be $100,000) awarded for the presentation of essentially old material is something scientists will not comprehend. Fancy awarding the American Chemical Prize of $25,000 to one who had written a summary of the theories of phlogiston!

# The Physical Properties of the Paraffin Hydrocarbons[1]

## By Robert E. Wilson and W. H. Bahlke

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THE value of a complete set of data on the physical properties of the normal paraffin hydrocarbons has warranted a rather thorough survey of the literature on this subject, from which a critical compilation of the best available data has been made. In many cases where observed data are not obtainable the missing figures have been calculated or extrapolated by such means (generally thermodynamical) as seemed most reliable in the judgment of the writers. In all cases the method has been given in detail, so that where additional data are desired they may be calculated or further extrapolated by similar means. In several cases a few of the experimental values are obviously wrong, and in such cases these values have been plotted, but disregarded in drawing the best representative curves. Since the results are to be used primarily by the oil industry, practical English units are used in presenting all the final results.

In using the extrapolated data for temperatures above 700° F. the thermal instability of all hydrocarbons must, of course, be kept in mind. While most of the figures above this point are therefore fictitious from a practical standpoint, the extrapolated critical data, etc., are presented because of their value in calculating various constants at lower temperatures.

*This paper compiles data from various sources in the literature on the vapor pressures, heats of vaporization, densities, critical constants, and specific heats of the normal paraffin hydrocarbons. These data are then treated theoretically with the aid of thermodynamics, the laws of corresponding states, and similar relationships, to choose between discrepant data, to fill in gaps, and to extrapolate to higher temperatures and to compounds of higher molecular weight. This results in giving a fairly complete set of approximate values for the more important physical constants for all the hydrocarbons from butane to tetracosane. The method of applying these results to actual refinery cuts is also discussed.*

### Vapor Pressure Data

The recommended vapor pressure curves for the normal paraffins from *n*-pentane to *n*-tetracosane, inclusive, are shown in Fig. 1, where the logarithm of the pressure in millimeters is plotted against the logarithm of the absolute temperature (degrees Kelvin). For convenience, additional temperature and pressure scales have been added, giving temperature in degrees Fahrenheit and pressure in pounds per square inch (gage pressure) above the normal boiling point and in millimeters at lower pressures. The experimental data corresponding with the circled points of this figure are taken from Beilstein (Vol. I) except for the four compounds, pentane, hexane, heptane, and octane, for which the data of Young[2] were used, and butane, for which the measurements of Burrell and Robertson and Siebert and Burrell were used.[3]

The method of plotting log *p* versus log *T* was adopted in order to make use of a very important generalization recently demonstrated by Hildebrand.[4]

Trouton's rule states that the molal entropy of vaporization (discussed later) is the same for all normal liquids at their boiling points, and the approximate Clausius-Clapeyron equation (also discussed later) states that $\dfrac{d \log p}{d \log T}$, or the slope of the vapor pressure curves in Fig. 1, is directly proportional to this molal entropy of vaporization. If both

these laws held accurately, the slope of the curves in Fig. 1 would be the same for all substances at their boiling points, and presumably along other lines of equal pressure, though the magnitude of the slope would, of course, change with the pressure.

Actually, owing to deviations from the perfect gas laws and other causes, this generalization is far from being true, especially for liquids boiling much outside the ordinary range of temperature. Hildebrand has suggested, however, that such a generalization might have much wider application if the comparisons between different liquids were made under conditions such that the mean distance between the molecules of the vapor was the same. Under these conditions deviations from the perfect gas law should be similar for the different substances. In other words, the slopes of the vapor pressure curve should be the same, not at the same pressures, but at equal vapor concentrations, or at corresponding values of

$$\frac{N}{v} = \frac{p}{RT}$$

where　$N$ = number of mols of vapor
　　　　$v$ = volume of vapor
　　　　$p$ = pressure of vapor
　　　　$T$ = temperature of vapor
　　　　$R$ = gas constant

Referring to Fig. 1, this ratio $\dfrac{p}{T}$ will be constant along lines of unit slope, the equation of which is

$$\log p - \log T = \log \frac{p}{T} = \text{constant}$$

According to Hildebrand, then, wherever any given one of these lines of unit slope intersects a vapor pressure curve, the slope of the latter should be the same for any (normal or nonassociated) liquid.

Since these lines of unit slope may be drawn at infinitesimal distances apart, it follows that, if the rule holds, any two vapor pressure curves must be parallel in the sense that the distance between the curves along any of the constant composition lines should be the same. Actually, Hildebrand has shown this to be approximately true for practically all liquids (except highly associated liquids such as water) on which good vapor pressure data are available.

If this generalization were rigidly true, it should be possible to construct all vapor pressure curves from a single complete one, given only *a single point* on each of the other curves to determine the distance between them along a line of unit slope. Since the method gives surprisingly good checks, even for such dissimilar substances as oxygen, hexane, and zinc, it should certainly be expected to hold with reasonable accuracy for a homologous series of compounds such as the paraffins, at least up to reasonably high pressures. However, in spite of this presumption of accuracy, it was not considered desirable to place entire reliance on any theory, but rather to use Hildebrand's method of representation as a basis for studying the deviations between all the observed data and the

[1] Received November 24, 1923.
[2] *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).
[3] *J. Am. Chem. Soc.*, **37**, 2188, 2683 (1915).
[4] *Ibid.*, **37**, 970 (1915).

Fig. 1.
Log Vapor Pressure
vs.
Log Temperature
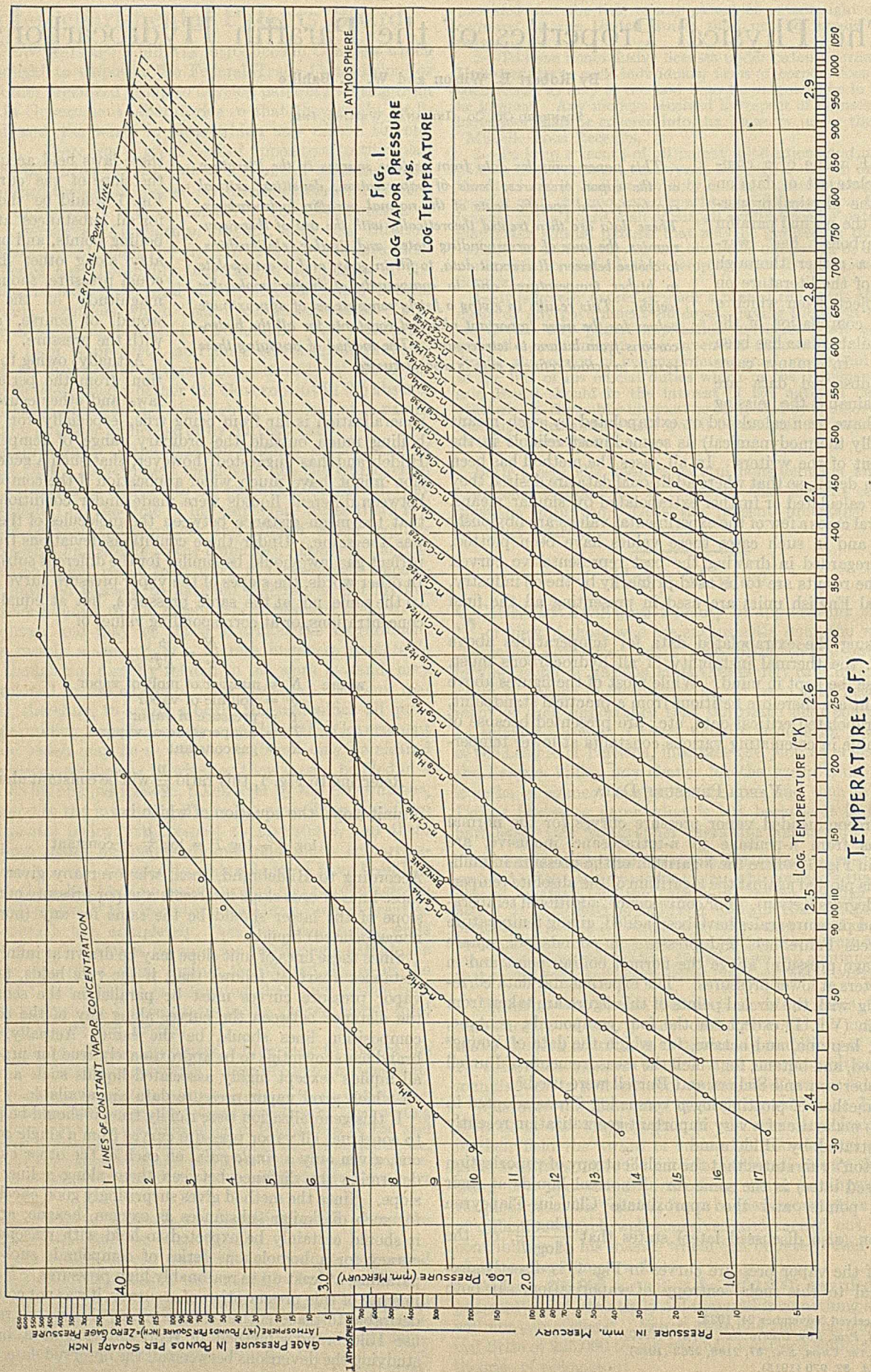
predictions drawn from the theory. If deviations did occur, they should certainly be small and systematic, and errors in individual observations should be shown up very quickly. By drawing deviation plots it should then be possible to extrapolate and interpolate with a relatively high degree of accuracy.

The accurate vapor pressure data of Young for pentane, hexane, heptane, and octane afford an opportunity to study the reliability of Hildebrand's relationship and the deviations therefrom over a very wide range of temperatures and pressures. These data were accordingly plotted on a large-scale log-log plot similar to Fig. 1, together with all available data on the boiling points at atmospheric and reduced pressures for the higher members of the paraffin series.

The best representative vapor pressure curves were then drawn through these points, as well as a series of lines of unit slope (see above). As pointed out above, the distance between two adjacent curves should be the same along all these lines if Hildebrand's equation held. Instead of assuming this, however, the curves were originally drawn on the basis of the experimental data alone, and then the distance between the curves along each line was measured. It was found that the distances along the different lines were not identical, but that the deviations were small and apparently systematic. This can best be seen by plotting the distance from one vapor pressure curve to the next along some line of unit slope against the number of carbon atoms.

Selecting unit slope lines Nos. 4, 9, and 16 as the basis of measurement, the results are plotted in Fig. 2 on semi-log paper. It should be kept in mind that if one vapor pressure curve is slightly misplaced it would tend to make one distance too short and the next distance too long, and most of the deviations which show up in Fig. 2 are of this nature. As a whole, it appears that the points tend to fall on a smooth curve which merges into a straight line beyond ten carbon atoms. It appears, however, that the distances along each line of unit slope are not exactly the same, but tend to increase gradually toward the lower pressures. This difference seems to be slightly accentuated as the number of carbon atoms increases. The maximum deviation between the distances along line 9 and line 16 is, however, surprisingly small, considering the wide range of pressures covered.



FIG. 2

DEVIATIONS FROM HILDEBRAND'S RELATIONSHIP
DISTANCES ALONG CONST. COMP. LINE 16 - △
DISTANCES ALONG CONST. COMP. LINE 9 - ○
DISTANCES ALONG CONST. COMP. LINE 4 - ☐

The vapor pressure curves on Fig. 1 were accordingly constructed by using the Hildebrand relationship corrected as indicated by Fig. 2. All distances were measured from the experimental curve for octane, which is undoubtedly very reliable. In spite of the fact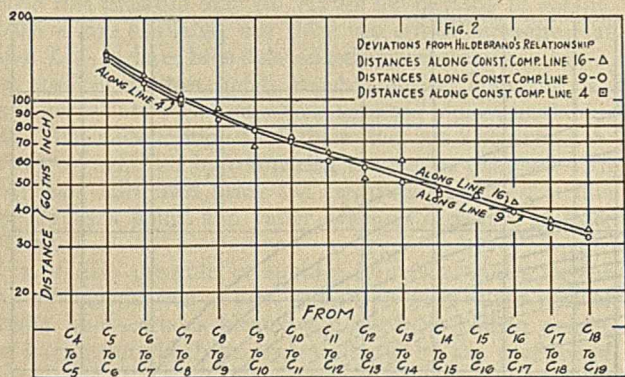 that all the other curves on Fig. 1 are thus calculated from a single one plus the smooth curves in Fig. 2, when all the observed data from the literature were plotted on the same figure it was found that the agreement was quite as good as could be expected. The only serious discrepancies are in the case of butane, where no smooth curve could fit the rather discordant data, and in the case of some of the higher hydrocarbons at low pressures

(10 to 20 mm.) where observations are likely to be rather inaccurate.

It is certain that the system of lines thus drawn is much more accurate than could have been obtained by attempting to draw lines precisely through the individual observed points, some of which are obviously in error. It also gives a reliable means for extrapolating the vapor pressure curves for the hydrocarbons above octane to pressures between one atmosphere and the critical points, in which region no data whatever appear to be available. The critical points are discussed in a later section.

### HEATS OF VAPORIZATION

For pure compounds the heat of vaporization may be calculated by a number of different equations, most of which agree fairly well with the observed values. However, each equation has its own particular use, depending upon the type of data available or the class of liquids to which the equation is to be applied. The writers have made a study of a number of equations in order to determine which should be used for paraffin hydrocarbons.[*]

In the equations given below the following symbols have been used:

$L$ = latent heat of vaporization
$M$ = molecular weight
$T$ = absolute temperature
$p$ = vapor pressure of the liquid
$V_l$ = volume of 1 mol of the liquid
$V_v$ = volume of 1 mol of the vapor
$P_c$ = critical pressure
$R$ = gas constant

1—The simplest expression which permits the calculation of the heat of vaporization is *Trouton's rule:*

$$\frac{ML}{T} = \text{constant} = 20.5 \qquad (1)$$

The expression $\frac{ML}{T}$ represents the *molal entropy of vaporization* at the normal boiling point and its approximate constancy was pointed out by Trouton as an empirical relationship.

2—Another expression is that deduced by *Clapeyron* on the basis of the first and second laws of thermodynamics, and is

$$\frac{dp}{dT} = \frac{L}{T(V_v - V_l)} \qquad (2)$$

Where accurate data as to the vapor pressure curve and the specific volumes of liquid and vapor are obtainable, this equation is unquestionably reliable. Indeed, its accuracy has been demonstrated by Mills[5] using the data of Young on pentane, hexane, heptane, and octane. Unfortunately, however, accurate data as to the specific volume of the vapor are seldom available.

3—Equation 2 can be modified to eliminate the specific volume terms by assuming that the saturated vapors obey the perfect gas law and that $V_l$ is negligible compared with $V_v$. The equation then takes the form

$$\frac{-d \ln p}{d\left(\frac{1}{T}\right)} = \frac{ML}{R} \qquad (3)$$

According to this *modified Clapeyron equation* the heat of vaporization can be calculated from the slope of the line obtained by plotting log $p$ against $\frac{1}{T}$. This equation is frequently used, but it must be remembered that, on account of the foregoing assumptions, deviations must be large for the higher hydrocarbons or for any hydrocarbon at high pressures.

4—*Nernst,*[6] by combining the Clapeyron equation with an empirical one of his own involving critical data, has developed the expression

$$ML = R \frac{T_1 T_2}{T_1 - T_2}\left(1 - \frac{p}{P}\right)\ln \frac{p_1}{p_2} \qquad (4)$$

$T_1$ and $T_2$ are two temperatures not far apart, say 20° C., and $p_1$ and $p_2$ are the vapor pressures at these two temperatures;

[5] *J. Am. Chem. Soc.*, **31**, 1099 (1909).
[6] "Theoretical Chemistry," **1916**, p. 295, *translated* by Tizard.

Table I—Latent Heats of Vaporization in B. t. u. per Pound

| Compound | Calcd. by Trouton's Rule | Deviation from Observed % | Calcd. by Clapeyron Equation | Deviation from Observed % | Calcd. by Modified Clapeyron Equation | Deviation from Observed % | Calcd. by Nernst Equation | Deviation from Observed % | Calcd. by Hildebrand Method | Deviation from Observed % | Observed | Observer |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pentane | 158.4 | +4.4 | 153.0 | +0.85 | 165.8 | +9.3 | 154.26 | +1.69 | 152.8 | +0.73 | 151.7 | Young |
| Hexane | 146.3 | +0.82 | 142.9 | −1.51 | 156.6 | +9.4 | 150.8 | +3.92 | 144.0 | −0.76 | { 147.4 | Tyrer |
|  |  |  |  |  |  |  |  |  |  |  | 142.9 | Mabery and Goldstein |
| Heptane | 137.0 | +0.14 | 136.8 | 0.0 | 149.4 | +9.2 | 139.5 | +1.97 | 136.8a | 0.0 | { 133.4 | Mabery and Goldstein |
|  |  |  |  |  |  |  |  |  |  |  | 133.2 | Ricardo |
|  |  |  |  |  |  |  |  |  |  |  | 136.8 | Mathewsb |
| Octane | 128.9 | +0.7 | 126.9 | −0.86 | 141.48 | +10.5 | 129.78 | +1.39 | 130.7 | +2.1 | 128 | Mabery and Goldstein |
| Brombenzene | 101.0 | −2.6 | 100.4 | −3.18 | 109.8 | +6.07 | ... | ... | 103.9 | +0.19 | 103.7 |  |
| Carbon tetrachloride | 83.9 | +0.24 | 83.5 | −0.24 | 89.8 | +7.3 | ... | ... | 82.3 | +1.57 | 83.7 |  |
| Chloroform | 103.4 | −2.64 | 109.8 | +3.4 | 112.9 | +6.3 | ... | ... | 103.5 | −2.5 | 106.2 | Mathews |
| Carbon bisulfide | 154.8 | +1.98 | 151.9 | +0.13 | 151.3 | −0.26 | ... | ... | 149.9 | +1.2 | 151.7 |  |
| Toluene | 153.7 | −1.6 | ... | ... | ... | ... | ... | ... | 155.5 | −0.45 | 156.2 |  |
| Benzene | 167.1 | −1.6 | 171.7 | +1.06 | 179.5 | +5.65 | ... | ... | 165.3 | −2.7 | 169.9 |  |
| Average deviation | ... | 1.7 | ... | 1.25 | ... | 8.2 | ... | 2.24 | ... | 1.22 | ... |  |

a Assumed as starting point.
b All Mathews' measurements were made at pressures slightly under 760 mm. His values have been corrected to 760 mm. by the authors, using the rate of change of heat of vaporization given by the Clapeyron equation.

$p$ is the vapor pressure at the temperature halfway between $T_1$ and $T_2$. Great accuracy is claimed by Nernst for this equation.

5—The *Hildebrand* method has already been discussed in connection with vapor pressures. Instead of assuming, as in Trouton's rule, that the molal entropy of vaporization is the same for all normal liquids at the same pressure, he postulates that it should be substantially the same at equal vapor concentrations—or, in other words, along the lines of unit slope in Fig. 1. If this relationship held and the heat of vaporization for any one liquid were known at different pressures, it should be possible to calculate the heat of vaporization of any other (normal) liquid at any desired pressure. While this generalization is probably not so accurate, especially at higher pressures, as the one regarding the slopes of the vapor pressure curves, it nevertheless holds remarkably well for all normal liquids at moderate pressures.

In calculating the heats of vaporization for various compounds by the Hildebrand method, the figures of Mills for heptane at different temperatures have been taken as the standard of reference. Mills' figures for heptane were calculated from the exact Clapeyron equation combined with the accurate data of Young on vapor and liquid densities and vapor pressures. Heptane was selected as the standard because the Mills value at atmospheric pressure checks very closely with the recent accurate observations of Mathews.[7]

In order to indicate the relative reliability of different methods

[7] Presented before the Division of Petroleum Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

of calculating heats of vaporization for nonassociated liquids, Table I has been prepared to cover all the reasonably accurate available data on hydrocarbons and several other normal liquids. The best data are undoubtedly those obtained very recently by Mathews.[7] A few scattered data are available for other hydrocarbons, but they are discordant and not worthy of consideration.

Wherever sufficient data are available, the exact Clapeyron equation, of course, shows up very well, but, as pointed out previously, it is not possible to use it for the higher hydrocarbons because of the absence of accurate data on vapor and liquid densities. The approximate Clapeyron equation shows wide deviations from the observed values, in spite of which fact it is often used to calculate such heats approximately. The Nernst method shows up fairly well, but again requires the use of critical data which are not available for the higher hydrocarbons.

The Hildebrand results show up somewhat better than Trouton's rule (average deviation 1.2 per cent instead of 1.7 per cent) and the difference is much more pronounced when comparison is made with very low or high boiling, nonassociated substances, such as oxygen and zinc, given in Table II.

Table II—Latent Heats of Vaporization
(B. t. u. per pound at 100 mm. pressure)

| Substance | Boiling Point at 100 Mm., °F. | L from Vapor Pressure Observationsa | L Calcd. by Hildebrand's Method | % Deviation | L Calcd. by Trouton's Rule | % Deviation |
|---|---|---|---|---|---|---|
| Oxygen | −313 | 103.4 | 102.3 | −1.1 | 121.9 | +18.1 |
| Hexane | 61 | 159.9 | 160.8 | +0.6 | 161.8 | + 1.2 |
| Zinc | 1395 | 851 | 866 | +1.8 | 759 | −10.8 |

a For the method of calculation see Hildebrand (*loc. cit.*).



Fig. 3.
HEAT OF VAPORIZATION
VS.
LOG. VAPOR PRESSURE
CALCULATED BY HILDEBRAND'S METHOD
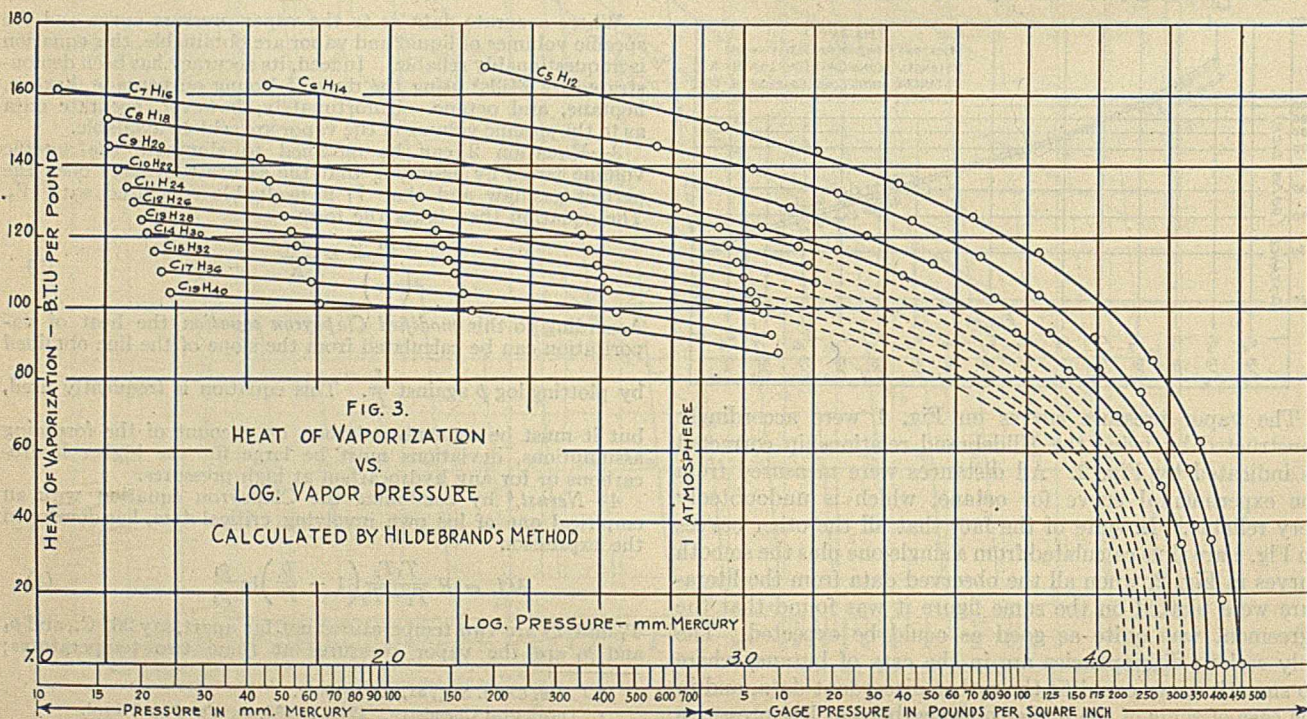
In this table are given the latent heats of vaporization at 100 mm. pressure of three compounds calculated by Hildebrand's method (based on the figures for heptane at various pressures) and by Trouton's rule. The "constant" entropy of vaporization used in the calculations by Trouton's rule was taken as 26.77, which is the average entropy of vaporization, at 100 mm. pressure, of the fifteen substances given by Hildebrand in his article. This table shows well the errors involved in the use of Trouton's rule for very low or high boiling substances.



FIG. 4.
HEAT OF VAPORIZATION
VS.
BOILING POINT (760 mm)
CALCULATED BY HILDEBRAND'S METHOD
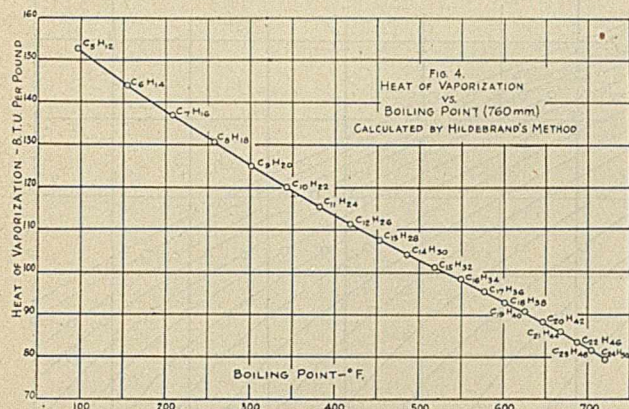
It therefore appears that Hildebrand's equation is the most reliable available method for determining the heats of vaporization of the higher hydrocarbons from low pressures up to 15 or 20 pounds gage pressure. It should be said, however, that Hildebrand's relationship cannot hold beyond the point where heats of vaporization begin to change rapidly as the critical point is approached, because the heat (and hence the entropy) of vaporization of any liquid at its critical point is zero, and the lines of unit slope are far from being parallel to the curve which includes all the critical points on Fig. 1. For example, the entropy of vaporization of octane is zero at its critical point and the line of unit slope which passes through the critical point of octane intersects the heptane curve at a point where its entropy of vaporization is about 5.2.

In order to get approximate values for this region, Hildebrand's equation is used to calculate the heats up to about 15 pounds pressure, and these curves are plotted in Fig. 3. Above this pressure only the curves for pentane to octane, inclusive, are available, but since the critical pressures (at which $L = 0$) have been determined approximately on Fig. 1, it is possible to draw fairly reliable dotted lines through the intermediate region in which data are almost unobtainable. The presumption that these lines are approximately correct is confirmed by comparing the results obtained with the values calculated using the extrapolated critical points together with liquid and vapor densities discussed in later sections.

Fig. 4 also presents in simpler form the values for the heats of vaporization at atmospheric pressure of the normal paraffin hydrocarbons plotted against their boiling points. The large errors likely to be introduced by the practice of using a single figure of 120 as the heat of vaporization of all petroleum distillates becomes obvious on studying this figure.

## CRITICAL DATA

The critical points of the hydrocarbons above octane have been extrapolated from the general trend of the line passing through the known critical points, and are therefore only approximate. However, calculations involving these extrapolated critical points are made in the following sections, and some checks with other data indicate that the results are nearly enough correct to be of considerable practical value.

The critical density may be calculated from these extra-

polated values by the following method: Van der Waals pointed out that the ratio

$$\frac{R \times \text{critical temperature}}{\text{critical pressure} \times \text{critical volume}}$$

should be constant for all substances and, according to his theory, equal to 2.67. The observed critical constants show that this ratio is nearly constant for all normal substances, but its average value is about 3.75. In only one or two cases does its value exceed 3.90. Young's values for this constant for the normal paraffin hydrocarbons which he measured are as follows:

| | | | |
|---|---|---|---|
| Pentane | 3.766 | Heptane | 3.854 |
| Hexane | 3.831 | Octane | 3.865 |

It will be noted that these values appear to be flattening off to a maximum around 3.90, so a reasonable extrapolation should be fairly reliable. By plotting these values against the molecular weight and combining this value of the ratio with the values for the critical pressure and the critical temperature obtained from Fig. 1, it is possible to approximate the critical volume of the higher hydrocarbons. The critical data calculated by this method are given in Table III.

TABLE III—CRITICAL CONSTANTS[a]

| COMPOUND | Critical Temperature ° F. | Critical Pressure Mm. | Critical Pressure Atm. | $\frac{RT_c}{P_cV_c}$ | $V_c$ | $D_c$ (G./Cc.) |
|---|---|---|---|---|---|---|
| Pentane | 386.9 | 25100 | 33.04 | 3.766 | 4.305 | 0.2323 |
| Hexane | 454.6 | 22510 | 29.63 | 3.831 | 4.266 | 0.2344 |
| Heptane | 512.3 | 20430 | 26.89 | 3.854 | 4.272 | 0.2341 |
| Octane | 565.2 | 18730 | 24.66 | 3.865 | 4.297 | 0.2327 |
| Nonane | 612 | 17380 | 22.86 | 3.871 | 4.311 | 0.2319 |
| Decane | 655 | 16140 | 21.24 | 3.877 | 4.348 | 0.2300 |
| Undecane | 697 | 15140 | 19.92 | 3.882 | 4.370 | 0.2288 |
| Dodecane | 735 | 14130 | 18.59 | 3.886 | 4.435 | 0.2255 |
| Tridecane | 770 | 13340 | 17.55 | 3.890 | 4.465 | 0.2240 |
| Tetradecane | 802 | 12590 | 16.56 | 3.893 | 4.505 | 0.2220 |
| Pentadecane | 832 | 11970 | 15.75 | 3.896 | 4.520 | 0.2212 |
| Hexadecane | 862 | 11480 | 15.10 | 3.898 | 4.537 | 0.2205 |
| Heptadecane | 889 | 10960 | 14.41 | 3.900 | 4.557 | 0.2195 |
| Octadecane | 915 | 10590 | 13.83 | 3.901 | 4.575 | 0.2186 |
| Nonadecane | 937 | 10210 | 13.43 | 3.902 | 4.541 | 0.2203 |

a The number of significant figures in some parts of this table is probably greater than is justified by the accuracy of the data, but their use seems desirable to make the various conversions more consistent.

## LIQUID DENSITIES

The theorem of corresponding states offers perhaps the best criterion for coördinating existing data and extrapolating the densities of the liquid hydrocarbons to higher tempera-



FIG. 5.
RATIO OF SPECIFIC VOLUME OF LIQUID TO CRITICAL VOLUME
VS.
RATIO OF TEMPERATURE TO CRITICAL TEMPERATURE

FIG. 6.
DENSITY OF LIQUID HYDROCARBONS
VS.
TEMPERATURE
$C_5H_{12} - C_{20}H_{42}$, INCLUSIVE
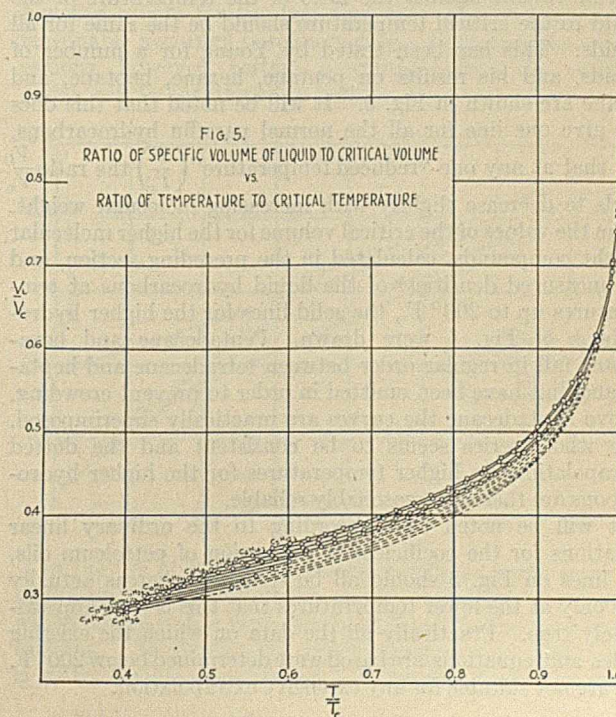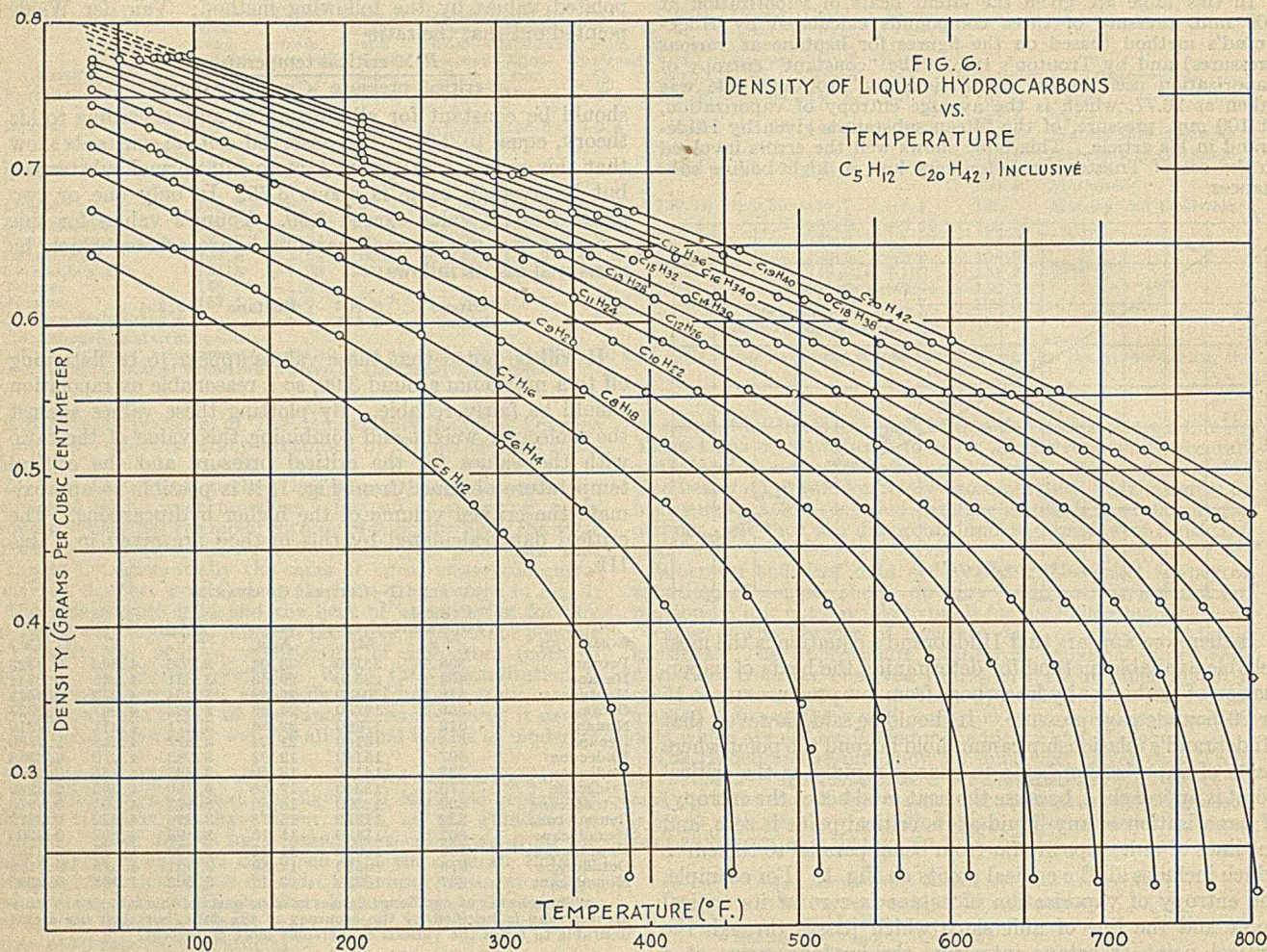
tures. According to this theorem the curve obtained by plotting the ratio of the specific volume of the liquid to the critical volume against the ratio of the temperature of the liquid to the critical temperature should be the same for all liquids. This has been tested by Young for a number of liquids, and his results on pentane, hexane, heptane, and octane are shown in Fig. 5. It will be noted that this does not give one line for all the normal paraffin hydrocarbons, but that at any one "reduced temperature" $\left(\dfrac{T}{T_c}\right)$ the ratio $\dfrac{V_l}{V_c}$ tends to decrease slightly with increasing molecular weight. From the values of the critical volume for the higher molecular weight compounds, calculated in the preceding section, and the measured densities[8] of the liquid hydrocarbons at temperatures up to 200° F., the solid lines for the higher hydrocarbons of Fig. 5 were drawn. Pentadecane and hexadecane fall in regular order between tetradecane and heptadecane, but have been omitted in order to prevent crowding. Above heptadecane the curves are practically superimposed. The whole series seems to be consistent and the dotted extrapolations to higher temperatures for the higher hydrocarbons are therefore reasonably reliable.

It will be noted that according to the ordinary linear equations for the coefficient of expansion of petroleum oils, the lines on Fig. 5 should all be straight, whereas actually it is only at the lower temperatures that this is even approximately true. Practically all the data on which the existing tables and equations are based were determined below 200° F. and are not suitable for any extensive extrapolation.

[8] Beilstein, Handbuch, Vol. I, 3rd ed., p. 102.

In order to make the results in Fig. 5 more readily available for practical purposes, the actual densities have been calculated and plotted against the Fahrenheit temperature in Fig. 6. While the ordinary tables or equations can be used up to 200° F. for the lighter hydrocarbons, or to somewhat higher temperatures for the higher hydrocarbons, reference should always be made to Fig. 6 to obtain results at temperatures above 200° F. if the calculated density at the higher temperature is below 0.65. For the compounds from $C_{15}H_{32}$ to $C_{20}H_{42}$, inclusive, the densities shown in Fig. 6 are represented by dotted lines at lower temperatures (below the melting point), for a petroleum product corresponding to the densities of these compounds would not freeze at as high a temperature as the pure hydrocarbon.

To show the errors involved in using the ordinary equation, suppose it is desired to know the volume occupied by a gallon of distillate measured at 60° F. when it is heated to 600° F. Its A. P. I. gravity is 61.2°, so that its density corresponds to that of decane. If the customary coefficient of expansion (0.0006) based on measurements at relatively low temperatures is used, the calculated volume at 600° F. is 32.4 per cent greater than its volume at 60° F., while the approximately correct value given by the decane curve in Fig. 6 indicates an expansion of 77 per cent between 60° and 600° F.

In using these curves it should be remembered that the density given is the density when the liquid is under its own vapor pressure, so that at relatively high temperatures (or preferably at densities below about 0.45) these curves are not accurate when the pressure is much in excess of the vapor pressure.

### Saturated Vapor Densities

It has been shown that the ratio of the observed densities of the saturated vapor to those calculated by means of the perfect gas law increases with increasing temperature until at the critical point the ratio is nearly four to one. It is therefore obvious that the use of the perfect gas law to calculate the saturated vapor volumes at relatively high pres-

FIG. 7.
RATIO OF SPECIFIC VOLUME OF SATURATED VAPOR TO CRITICAL VOLUME
vs
RATIO OF VAPOR PRESSURE TO CRITICAL PRESSURE

X = PENTANE
☐ = HEXANE
△ = HEPTANE
○ = OCTANE
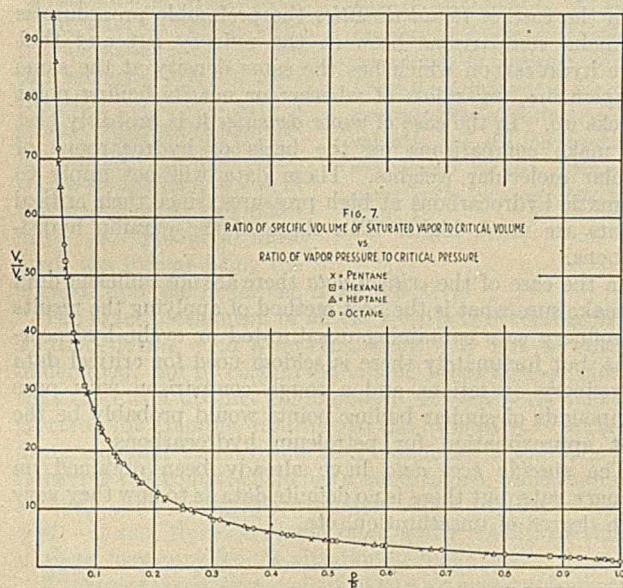
sures will give rise to large errors. Even at their normal boiling points the observed vapor densities are from 5 (for the lighter hydrocarbons) to 15 per cent higher than those calculated on the basis of the perfect gas law. However, by making use again of the theorem of corresponding states, it is possible to obtain values which are close to all available observations.

In Fig. 7 the ratio of the specific volume of the saturated vapor to the critical volume has been plotted against the ratio of the vapor pressure to the critical pressure for the four normal hydrocarbons which Young measured. The points all fall very close to the same line, so that the use of this line for the hydrocarbons of higher molecular weight should not introduce any large error into calculations of their vapor densities.

Since the foregoing sections supply approximate values for the specific volume of both liquid and vapor, it should be possible to calculate the heat of vaporization by means of the more exact Clapeyron equation with a fair degree of accuracy and compare the resulting value with that obtained by the Hildebrand method. For instance, the heat of vaporization of pentadecane at 33.9 pounds per square inch (gage pressure), calculated from the values of specific volumes of liquid and vapor given by these curves, is 84.3 B. t. u. per pound. Hildebrand's method gives 90 B. t. u. per pound at the same point. This agreement is considered reasonably good, because the Hildebrand values are, for reasons discussed in a previous section, undoubtedly somewhat high at such pressures.

### Specific Heats

Very few data on the specific heats of petroleum distillates over any considerable temperature range have been published. Wilson and Barnard[9] have measured the specific heats of gasoline and kerosene up to 400° C. and found that they were expressed by the following formula:

[9] *J. Soc. Automotive Eng.*, **10**, 65 (1922).

$$\frac{dQ}{dT} = 0.5 + 0.000333\,(t-32), \text{ where } t = \text{temperature in ° F.}$$

Their data unfortunately combined specific heats of both liquid and vapor, which are not necessarily the same, although probably similar.

Karawajeff[10] found that for heavy distillates between 100° and 400° C. the specific heat could be represented by the formula

$$\frac{dQ}{dT} = 0.4825 + 0.00077\,(t - 100)$$

or for degrees Fahrenheit:

$$\frac{dQ}{dT} = 0.4055 + 0.000428\,(t - 32)$$

Recently Leslie and Geniesse[7] have measured the specific heats of a number of lubricating oils up to 290° F. The average of their measurements is given by the formula

$$\frac{dQ}{dT} = 0.3481 + 0.000823\,(t - 32)$$

The specific heats calculated from these three formulas are shown graphically in Fig. 8. The formulas are obviously not wholly consistent, but the results do bring out two important points, as follows: (1) specific heats increase rapidly with increasing temperature; (2) specific heats decrease as molecular weight increases.

If the curves in Fig. 8 are used with judgment, the results will at any rate be far more reliable than those obtained by following the customary practice of using 0.5 for all specific heats. If the temperature range involved is at all large, the specific heat corresponding to the mean temperature is, of course, the one to employ.

Some experimental work should certainly be done to clear up the existing discrepancies and uncertainties in these specific heat data, and especially in the specific heats of vapors, on which a negligible amount of work seems to have been done.

### Application of Results to Refinery Cuts

Since the pure hydrocarbons from which these cuts have been developed are largely laboratory curiosities, the compilation and extrapolation of these data would scarcely be justified except for the fact that they can be applied with reasonable accuracy to refinery cuts. In making these applications, however, certain precautions must be observed which will be mentioned in detail.

FIG 8.
TRUE SPECIFIC HEAT
vs.
TEMPERATURE

LIGHT DISTILLATES (WILSON & BARNARD)
HEAVY DISTILLATES (KARAWAJEFF)
LUBRICATING OILS (LESLIE)
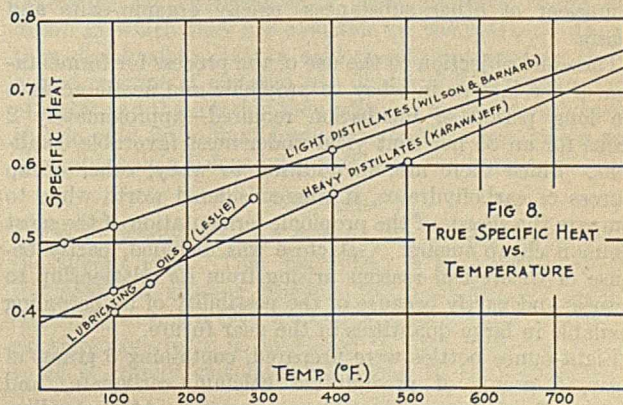
In the use of the *vapor pressure* results accurate measurements on refinery cuts have shown that these give curves which belong to the same family as those for the pure hydrocarbons. To predict the vapor pressure when a given cut is heated up in a closed vessel it is therefore necessary merely

[10] *Petroleum*, **9**, 550 (1914).

to know its boiling point. This is, however, not the same as the initial boiling point in a regular Engler distillation where the thermometer is in the neck of the flask, but rather the true initial boiling point with the thermometer in the liquid, which is generally from 30° to 60° F. higher.

The curves may similarly be used to determine the vacuum or the amount of steam required to bring a given fraction over below a certain temperature, but here again the boiling point at atmospheric pressure should be determined with the thermometer in the liquid at the time when the desired cut has been distilled off.

Incidentally, it should be noted that the vapor pressure curve of unsaturated and cyclic hydrocarbons checks up very closely with those for saturated hydrocarbons of similar boiling points. (The curves cannot, however, be applied with equal accuracy to alcohols, esters, or other organic compounds containing elements besides carbon and hydrogen.) In any such interpolations the vapor pressure and other curves should be considered as representing a family of essentially parallel curves, and it is not necessary to follow any particular line but rather to determine the atmospheric pressure boiling point of the cut exactly and assume a line passing through this point which will fit in with the family of curves.

In the case of *heats of vaporization* the figure usually desired is the heat of vaporization of an entire cut. For this purpose the average boiling point of the same should be obtained by averaging the temperatures at all points from initial to the maximum. In this case again the thermometer

should be in the liquid, but the error is not large if the ordinary vapor temperature results are used, since the heat of vaporization does not change very rapidly with the boiling point. Reference should be made to Fig. 4 for results at atmospheric pressure, or to Fig. 3 for results at other pressures, after determining what hydrocarbon most nearly corresponds to the average boiling point of the cut in question at atmospheric pressure.

In the case of *liquid densities* the preferable procedure is to make comparisons between the refinery cut and that pure hydrocarbon which has the same density at the same temperature, regardless of whether or not its boiling point checks up. In the case of *vapor densities* it is probably best to make comparisons on the basis of hydrocarbons of similar molecular weights. These data will not apply to aromatic hydrocarbons at high pressures, since their critical points are much higher than those of the paraffin hydrocarbons.

In the case of the *critical data* there are not sufficient data to make sure what is the best method of applying the results to refinery cuts containing unsaturated or cyclic hydrocarbons, but fortunately there is seldom need for critical data in refinery operations and a rough comparison with pure compounds of similar boiling points would probably be the best approximation for petroleum hydrocarbons.

The *specific heat data* have already been obtained on refinery cuts, but there is no definite data as to how they vary with degree of unsaturation, etc.

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# The Rates of Fermentation of Sugars by the Propionic Organism[1]

By E. O. Whittier, J. M. Sherman, and W. R. Albus

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PREVIOUS work by Sherman and his associates[2] on the propionic fermentation has dealt with its bacteriological and chemical features, especially in their bearing on the use of the propionic organism in the manufacture of Swiss cheese and in the production of propionic acid in quantity from whey. Among the points established was the fact that the organism ferments not only lactose, but also a number of other substances, chiefly organic salts and sugars.

The chief objection to the use of the process for fermentation of the lactose in whey to propionic and acetic acids is the long period of incubation required—approximately 2 weeks for an 85 per cent yield under most favorable conditions. Since there are, in addition to whey, other cheap sources of carbohydrates, it was considered worth while to compare the speeds of the propionic fermentation of the most common cheap sugars. Galactose was included, partly because of theoretical reasons arising from its relationship to lactose, and partly because of the possibility of its becoming available in large quantities in the near future.

Eight-ounce bottles were prepared, containing 5 grams of sugar, 5 grams of precipitated calcium carbonate, and 1 gram of dried yeast, in 100 cc. of water. After sterilization each bottle was inoculated with 1 cc. of a culture of *Bacterium acidi-propionici* (d) and a loopful of a culture of

[1] Received September 26, 1923.

[2] Sherman and Shaw, *J. Gen. Physiol.*, **3**, 657 (1921); Sherman, *J. Bact.*, **6**, 379 (1921); Sherman and Shaw, *Sci. Proc. Soc. Am. Bacteriologists, Abstracts Bact.*, **6**, 16 (1922); Shaw and Sherman, *J. Dairy Sci.*, **6**, 303 (1923); Sherman and Shaw, *J. Biol. Chem.*, **56**, 695 (1923); Whittier and Sherman, This Journal, **15**, 729 (1923).

*Lactobacillus casei*, and incubated at 30° C. for 16 days. The volatile acids produced were distilled off and determined by the method of Duclaux. The results are shown in Table I.

Table I—Relative Speed of Fermentation of Several Sugars by the Propionic Organism

| SUGAR | GRAMS OF ACID PRODUCED | | PER CENT OF THEORETICAL YIELD | |
|---|---|---|---|---|
| | Propionic | Acetic | Propionic | Acetic |
| Lactose | 1.2967 | 0.3863 | 47.3 | 34.8 |
| Galactose | 1.4493 | 0.4430 | 52.9 | 39.9 |
| Glucose | 1.5351 | 0.4528 | 56.0 | 40.8 |
| Sucrose | 1.6638 | 0.5008 | 57.6 | 42.8 |
| Maltose | 2.1290 | 0.7928 | 77.7 | 71.4 |

Variations wider than expected were obtained in the amounts of volatile acid produced in the same period from the different sugars. Since the time of incubation was chosen so that none of the fermentations was complete, the amounts of volatile acids found should be a fairly accurate measure of the relative rates of fermentation. This statement may be objected to on the basis that the per cent of theory yield is the strictly scientific measure. However, the choice of either basis will give identical ratios in the cases of the sugars used except in those where sucrose is concerned. Glucose, galactose, and sucrose are fermented by the propionic organism somewhat more rapidly than lactose; weight for weight, sucrose has an advantage which does not appear when the theoretical basis is chosen; maltose is fermented about 60 per cent faster than lactose, and about 30 per cent faster than the other sugars. The relative advantage of these sugars in the commercial production of propionic acid would depend, of course, on relative cost and availability as well as the speed of fermentation.

# An Electrometric Study of the Titration of Boric Acid[1]

### By M. G. Mellon and V. N. Morris

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I T IS well known that the presence of certain polyhydroxy organic compounds enables one to obtain a sharp end point when titrating boric acid with a strong base, using phenolphthalein as the indicator. Of the compounds acting in this way glycerol and mannitol are probably most used, the former being the cheaper and the latter the more effective.

*An electrometric determination of the pH curve for the neutralization of boric acid in the presence of certain polyhydroxy organic compounds indicates a wide variation in the effectiveness of these compounds in changing the position of the curve for boric acid alone. From the standpoint of adaptability for use in the accurate volumetric determination of boric acid, hydroxy acids and polyphenols are least valuable and the polyalcohols most valuable under the conditions maintained in this work. From the standpoint of effectiveness along with low cost, invert sugar is the most valuable substance studied.*

The exact mechanism of all the reactions occurring in the solution during such a determination may not be entirely understood, but by certain individuals it has been considered that there is a distinct combination between boric acid and glycerol, for example, resulting in the formation of an ester-like compound which reacts as a monobasic acid. The ionization of this complex acid has a much higher value than that of boric acid, being approximately equal to that of acetic acid. It can, therefore, be titrated under conditions similar to those necessary for the titration of acetic acid.

The recent development of apparatus for making electrometric titrations has provided a convenient and effective means for studying the course of neutralization reactions such as that mentioned. The pH curve which may be plotted for such a titration gives one a basis for considering the change of hydrogen-ion concentration during the titration, since the pH value at any point in the neutralization is the logarithm of the reciprocal of the hydrogen-ion concentration. In order to ascertain the effect of glycerol upon the acidic properties of boric acid, for instance, one has merely to determine the pH curve for the titration of the acid with and without the addition of glycerol.

The object of the present investigation was to make such an electrometric study of the effect of a number of polyhydroxy organic compounds upon the acidic properties of boric acid with the ultimate aim of comparing the effectiveness, convenience, and cost of these compounds with glycerol for use in the volumetric determination of boric acid.

### Previous Work

Klein[2] seems to have been the first to report the fact that solutions of boric acid show the properties of a stronger acid on the addition of certain polyalcohols and sugars. Thomson[3] discovered that boric acid could be determined satisfactorily by titration in the presence of glycerol, using phenolphthalein as the indicator. Certain other compounds were found to act similarly; but not until the development both of the scheme for determining pH curves and of the modern conception of the relationship of neutralization indicators to these curves did we have an easily understandable basis for making such determinations properly.[4]

Magnanini[5] noticed that the electrical conductivity of the aqueous solution of boric acid is markedly increased by the addition of certain of these hydroxy organic compounds, and he determined the effect of a number of them. Some years later Böeseken and Van Rossem[6] took up this study, hoping to be able to obtain from a determination of the conductivity of the system some knowledge of the configuration of the organic compound contained therein. Continuing the work of this first paper, Böeseken[7] and his students have published more than twenty-five others. They conclude that the increase in the electrical conductivity of polyalcohols, polyphenols, hydroxyacids, ketonic acids, etc., with boric acid is due to the formation of complex acids stronger than the components. In general, these complexes are formed when two OH groups are situated on the same side of the adjacent carbon atoms to which they are bound. No effect, or occasionally a small decrease in the conductivity, occurs when the compounds do not have such a configuration.

For this investigation a number of the compounds used by Böeseken were selected, including polyalcohols, hydroxy acids, etc. During the course of the work a paper by Van Liempt[8] dealing with several of these compounds came to the attention of the authors. Van Liempt directed attention to the effect upon the curves, for glycerol, mannitol, fructose, and invert sugar, of varying the ratio of the amounts of the organic compounds and the boric acid.

### Materials

Commercial compressed hydrogen was used for the hydrogen electrode after being passed through the customary purification train. The calomel electrode was made in the usual way using normal potassium chloride. The sodium hydroxide used for titrating the boric acid was prepared free from carbon dioxide. Recrystallized, air-dried boric acid was used to make up a stock solution. This solution was checked frequently against the standard base, using mannitol and phenolphthalein.[9] The results indicated that there was practically no change in the concentration of the acid over a period of more than 2 months. Most of the organic compounds were used as purchased, since it seemed desirable to determine the effectiveness of these materials in the condition in which they are available on the market. In case they dissolved to give an acid or alkaline reaction the required amount of material was dissolved in a small amount of water and the solution then adjusted carefully with hydrochloric acid or sodium hydroxide until just colorless with phenolphthalein before being added to the boric acid.

### Method

The apparatus used for determining the pH curves was of the Wendt type. This instrument is so constructed that the potential existing between the hydrogen and calomel electrodes during a titration can be read directly. From the electromotive force as measured in such a system the pH value is readily calculated according to the equations:[10]

$$E_{18}° = 0.058 \log \frac{1}{c} + 0.285$$

$$pH = \frac{E_{18}° - 0.285}{0.058}$$

[1] Presented before the Division of Industrial and Engineering Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] *Bull. soc. chim.*, **29**, 195 (1878).

[3] *J. Soc. Chem. Ind.*, **12**, 432 (1893).

[4] Prideaux, "Theory and Use of Indicators," 1917, p. 225.

[5] *Gazz. chim. ital.*, **20**, I, 428; II, 215 (1890); **21**, II, 134 (1891).

[6] *Rec. trav. chim.*, **30**, 392 (1912).

[7] See *Rec. trav. chim.*, **40**, 553 (1921) and *C. A.*, **16**, 906 (1922) for a summary of this work and references to the various papers.

[8] *Rec. trav. chim.*, **39**, 358 (1920); *Z. anorg. Chem.*, **111**, 151 (1920).

[9] Blasdale, "Quantitative Chemical Analysis," 1914, p. 301

[10] Central Scientific Co., Chicago, *Bull.* **86**.

When an open beaker is used for the titration, an instrument of this type does not provide against errors arising from changes of temperature or from absorption of carbon dioxide during a titration. From the nature of the present work no serious
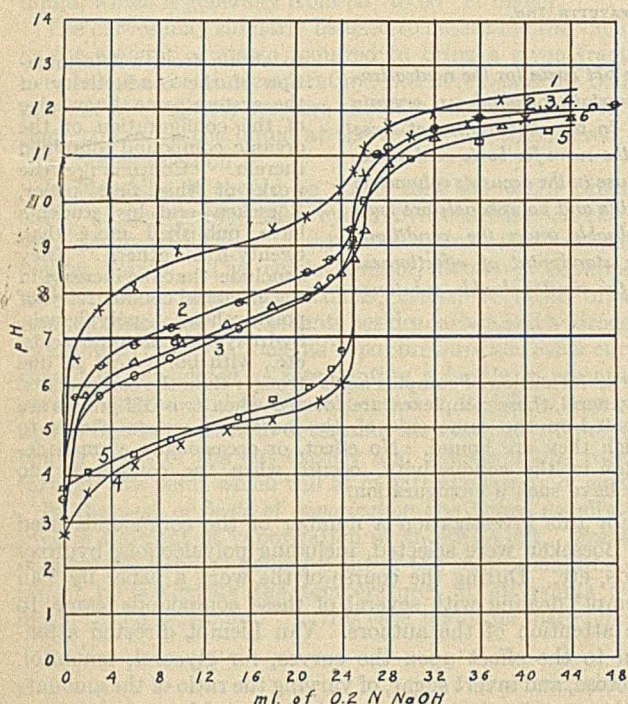


Fig. 1—Titration of Boric Acid (50 Ml. of a 0.0994 $N$ Solution) in Presence of Polyalcohols: (1) Acid Alone, (2) Glycerol, (3) Erythritol, (4) Mannitol, (5) Manna, (6) Glycerol and Sufficient Sodium Chloride to Saturate the Solution

error should be involved through neglect of these factors. Some determinations were made with an electrode plated first with gold, but finally only a thin coating of platinum black was deposited directly upon the platinum. In general, the instrument worked very satisfactorily when the electrode was replatinized frequently. Occasionally, a sluggishness of the galvanometer and fluctuations of the millivoltmeter were encountered, particularly with boric acid alone and with lactic acid. In such cases what seemed to be an average value was taken. If all the organic compound failed to dissolve at first, as dulcitol, lactose, and gallic acid, the titration was started anyway, the undissolved portion going into solution before the completion of the neutralization.

The general procedure consisted in titrating a definite volume of a standard solution of boric acid containing a definite amount of the organic compound. In nearly all cases the latter was weighed and added to the solution just before beginning the titration. Since it was desired to determine the relative effect of the organic compounds, some basis of comparison was necessary. 25, 30, or 50 ml. of the boric acid solution (0.0994 $N$) were used, and to it was added the organic compound in the ratio of four mols of the organic compound to one of the acid, for all compounds except the acids. They were used on the basis of one equivalent of organic acid to one mol of boric acid. Lack of a sufficient amount of the rarer and more expensive compounds prevented the use of a larger ratio, although this would have been desirable in some cases. Phenolphthalein was present in the solution being titrated, its change of color serving as a check on certain phases of the work. There was a sharp change in color only when the compounds gave curves having a vertical portion through the pH range of the indicator.

## Experimental Data

In making the various titrations practically the same procedure was followed throughout, except in a few cases when some difficulty necessitated certain modifications. These are mentioned in connection with the measurements on the compounds involved.

The original data from which the pH curves were calculated have not been included. The curves shown herewith are plotted from the titrations in the usual way with abscissas representing milliliters of standard base and ordinates representing pH values.[11] Occasionally, portions of two curves have been combined in the graph, if they were so close together as to be practically indistinguishable on a reduced basis. It will be noted that the curve for boric acid has been repeated several times, since the relative position of the various curves makes the effect of the different organic compounds immediately evident. The compounds used have been grouped as polyalcohols, sugars, polyphenols, and acids.

Polyalcohols—Of the polyalcohols selected three are stereoisomers—mannitol, sorbitol, and dulcitol. Further, glycerol has three carbon atoms to the molecule, erythritol four, and the others six. Manna was also used, as Miss Iles[12] has recently recommended it as a substitute for the purified and much more expensive mannitol. She stated that 5 grams are equivalent to about 25 ml. of 80 per cent alcohol. The crude product was used as purchased, except for neutralization of the solution. In this condition it is stated to contain about 50 per cent mannitol. On the basis of the approximate analysis of manna available,[13] it was calculated that 7 grams would contain an amount of polyalcohols equivalent to the other alcohols used.

The effect of an increasing number of carbon atoms and OH groups in the molecule upon the position of the curve is plainly shown in Fig. 1 by Curves 1, 2, 3, and 4. The ad-

[11] This Journal, 15, 182 (1923).
[12] Analyst, 43, 323 (1918).
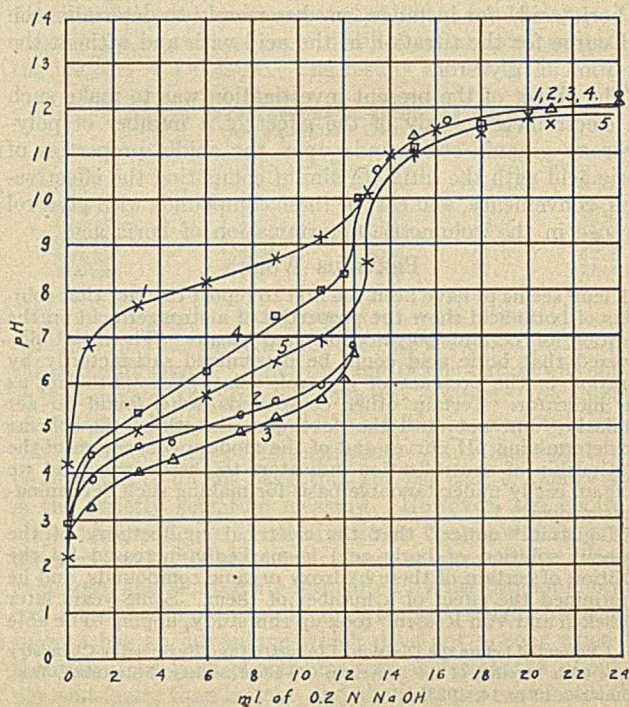[13] Thorpe "Dictionary of Applied Chemistry," Vol. III, 1912, p. 398.



Fig. 2—Titration of Boric Acid (25 Ml. of a 0.0994 $N$ Solution) in the Presence of Polyalcohols: (1) Acid Alone, (2) Dulcitol, (3) Sorbitol, (4) Mannitol, (5) Mannitol with Sufficient Sodium Chloride to Saturate the Solution

vantage of mannitol in effectiveness is evident, although even the proportion of glycerol used would enable one to make the usual acidimetric titration by using an indicator of the proper pH range. According to Gilmour,[14] mannitol is about eleven times as effective as glycerol. Curve 5 is for manna. Prideaux[15] has mentioned the effect of sodium chloride upon the curve for mannitol. Curve 6 shows the drop produced on the curve for glycerol by adding sufficient sodium chloride to saturate the solution.

In Fig. 2 are shown the curves for dulcitol and sorbitol, isomers of mannitol, determined upon the same basis as Curve 4 of Fig. 1. Curve 4, Fig. 2, is for mannitol on a ratio of 1:1 instead of 4:1, the proportion used for the others. Curve 5 then shows the drop produced on No. 4 by the addition of sufficient sodium chloride to saturate the solution. No explanation is offered for the horizontal shift in the vertical portion of the curve.

SUGARS—As compounds closely related chemically to the members of the preceding group, a number of the sugars were selected. In Fig. 3 are shown the curves for xylose, rhamnose, mannose, and fructose, representing, respectively, a pentose, a methylpentose, a hexose of the aldose group, and a hexose of the ketose group. Only small amounts of these compounds were available, so the location of the curves could not be checked. In Fig. 3 the scale for abscissas is double that for the others.

In Fig. 4 the curves are for the two disaccharides, sucrose and lactose, the dextrorotatory monosaccharide, dextrose, and the combination of dextrorotatory and levorotatory monosaccharides as found in invert sugar. The latter was made according to the directions of Gilmour,[14] which consist in boiling the calculated weight of sucrose in a small volume of water, adding 1 ml. of 0.2 $N$ hydrochloric acid, shaking, cooling, adding 1 ml. of 0.2 $N$ sodium hydroxide, and making up to 50 ml. To this solution the calculated weight of boric acid was added and the whole titrated.

[14] *Analyst*, **46**, 3 (1921).
[15] "Theory and Use of Indicators," **1917**, p. 282.
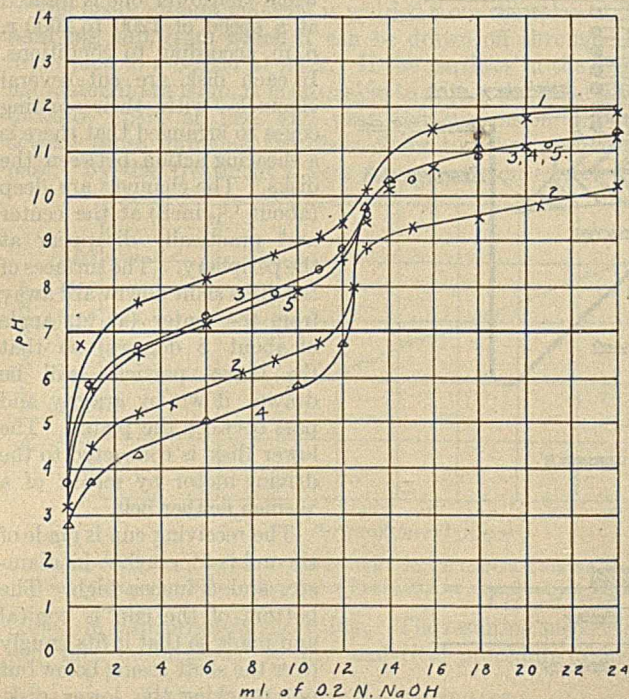
FIG. 3—TITRATION OF BORIC ACID (25 ML. OF A 0.0994 $N$ SOLUTION) IN THE PRESENCE OF SUGARS: (1) ACID ALONE, (2) XYLOSE, (3) RHAMNOSE, (4) FRUCTOSE, (5) MANNOSE

OTHER COMPOUNDS—Several other types of organic compounds were used, but none of them gave a curve with a vertical portion which would indicate the possibility of making a volumetric determination, and the results have not been
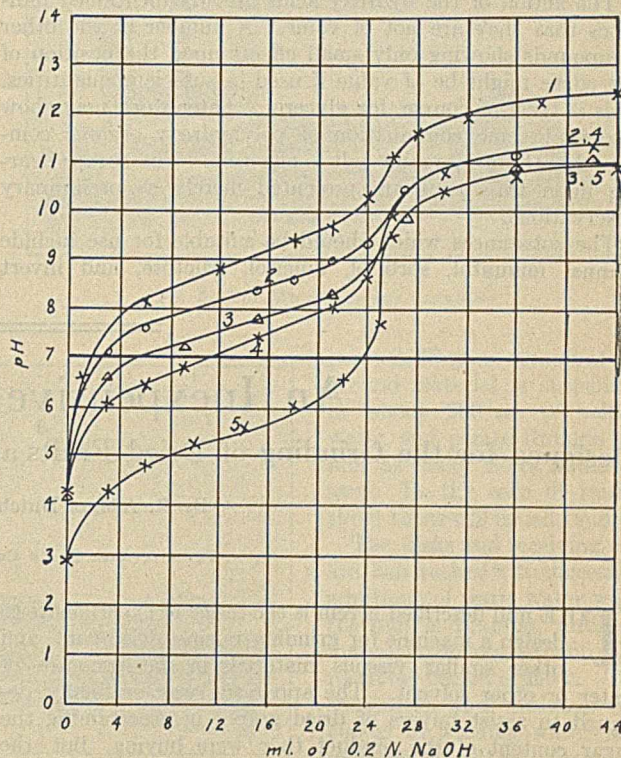
FIG. 4—TITRATION OF BORIC ACID (50 ML. OF A 0.0994 $N$ SOLUTION) IN THE PRESENCE OF SUGARS: (1) ACID ALONE, (2) SUCROSE, (3) LACTOSE, (4) DEXTROSE, (5) INVERT SUGAR

included. A marked drop in the curve for boric acid was obtained with the polyphenols, pyrocatechol and pyrogallol. Such acids as glycolic, oxalic, and gallic gave a different type of curve than the polyalcohols, since with these acids there is apparently involved a successive neutralization of the organic acid and the boric acid. Some downward displacement of the curve was evident with all these compounds.

## DISCUSSION

An inspection and comparison of the preceding curves leads to several conclusions regarding the pH curve for the titration of boric acid when determined in the presence of various polyhydroxy organic compounds.

The general effect evident is a downward displacement of the curve, the portion preceding the point of neutralization being affected most. There is also evident a wide variation in the relative displacement produced by the different compounds. From our present knowledge of the course of neutralization of acids of different degrees of ionization, we should anticipate a drop in the first half of the pH curve upon the addition of any substance which forms a complex acid more highly dissociated than boric acid itself. With some of the compounds studied the shift in the curve is greater than the distance between the curves for acetic and hydrochloric acids, showing that, in these instances, the complex acid has a relatively high degree of ionization.

Only a few of the compounds investigated give, for the proportions used, the type of curve necessary for an accurate volumetric determination of boric acid—that is, a curve with a vertical portion of sufficient length to pass through the pH range of a suitable indicator. Böeseken has shown that

the electrical conductivity of boric acid is increased more or less by a considerable number of polyhydroxy organic compounds, but it is evident that they are not necessarily of value, therefore, for use in determining boric acid.

The action of the hydroxy acids already mentioned indicates that they are not of value. A number of the other compounds showing only small effects upon the position of the curve might be of value if used in sufficient quantities. This is true, of course, for glycerol. Later work may show also that some combination of polyhydroxy organic compound with an inorganic salt is effective. The curves bearing upon this point are presented merely as preliminary observations.

The substances which should be suitable for use include manna, mannitol, sorbitol, dulcitol, fructose, and invert sugar. Of this list sorbitol, dulcitol, and fructose are too expensive for extensive use, leaving for consideration mannitol, manna, and invert sugar. The curve for mannitol has the longest vertical portion, indicating that it is the most effective substance for the proportions used. Both manna and invert sugar give curves lying close to that for mannitol. Their vertical portion is shorter but properly located for a satisfactory volumetric determination of boric acid, using either of these substances along with phenolphthalein or cresol red as an indicator. Several determinations were made in this way in order to check the accuracy of such a conclusion. According to the prevailing price of chemicals, invert sugar is the cheapest material to use, although preparation of a solution of it involves more time than weighing mannitol or manna directly.

# An Inexpensive Laboratory Mill[1,2]

## Designed for the Grinding of Dried Fruits and Similar Materials in the Presence of a Liquid

By R. Adams Dutcher and John F. Laudig

PENNSYLVANIA STATE COLLEGE, STATE COLLEGE, PA.

THE mill described herein is the result of experiments to design a machine for grinding raisins, dried fruit, and other similar viscous materials in the presence of water or other solvent. The apparatus was originally designed to assist buyers of dried grapes in ascertaining the sugar content of the product they were buying, but the writers believe that the mill could be used in a variety of ways in most laboratories, especially in the preparation of colloidal materials and in the grinding of many agricultural, biological, and pharmaceutical materials. This mill was constructed in the college shops at a cost of about $30.00.

In order to obtain the information necessary for properly classifying the dried fruit, the sugar content must be estimated while the shipment is being unloaded and graded, which requires about twenty minutes. The method described in this paper gives fairly accurate results on the determination of the sugar content of dried raisins in a very short time, even in the hands of a nontechnical worker.

### DESIGN

In designing the mill shown in Figs. 1 to 4, the following conditions had to be met:

1—Gummy materials had to be ground in the presence of a solvent to remove the sugars as rapidly as possible from the tissues.

2—The material had to be ground to a very fine state of subdivision to insure complete solution of the sugars present.

3—The mill had to be so constructed that no material could be lost during the grinding process.

4—It was also essential that the mill be easily and quickly dismantled and reassembled.

Fig. 1 shows a cross section of the mill as finally built. It consists primarily of two steel disks $4\frac{1}{2}$ inches in diameter, the upper one being stationary while the lower one is rotated at a speed of 1200 to 2000 r. p. m. according to conditions. In each disk are cut several channels with their cutting edges so arranged that there is a shearing action between the disks. The channels are deep (about $\frac{1}{16}$ inch) at the center and practically disappear at the periphery. The surfaces of the disks slant downward away from the center (at an angle of about 5 degrees) so that the larger particles will be drawn down by gravity and pass between the plates. The lower disk is connected to the driving motor by means of a $\frac{1}{4}$-inch leather belt.

The receiving cup is made of tin and is $5\frac{1}{2}$ inches in diameter and 5 inches high. The bottom of the cup is conical and made so that it fits snugly over the shaft casing below but not touching the lower disk, as shown in Fig. 1. The interior surface of the cup is perfectly smooth, any crevices
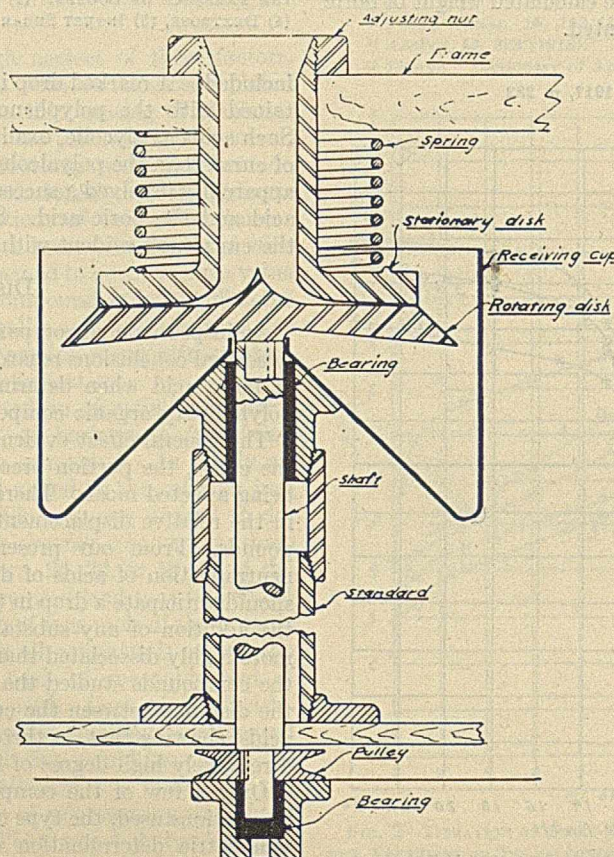
FIG. 1—A CROSS SECTION OF THE MILL SHOWING DISKS, ADJUSTING MECHANISM, RECEIVING CUPS, AND DRIVING SHAFT
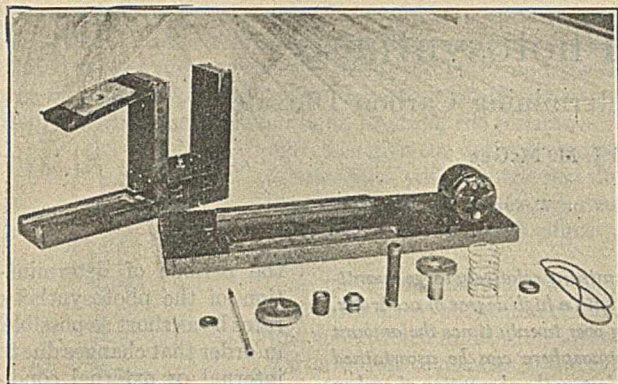
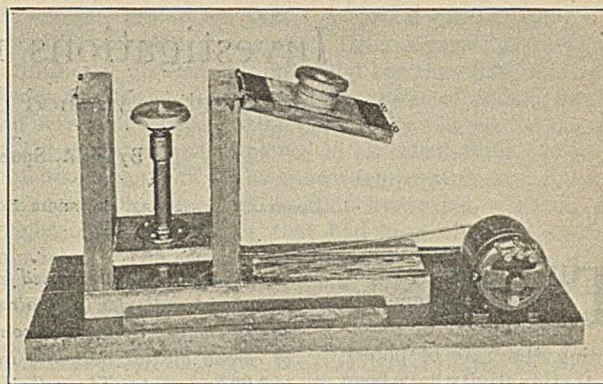FIG. 2—THE MILL DISMANTLED SHOWING ALL PARTS EXCEPT THE
RECEIVING CUP



FIG. 3—THE MILL OPEN FOR CLEANING

being filled with solder. This facilitates cleaning. The receiving cup and lower disk are removable and the upper disk is held in place by a hinged crosspiece on the frame. An adjusting nut at the top of the stationary disk permits regulation of the distance between the plates, and a strong spiral spring imparts the necessary pressure to the grinding surfaces. The framework is constructed of wood 2 inches thick, except for the hinged member carrying the upper disk, which is $1^1/_2$ inches thick. When assembled the



FIG 4—THE MILL COMPLETE AND READY FOR GRINDING

mill and frame are $17^1/_4$ inches thick and 25 inches long. (Figs. 2, 3, and 4.) The upper disk is screwed on to a piece of 1-inch pipe, which provides means for both mounting the disk and charging the mill.

The finely ground material is whirled from the rotor to the receiving cup, from which it can be drawn off through the drain pipe to a beaker or flask. If the particles in the original material are large, it is advisable to adjust the disks some distance apart at first and pass the suspension through several times, bringing the disks closer together after each pass. By this treatment a very fine suspension can be ob-

per. A 50-gram sample of the ground material is suspended in about 200 cc. of boiling water and passed through the mill as many times as necessary. In the case of raisins three times will usually suffice.

The disks and receiving cup are then washed with successive additions of warm water while the mill is running, until all materials are washed into the receiving beaker or flask. The suspension and washings are cooled in running water and made up to 500 cc. volume at 20° C. If analyses are not to be made immediately, four or five drops of toluene should be added to prevent the development of molds.

A few drops of the raisin suspension are then placed between the prisms of an Abbé refractometer and the refractive index of the solution is read. By the use of Chart 1 it is possible to read the percentage of reducing sugars present with a reasonable degree of accuracy. Determinations can be made by this method in less than 20 minutes.

### ACKNOWLEDGMENT
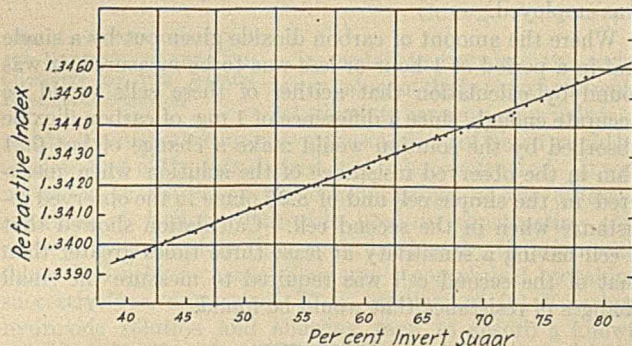
CHART 1—RELATION OF REFRACTIVE INDEX TO CONCENTRATION OF RE-
DUCING SUGARS IN RAISIN SOLUTIONS PREPARED BY THE COLLOID MILL

tained in a surprisingly short time. The resulting suspension can then be subjected to any analytical procedure desired.

### DETERMINATION OF RAISIN SUGARS

To insure uniform sampling and facilitate grinding, about 200 grams of raisins are passed through an ordinary food chop-

## French Physical Society Anniversary

The semicentennial of the organization of La Société Française de Physique was celebrated in Paris, December 10 to 15, by a series of lectures by distinguished physicists given in the Amphitheatre de Physique at the Sorbonne, and by other functions. The most interesting lectures were by Lorenz on "The New Mechanics;" Lord Rayleigh on "Iridescence;" Stormer on "The Aurora Borealis;" and by Knudsen on "The Mechanism of Evaporation and Condensation." On Wednesday evening, the 12th, there was an elegant banquet at which several hundred physicists from the principal countries of Europe were present. Thursday afternoon, the 13th, there was a "Séance Solennelle" in the Grand Amphitheatre of the Sorbonne, with Alexandre Millerand, President of the Republic, in the chair. On this occasion, in addition to addresses on the history of the society, there was an address by Charles Fabry on "Explorations in the Field of Radiation."

An exposition of physics in the Grand Palais, which was originally planned to last for two weeks, proved to be so popular that it was continued for a third week. The exposition contained both scientific and commercial exhibits from all fields of physics, the exhibition of electrical apparatus being especially prominent.

The entertainment of delegates to this celebration was provided for with true French hospitality.—W. A. NOYES

# Investigations in Photosynthesis[1]

## An Electrometric Method of Determining Carbon Dioxide

By H. A. Spoehr and J. M. McGee

Coastal Laboratory, Carnegie Institution of Washington, Carmel, Calif.

T HE methods which have been generally employed for determining the rate of photosynthetic activity have been based upon three principles: (1) the liberation of oxygen, (2) the absorption of carbon dioxide, and (3) the formation of organic substance. While the use of each of these principles possesses certain definite advantages in interpreting the phenomenon of photosynthesis, they are not all of them amenable to the same degree of accuracy and ease of application. On account of the fact that in determining photosynthetic rates it is essential that consideration be also given to the rates of respiration, it has been found that a method based upon the differential determination of the concentration of carbon dioxide in the medium surrounding the plant affords the easiest, as well as the most accurate, method of determining the rate of carbon dioxide fixation by the plant. This does not imply that it is the only method which should be employed in the study of the photosynthetic process; in fact, data obtained by means of the other principles are of equal significance in gaining a clearer conception of the mechanism of the process. However, the determination of carbon dioxide can be accomplished with greater accuracy and ease than of either oxygen or the synthesized products.

*A method has been devised for determining relatively large quantities of carbon dioxide in an air stream with a high degree of accuracy, so that changes in a stream containing over twenty times the amount of carbon dioxide normally in the atmosphere can be ascertained to 0.002 per cent. The method is based upon the absorption of carbon dioxide in barium hydroxide solution and the determination of the change in concentration of the latter through electrical resistance measurements. The necessary precautions and apparatus are described as well as the mode of constructing a resistance-concentration curve by using, instead of standard hydrochloric acid, the carbon dioxide in the atmosphere. The latter thus served as a very dilute solution of carbon dioxide of known concentration of which carefully measured volumes were used to standardize the barium hydroxide solution.*

### Principle of Method

The general principle of the electrometric determination of carbon dioxide, as used in this laboratory, has already been described;[2] it has since been amplified and improved to yield more accurate results, so that 0.002 per cent of carbon dioxide by volume can be determined with certainty. The method is based upon the absorption of the carbon dioxide in an air stream by means of barium hydroxide, and the determination of the strength of the barium hydroxide solution from its electrical conductivity. As first devised, the method was used for determining the carbon dioxide emission from an entire plant or a larger number of leaves; it has since been perfected so that the carbon dioxide exchange of a single excised leaf can be determined with a high degree of accuracy.

### Precautions Necessary

In employing the method of differential determinations of carbon dioxide for determining photosynthetic activity, a number of factors must be given careful consideration. For reasons which have already been discussed,[3] when working with land plants it is advantageous to use a single excised leaf. Moreover, it is desirable that the carbon dioxide concentration of the air be increased five to twenty times that of normal air. On the other hand, it is essential that the periods of determination of the photosynthetic rates be as short as possible, in order that changes due to internal or external conditions can be detected readily. But the amount of carbon dioxide given off or fixed by a single leaf in as short a period as, say, 15 minutes, is exceedingly small. The problem then resolves itself into absorbing so completely the relatively large amounts of carbon dioxide in the air stream that the very slight differences in the carbon dioxide exchange of the leaf can be determined with sufficient accuracy. It is therefore necessary to adjust several factors in the experimental procedure so that the differences in the rate of photosynthesis and respiration fall within the experimental error of the method.

It is necessary to have the volume of the absorbing solution and the measurements of the resistance commensurate with the accuracy required. When a relatively large amount of carbon dioxide is to be absorbed, as is the case when the periods of determination are long and several leaves are used in the respiration chamber, 125 cc. of 0.12 N barium hydroxide solution and a simple cell consisting of a wide-mouthed glass vessel with dip electrodes can be used. Such a cell, described in a former report,[4] had a cell constant of 1.284 at 25° C. and had an observed resistance of 96.6 ohms when filled with 0.1 N potassium chloride solution.

When the carbon dioxide emitted or absorbed by a single leaf during a period of 2 or more hours was to be measured, a pipet-shaped cell,[5] the observed resistance of which was 1940 ohms at 25° C. and which had a cell constant of 25.026, was employed.

Where the amount of carbon dioxide given out by a single leaf in a period of 1 hour or less was to be measured, it was found by calculation that neither of these cells would be accurate enough, since a difference of 1 mg. of carbon dioxide absorbed by the solution would make a change of but 0.21 ohm in the observed resistance when measured in the simple cell and of 8.26 ohms in the observed resistance when in the second cell. Calculation showed that a cell having a sensitivity at least three times greater than that of the second cell was required to measure the small changes of resistance that would be found.

### Apparatus

The accuracy of this method is limited by the accuracy with which the resistance of the solution can be determined. The most convenient source of current is the commercial 110-volt, 60-cycle alternating current, and a very convenient combination set-up of bridge and dial resistance boxes with

[1] Received September 12, 1923.
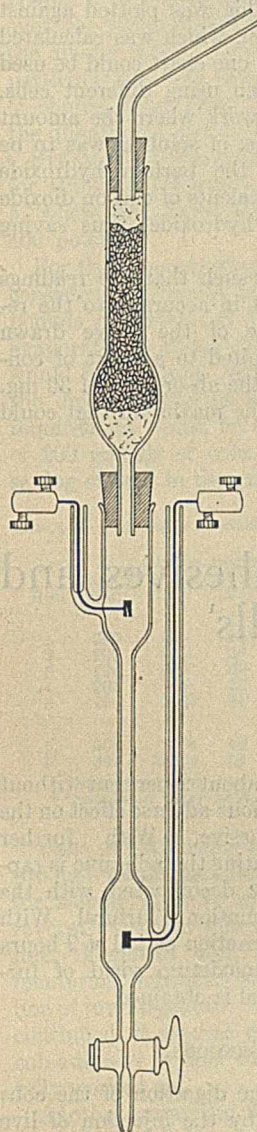[2] Spoehr and McGee, *Carnegie Inst. Pub.*, **325**, 28, 89 (1923).
[3] *Ibid.*, **325**, 22 (1923).
[4] *Carnegie Inst. Pub.*, **325**, 28 (1923).
[5] *Ibid.*, **325**, 89 (1923).

galvanometer can be obtained for such a current. The sensitivity of an electrolytic cell is proportional to its resistance limited by the accuracy of the resistance boxes and the degree of polarization and self-induction set up in the system used. With these considerations in mind, the resistance required to give the desired accuracy for the work with a single leaf during short periods was found, when calculated, to be 6000 ohms or more.

A cell having this resistance when filled with 0.1 $N$ potassium chloride was constructed and tested to see if the errors due to polarization or self-induction were too large to be negligible. Since these errors were found to be very small, a cell was devised that would have this resistance and yet would not require a large volume of solution and that could be filled without exposing the solution to the carbon dioxide of the air. A pipet-shaped cell of 30-cc. capacity having two bulbs was found to meet all these requirements better than any other form in common use. The bulbs of such a cell served as the electrode chambers. The electrodes (0.25 sq. cm. in area) must be small in order to give the desired resistance. These were placed with the flat side vertical so that air bubbles which might form in the solution did not collect on the electrodes and change the resistance. Errors due to this last cause may be minimized by warming the solution to be tested to the temperature of the thermostat before filling the cell. The pipet cell was fitted with a glass stopcock in the inlet tube and with a soda lime tube fitted into the upper bulb to protect the solution from the carbon dioxide of the air.

### RESISTANCE-CONCENTRATION CURVE

In order to translate the resistance values of the barium hydroxide solution into concentration values, a resistance concentration curve, the accuracy of which would be equal to that of the data desired, had to be constructed. It was necessary to determine the concentrations of the different solutions of barium hydroxide used in constructing this curve more accurately than could be done by titration with dilute hydrochloric acid. This was accomplished by taking successively a number of 75-cc. portions of 0.1 $N$ barium hydroxide solution and allowing each to absorb a known quantity of carbon dioxide, permitting the barium carbonate to settle out, and determining the resistance of the clear supernatant solution at 25° C.

When attempting to measure a quantity of carbon dioxide of less than 10 mg. it was found imperative that all containers for the barium hydroxide solution be free of carbon dioxide. In all this work the absorption tubes, sample bottles, pipet, etc., were swept free of carbon dioxide, before being used, by a stream of air passed through soda lime. The work



FIG. 1—ELECTROLYTIC CELL FOR DETERMINING THE CONDUCTIVITY OF THE BARIUM HYDROXIDE SOLUTION

of Benedict[6] has shown that the carbon dioxide content of dry air is remarkably constant. His analysis of dry air from various open air sources differed by less than 0.002 per cent. Hence air was used as a constant source of carbon dioxide and his average value of 0.031 per cent by volume, the average of 212 analyses, was employed in all calculations. When a measured volume of air at known temperature and pressure was drawn through the barium hydroxide solution, the weight of carbon dioxide that had been absorbed could be calculated. The atmosphere was thus used as a very dilute solution of carbon dioxide of known concentration, each liter of which, when dry, contains 0.6076 mg. of carbon dioxide.

TABLE I—SPECIFIC RESISTANCE OF VARIOUS CONCENTRATIONS OF BARIUM HYDROXIDE SOLUTIONS AT 25° C. WITH THE CARBON DIOXIDE EQUIVALENT OF 75 Cc. OF THE SOLUTION

| Volume of Water Displaced Liters | Volume of Dry Air at 0° C. and 760 Mm. Liters | Weight of $CO_2$ in Dry Air Grams | $CO_2$ Equivalent of 75 Cc. of Ba (OH)$_2$ Solution Grams | Specific Resistance Ohms |
|---|---|---|---|---|
| 0 | 0.0000 | 0.000000 | 0.176938 | 46.893 |
| 2 | 1.7534 | 0.001065 | 0.175873 | 47.157 |
| 3 | 2.6502 | 0.001610 | 0.175328 | 47.320 |
| 3 | 2.6273 | 0.001596 | 0.175342 | 47.307 |
| 5 | 4.4086 | 0.002678 | 0.174260 | 47.601 |
| 10 | 8.8300 | 0.005365 | 0.171573 | 48.272 |
| 15 | 13.2940 | 0.008077 | 0.168861 | 49.001 |
| 15 | 13.2550 | 0.008054 | 0.168884 | 49.050 |
| 20 | 17.9030 | 0.010878 | 0.166060 | 49.627 |
| 25 | 22.3910 | 0.013605 | 0.163333 | 50.404 |
| 30 | 26.8440 | 0.016311 | 0.160627 | 51.051 |
| 35 | 31.2960 | 0.019016 | 0.157922 | 51.864 |
| 40 | 35.844 | 0.021779 | 0.155159 | 52.782 |
| 45 | 40.428 | 0.024564 | 0.152374 | 53.723 |
| 50 | 44.843 | 0.027247 | 0.149691 | 54.690 |

The apparatus by which a measured volume of air could be drawn through barium hydroxide solution consisted of ten-bulb absorption tubes, the air entering the solution through narrow tubes inserted in the lower end of the absorption tubes. The latter were filled with 75 cc. of the barium hydroxide solution and air was drawn from out of doors by means of a Mariotte bottle aspirator. The rate at which the air was drawn through the apparatus was regulated by means of a needle valve. The water from the outlet tube of the aspirator was collected and its volume measured, in order that the volume of air that had entered the aspirator might be known. A water-filled pressure gage attached to the aspirator permitted the air pressure inside to be measured, and the temperature was determined from a thermometer placed beside the bottle. The determinations with volumes of air greater than 15 liters were made in an underground constant-temperature room in which the temperature varied but 0.9 degree during the entire time the determinations were being carried out. The contents of the absorption tube, when the desired volume of air had been drawn through,

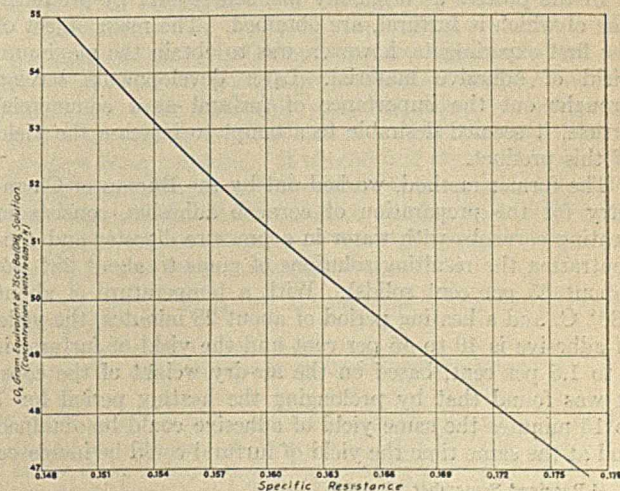[6] Benedict, *Carnegie Inst. Pub.*, **166**, 114 (1912).



FIG. 2—SPECIFIC RESISTANCE CURVE OF BARIUM HYDROXIDE USED IN CARBON DIOXIDE DETERMINATIONS

were immediately transferred to a sample bottle free of carbon dioxide and sealed with paraffin until the resistance could be determined. Thus the temperature, pressure, and weight of carbon dioxide absorbed from each volume of air were calculated and the specific resistance determined, as shown in Table I.

As examples of the accuracy of this method, two determinations of the carbon dioxide in 3 liters of air showed a difference of 0.05 mg. carbon dioxide and two determinations of the amount in 5 liters of air a difference of 0.11 mg. carbon dioxide. These differences are equivalent to a difference of 0.001 per cent by volume of carbon dioxide in the determinations, an order of accuracy equal to that obtainable with the Sonden air analysis apparatus, hitherto the most accurate devised. Using the cell with a cell constant of 85.204, a difference of 1 ohm in the observed resistance of the barium hydroxide solution, when calculated as specific resistance, was equal to 0.45 mg. carbon dioxide on the middle portion of the curve. Hence a milligram of carbon dioxide when absorbed would change the observed resistance of the solution 21.7 ohms. Since the change of resistance with concentration is not linear, an ohm will have a slightly

different equivalent value in milligrams of carbon dioxide on different portions of the curve.

From the data so obtained, knowing the original concentration of the solution, the carbon dioxide gram equivalent of each 75-cc. portion, after the desired volume of air had been drawn through, was calculated. This was plotted against the specific resistance of the solution, which was calculated from the observed resistance so that one chart could be used to translate the data obtained when using different cells. Since the curve was to be used in work where the amount of carbon dioxide absorbed by 75 cc. of solution was to be determined, the concentration of the barium hydroxide solution was expressed in gram equivalents of carbon dioxide instead of equivalents of barium hydroxide, thus saving much labor in calculating results.

The data were plotted on a scale such that the readings from the chart would be equivalent in accuracy to the resistance measurements. The range of the curve drawn through the points so plotted is limited to a chart of convenient size. A curve allowing for the absorption of 30 mg. of carbon dioxide was found to be the maximum that could be drawn with accuracy.

# The Simultaneous Production of Pentosan Adhesives and Furfural from Corncobs and Oat Hulls[1]

By Frederick B. LaForge

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

*This article describes in detail the process worked out at the Bureau of Chemistry experimental plant for the production of pentosan adhesives and furfural from corncobs and oat hulls. The yields of the two products from both of the raw materials were determined, as well as the steam consumption, time of the reaction period, and the proper proportion of water to raw material.*

*Special reference is made to the use of pentosan adhesives for briquetting anthracite coal.*

PENTOSAN adhesives are thick solutions of gums obtained by extracting various materials, such as corncobs and oat hulls, with superheated water and concentrating the extract. Previous reports on this subject by the Bureau of Chemistry have not described the process in detail.[2] Owing to the simplicity of the method used and the easy availability of the raw materials, these adhesives can be manufactured at a comparatively low cost.

In the process as originally planned several by-products, one of which is furfural, are obtained. The main object of the first experiments, however, was to obtain the maximum yield of adhesive material. Later developments having brought out the importance of furfural as a commercial article, it seemed desirable to attempt to increase the yield of this product.

The former method, worked out by the Bureau of Chemistry for the preparation of corncob adhesive, consists in heating corncobs with water in a pressure digester and concentrating the resulting solutions of gums to about 28° Bé. (about 65 per cent solids). With a temperature of about 180° C. and a heating period of about 28 minutes, the yield of adhesive is 40 to 45 per cent and the yield of furfural is 1 to 1.5 per cent, based on the air-dry weight of the cobs. It was found that by prolonging the heating period for 7 to 15 minutes the same yield of adhesive could be obtained and at the same time the yield of furfural could be increased

to about 2 per cent without serious adverse effect on the adhesive. With further heating the adhesive is rapidly decomposed, with the formation of furfural. With a reaction period of 2 hours a maximum yield of furfural is obtained.

## ADHESIVES FROM CORNCOBS

SEMICOMMERCIAL PLANT[3]—For the digestion of the cobs a cylindrical steel digester, heated by the injection of live steam, was employed. The average charge consisted of about 200 pounds of cobs and 850 pounds of water at room temperature, or 950 pounds when hot water was used. At the end of the heating period the pressure was relieved by blowing off through a condenser, after which the contents of the digester were discharged by means of a valve into a drain box. The solid residue was then further freed from the absorbed liquor by means of a hydraulic press. As a rule the press cake was moistened with water and the pressing operation was repeated. The discharge and wash liquors were evaporated to the proper consistency in an open steam-jacketed kettle.

Most of the furfural formed in this process was found in the condensed blow-off vapors, the furfural content of the distillates varying from 0.75 to 1.00 per cent. A large part of the total quantity produced, however, was found in the discharge liquor in about 0.1 per cent concentration. This fraction was determined by analysis, but was not generally isolated. In commercial practice, the portion contained in the discharge liquor would be recovered as a weak solution

[2] THIS JOURNAL, 10, 925 (1918); U. S. Patent 1,285,247 (November 19, 1918); *Chem. Age* (*N. Y.*), 28, 332 (1920).
[3] THIS JOURNAL, 15, 823 (1923).

and used in a subsequent charge. The quantity of furfural contained in the liquor remaining in the press cake was practically negligible.

Data from several typical runs are given in the table. In some cases the adhesive was evaporated to concentrations greater or less than 28° Bé. Calculated to this figure, however, the yields varied from 41 to 44 per cent of the weight of the air-dry cobs. The quantity of steam consumed for any particular run may be calculated by subtracting the quantity of charge water from the quantity of discharge liquor plus the quantity of distillate obtained.

▶ STEAM CONSUMPTION—The quantity of steam required for Runs 1 to 4 was approximately 500 pounds. For Run 5, where hot water was used, the requirement was about 400 pounds.

For the concentration of the discharge liquor to the proper consistency it would be necessary to evaporate about 1000 pounds of water. If the liquor were fed to a single-effect evaporator at about 70° F., approximately 1,120,000 B. t. u. would be required. Since the average heat requirement for the digestion process is around 500,000 B. t. u., the total requirement would be about 1,700,000 B. t. u. for a charge of 200 pounds of cobs. This is assuming that there is no saving of heat in the process.

TABLE I—ADHESIVE-FURFURAL RUNS USING CORNCOBS AND OAT HULLS

| Run | Material Lbs. | Charge Water Lbs. | Heating Period Min. | Discharge Liquor Lbs. | Distillate Lbs. | Yield of Adhesive of 28° Bé. Lbs. | Per cent | Yield of Furural[b] Per cent |
|---|---|---|---|---|---|---|---|---|
| | | | | *Corncobs* | | | | |
| 1 | 200 | 865 | 28 | 1171 | 200 | 88 | 44 | 1.50 |
| 2 | 200 | 865 | 28 | 1200 | 175 | 86 | .43 | 1.16 |
| 3 | 196 | 865 | 32 | 1172 | 196 | 88 | 45 | 1.35 |
| 4 | 203 | 865 | 35 | 1155 | 195 | 85 | 42 | 1.81 |
| 5 | 200 | 950[a] | 43 | 1090 | 270 | 82 | 41 | 2.04 |
| | | | | *Oat Hulls* | | | | |
| 6 | 200 | 930[a] | 43 | 1093 | 230 | 122 | 61 | 0.73 |
| 7 | 202 | 1000[a] | 52 | 1179 | 247 | 112 | 55 | 1.00 |

[a] Temperature of charge water, 90° C.
[b] Calculated from analysis by phloroglucinol method.

USES OF THE ADHESIVE—It was expected that the corncob product would find its principal application as a substitute for silicate of soda in pasting fiber container board, and several mill runs were made to test its adaptability in this line. Facilities were not available for systematic experimentation, however, and it was impossible to continue this line of investigation. Up to the time when the work was discontinued, it seemed probable that the application of corncob adhesive in fiber container manufacture could be successfully worked out.

Another promising field for this material seemed to be in its use as a substitute for cheaper grades of glue and dextrin in lines where appearance and strength were not of first importance. Thus it would probably be suitable as an adhesive for certain types of paper bags, cartons, etc. Corncob adhesive has also been used with some success as a wall-sizing material. Still another use which suggests itself is that of a foundry core-binder.

The most promising field for this adhesive, however, has been opened up recently in its application as a binder in the manufacture of anthracite coal briquets. In the now rapidly expanding briquet industry, the culm and other fines resulting from the grading and screening of the more easily marketable sizes of anthracite coal are compressed with automatic machinery into briquets. In this process various binders are used, pitch being the one most widely employed. After the briquets are molded they are usually subjected to heat treatment to remove the volatile constituents. The requirements for an ideal briquet are as follows: They must be waterproof and practically odorless and dustless; they must not contain large quantities of ash and sulfur; and they must not soften under heat. The binder must be cheap and available in large quantities. For briquets for domestic use none of the binders now employed are entirely satisfactory.[4]

Experiments made by a commercial concern in coöperation with the bureau indicate that a binder consisting largely of corncob adhesive will meet all the desired conditions if it can be produced cheaply enough to enable it to compete with those now in use.

BY-PRODUCTS AND THEIR USES—If adhesive alone were manufactured by the process worked out in this bureau, its cost would probably be somewhat too high to permit its use in this industry. It seems probable, however, that with a market for the by-product, furfural, produced in the manufacturing process, the cost of adhesive could be reduced to the point where its employment in this field could be considered.

The cellulosic residue resulting from the digestion of cobs under the conditions described is usually delivered by the press with a moisture content of about 60 per cent, and about 125 pounds, calculated as dry material, are produced from 200 pounds of cobs. In the dry state it has a B. t. u. value of about 9000. Thus in commercial practice the residue, if used for fuel for the process, will furnish a very substantial part of the heat requirement.

Several other uses for this material have been worked out. For instance, a satisfactory substitute for wood flour and a short fiber pulp can be prepared from it by extracting with weak caustic soda solution.[5] Promising results have also been obtained by using the untreated residue for the manufacture of wood substitutes and of wall board.[6]

A small quantity of acetic acid is obtained in the digestion process, but it is doubtful whether it would pay to recover it.

### ADHESIVE FROM OAT HULLS

Although the quantity of oat hulls produced in the United States is very much less than the quantity of corncobs, this material is an important source of adhesive and furfural. Large quantities of hulls are produced at oatmeal factories, where their disposal is often a problem. The process employed for the treatment of oat hulls is practically identical with that used for corncobs.

The yield of adhesive from oat hulls is greater than that obtained from corncobs. (Runs 6 and 7 of the table.) On the other hand, the yield of furfural is much smaller. The yield of adhesive given in the table is the quantity actually obtained on evaporation of the total extract recovered. In general, the pentosans from oat hulls seem to be more resistant to the action of superheated water than those resulting from the treatment of corncobs under the same conditions. The steam consumption is the same for the treatment of oat hulls as for corncobs.

PROPERTIES AND USES OF OAT HULL ADHESIVE—The concentrated extract obtained from the digestion of oat hulls resembles very closely the product obtained under the same conditions from corncobs. Oat hull adhesive, however, is somewhat lighter in color and is less hygroscopic than the product from corncobs. It should find the same application as corncob adhesive and should offer some advantages over that material for fiber container pasting and similar uses. Oat hull adhesive seems to be the equivalent of corncob adhesive in coal briquet manufacture.

[4] Briquetting Circular No. 1, Vulcan Iron Works, Wilkes-Barre, Pa., 1922, p. 2.
[5] *Chem. Age* (*N. Y.*), **28**, 334 (1920).
[6] Gruber and Bashioum, U. S. Patent 1,427,378 (August 29, 1922).

Robert A. Millikan, chairman of the executive board of the California Institute of Technology, who recently received the Nobel Prize in physics, has been awarded the Hughes Medal by the Royal Society of London in recognition of his work on the determination of physical constants.

# The Interfacial Tension between Petroleum Products and Water[1]

By E. M. Johansen

New England Oil Refining Co., Fall River, Mass.

THE well-known drop method was employed for determination of the interfacial tension, partly on account of its connection with the original problem and also because it was found to have certain advantages over other methods, especially in the case of viscous oils. The Donnan[1],[*] pipet was first tried, but was found to be unsatisfactory in a number of cases. Special forms of apparatus were constructed by using materials readily available in a laboratory, and were used in a series of experiments, during which several hundred determinations were made with a satisfactory degree of accuracy.

*The author once had occasion to estimate the number of drops that were formed when equal volumes of various kinds of cylinder oils were passed through an ordinary Detroit sight feed lubricator. This led to an investigation of the interfacial tension relations between oil and water and aqueous solutions, which proceeded intermittently from 1915 to 1922. During this time numerous data were collected and the relations between interfacial tension and a number of other subjects were studied. The following is a short review of some of the results of this work.*

## Apparatus and Procedure

One type of apparatus was designed for determination of the mass of a drop of water falling through a body of oil. In a second type of apparatus drops of oil were allowed to rise through a body of water. The first type was used in the case of clear, transparent oils, while the second type served for the examination of turbid, nontransparent oils. The two types of apparatus are constructed and operated in the following manner:

In the first apparatus (Fig. 1) drops of water are allowed to form at the lower end of a tip of glass or Monel metal, perforated by a capillary orifice. The lower plane of the tip, at which the drop is formed, is circular and has a sharp and true edge. The tip is firmly fastened in a double rubber stopper, which serves as connection between a lower bulb containing some water and the oil to be tested, and an upper bulb containing water. The surface of the oil in the lower bulb is set level with a mark on the bulb. The water from the upper bulb is allowed to enter the oil and forms drops in the oil at the lower surface of the tip, the speed of formation of the drops being regulated by a stopcock at the top of the upper bulb. The drops, upon falling from the tip, are counted, and the water accumulating in the lower bulb is drawn off by a tube and clamp into a graduated cylinder. When a sufficient number of drops have been drawn off, the surface of the oil in the lower bulb is set level with the mark. The volume of one drop is found by dividing the total volume of water drawn off by the number of drops.

The diameter of the lower plane of the tip should be accurately determined. The formation of the drops should take place at a slow rate, as too high results will be obtained if the drops are allowed to form too rapidly. When using a glass tip of 4 to 5 mm. diameter, 1 minute or slightly less should be required for the formation of one drop in the case of oils having a viscosity of 270 seconds (Saybolt Universal at 37.78° C.) or higher. Two drops per minute are found satisfactory for oils of lower viscosity, while for oils of very low viscosity (kerosene, gasoline) a rate of three to four drops per minute will be right. The apparatus is placed in a water bath, the temperature of which can be regulated.

The second apparatus (Fig. 2) consists of two glass bulbs connected by a U-tube by means of two rubber stoppers. One end of the tube is ground so as to have an opening with a true and sharp inner edge. The diameter of this opening is carefully measured. The oil to be tested is placed in the upper bulb, while the lower bulb is about half filled with water, in which the calibrated end of the U-tube is immersed. By applying suction to the bulb containing the water, drops of oil are formed at the calibrated end of the tube, below the water, and rise through this. The drops are counted, and the total volume of oil drawn into the water bulb is measured by aid of a pipet attached to the oil bulb, and into which is drawn a volume of water or other liquid equal to the total volume of the drops. The rate of formation of drops should be one to two drops per minute in the case of viscous oils, or three to four drops per minute in the case of kerosene or gasoline, when the diameter of the orifice where the drops are formed is between 3.5 and 7.5 mm. The whole apparatus is placed in a water bath.

The first apparatus is more easily operated than the second, which also in some cases requires the introduction of correction factors for the temperature of the air and for the vapor tension of the material under examination, as, for instance, in the case of gasoline.

After the volume of one drop is found by aid of either of the foregoing methods, the mass of one drop is calculated, using in this calculation the difference between the specific gravity of water and the specific gravity of the oil, both measured at the experimental temperature, for transforming the volume into weight. It is remarkable that several experimenters[2],[3] have neglected this necessary calculation, assuming that the interfacial tension is proportional to the volume of the drops.

From the mass of the drop the interfacial tension is calculated. The method first followed was that recommended by Morgan[4]—i. e., calibrating the tips by examining a liquid of known interfacial tension (such as benzene) towards water, and calculating from the results a factor for each tip. When using this method, however, it was found that the values obtained by the two apparatus did not agree in the case of oils having a tension or a specific gravity considerably different from those of benzene. After partially successful attempts to overcome this difficulty, the method described by Harkins and Brown[5] was tried and found to give excellent results. This method takes into consideration the relation between the dimensions of the tip and those of the drop, and produces the means of calculating the mass of an *ideal* drop—i. e., a drop which would fall from a tip if the volume of the drop were proportional to the circumference of the tip. The development of this method, as well as other important matter in connection with interfacial tension, is fully described in the articles by Harkins and his students.[6]

## Results

The results of comparative determinations of the interfacial tensions between various oils and petroleum products and water when using both forms of apparatus are given in Table I. Satisfactory agreement between the results obtained when using both forms of apparatus will be found in the case of oils that contain or produce no water-soluble substances adsorbable at the interface, if the drops are allowed to form sufficiently slowly and at the same rate of speed. If water-

[1] Presented before the Division of Petroleum Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[*] Numbers in text refer to bibliography at end of article.

soluble adsorbable matter is present or formed, the second apparatus will give somewhat lower results than the first, on account of contamination of the water through which the drops of oil must rise.

The interfacial tensions between a number of representative petroleum products and water are given in Table II.
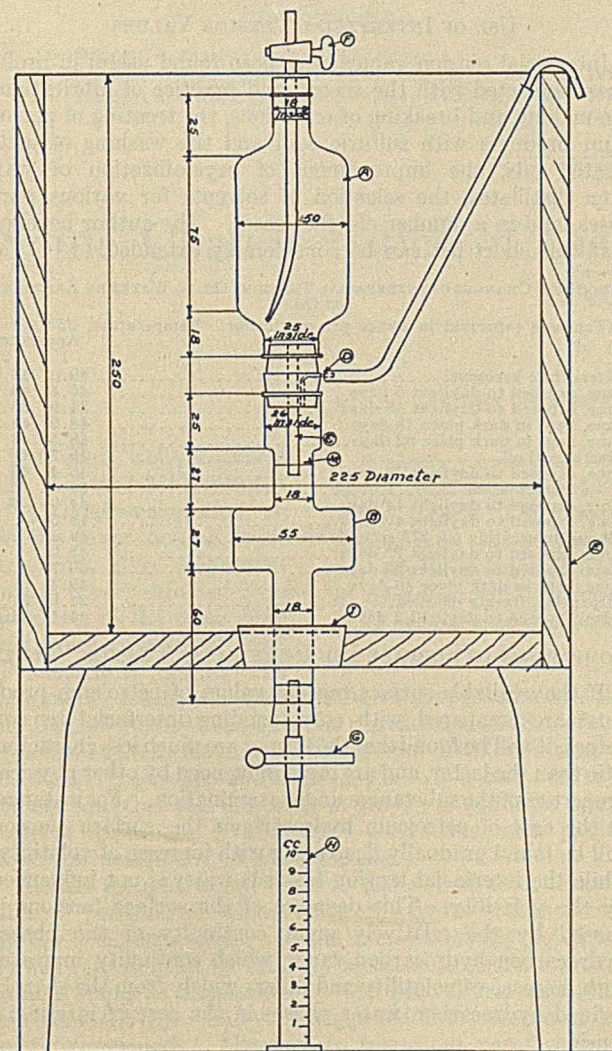


Fig. 1

*A* = bulb for water; *B* = bulb for oil; *C* = tip; *D* = air escape; *E* = water bath; *F* = glass stopcock; *G* = pinchcock; *H* = graduate; *I* = rubber stopper; *M* = mark. Dimensions are given in millimeters.

Increase in temperature causes a decrease in the interfacial tension between oil and water. This decrease varies considerably in the case of different materials, as may be noticed in Table III.

Relatively few data referring to the interfacial tension between water and petroleum products are found in the literature,[7] and still less is published about the practical applications of the values found by measuring the tension.[8] There are, however, many cases in which the determination of the interfacial tension between water and oil will be found of value. While this determination seldom will be found useful as a routine test, it will often give interesting and important information in research work.

The value of the interfacial tension between two immiscible liquids is generally very much influenced by small additions of substances that are adsorbed at the interface. A variation of the interfacial tension from the normal value is thus a very good indication of the presence of such substances. For instance, the presence in petroleum products of small amounts of organic acids, which cannot be demonstrated by ordinary analytical methods, may readily be proved by determination of the interfacial tension between the oil and the water, and oil and a dilute solution of alkali. The value of the latter tension will be found very much lower than the former, if acids are present. It was also readily proved by this method that petroleum hydrocarbons, exposed to light in a partly filled bottle, will change quite rapidly with the formation of adsorbable acid products. If not exposed to light very little change, or none at all, will take place. It is interesting to note that very highly refined petroleum products, such as white medicinal oils, which do not absorb bromine or iodine and thus apparently are fully saturated, change rapidly. Examples of the changes are given in Table IV.

TABLE I—COMPARATIVE DETERMINATIONS OF INTERFACIAL TENSIONS
(Tensions expressed in dynes per centimeter. Temperature, 25° C. (77° F.))

| | | 1 | 2 |
|---|---|---|---|
| Benzene | | 34.2 | 34.0 |
| Motor gasoline | | 38.9 | 38.7 |
| Mineral spirits | | 42.6 | 42.0 |
| Water-white kerosene | | 48.5 | 48.7 |
| Mineral seal oil | | 49.7 | 49.5 |
| Nonviscous lubricating oil | | 51.6 | 50.9 |
| Lubricating oil, filtered | 95 seconds viscosity | 53.4 | 54.0 |
| | 135 seconds viscosity | 54.3 | 53.9 |
| White medicinal oil | | 55.0 | 55.3 |
| Turpentine | | 14.1 | 14.8 |
| Turpentine, freshly distilled | | 21.1 | 21.2 |
| Oil of eucalyptus | | 15.1 | 15.1 |
| Prime lard oil | | 20.2 | 19.8 |
| Hexadecylene ("Cetene") | | 50.1 | 50.3 |
| | 95 seconds viscosity and 1% oleic acid | 30.1 | 30.0 |
| | 95 seconds viscosity and 10% oleic acid | 17.2 | 18.0 |
| | 95 seconds viscosity and 10% lard oil | 27.6 | 26.8 |
| Lubricating oil | 220 seconds viscosity | 47.3 | 47.0 |
| | 220 seconds viscosity and 1% copper oleate | 30.3 | 31.0 |
| | 220 seconds viscosity and 2.5% blown cottonseed oil | 19.9 | 20.5 |
| Red paraffin oil, 275 seconds viscosity | | 38.9 | 38.7 |

An interesting fact was observed by aid of the determination of the interfacial tension—i. e., that when xylene and petroleum naphtha having the same boiling points were mixed and the mixture was filtered through fuller's earth, the first fraction of filtrate was free from xylene, the latter apparently being adsorbed by the earth. The fraction obtained was too small to be examined by the ordinary methods, but when examined as to its interfacial tension it was found that, instead of the relatively low tension of the original mixture, the fraction showed the high tension of the naphtha used in preparing the mixture.

Petroleum oils of high viscosity are often used as viscosimetric standards, as, for instance, in the determination of the relations between absolute or kinematic viscosity de-

TABLE II—INTERFACIAL TENSIONS BETWEEN WATER AND PETROLEUM PRODUCTS

| | | Apparatus | Temperature °C. | Dynes per Cm. |
|---|---|---|---|---|
| Pentane | | 1 | 25 | 50.3 |
| 72 Bé. solvent | | 1 | 25 | 48.5 |
| Straight run gasoline | | 1 | 25 | 50.5 |
| Cracked gasoline | | 1 | 25 | 44.8 |
| Mineral spirits (55 Bé.) | | 1 | 25 | 49.8 |
| Turpentine substitute | | 1 | 25 | 47.5 |
| Water-white kerosene | | 1 | 25 | 48.0 |
| Mineral seal oil | | 1 | 25 | 47.5 |
| Paraffin oil | 100 seconds viscosity | 1 | 25 | 41.7 |
| | 275 seconds viscosity | 1 | 25 | 42.5 |
| Lubricating oil | filtered, 150 seconds viscosity | 1 | 25 | 47.5 |
| | filtered, 200 seconds viscosity | 1 | 25 | 52.8 |
| | filtered, 275 seconds viscosity | 1 | 25 | 49.2 |
| | (California) 260 seconds viscosity | 1 | 25 | 33.2 |
| | (California) 600 seconds viscosity | 1 | 25 | 39.7 |
| Cylinder oil | unfiltered | 2 | 65.6 (150° F.) | 28.5 |
| | filtered | 1 | 51.7 (125° F.) | 47.5 |
| | highly filtered | 1 | 65.6 | 52.9 |
| | dark (No. 5) | 2 | 65.6 | 35.2 |
| Petrolatum | filtered (No. 0) | 2 | 65.6 | 44.2 |
| | first from filter | 1 | 65.6 | 50.2 |
| White amorphous wax from petrolatum | | 1 | 79.4 (175° F.) | 43.0 |
| Paraffin wax, 55.6° C. melting point | | 1 | 65.6 | 49.8 |

termined by a long tube viscometer and viscosity as expressed by the Saybolt viscometer, or by other viscometers in commercial use. It is of importance that such oils should be as free as possible from adsorbable substances, as the latter may under certain conditions more or less clog the relatively long tube of the viscometer used as standard, and thus cause
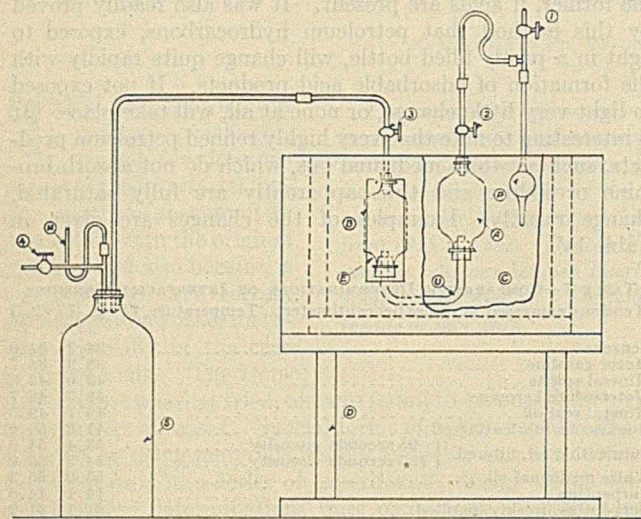


Fig. 2

1, 2, 3, 4 = stopcocks; $P$ = pipet; $M$ = manometer and suction arrangement; $S$ = suction bottle; $U$ = U-tube and tip; $C$ = bath made of 2.5 cm. (1 inch) wood inside width 25 cm. (10 inches); $B$ = glass bulb for water; $A$ = glass bulb for oil; $D$ = wooden stand 30.5 cm. (12 inches) wide; $E$ = glass window.

errors by slowing down the flow. Cases have occurred in the experience of the author in which the flow of oil through long, narrow tubes was slowed down as much as 14 per cent during 2 hours. The determination of the interfacial tensions between water and the oil in question is a good criterion of the freedom of the latter from objectionable matter, which should be removed by repeated purification of the oil until the tension reaches a constant high value.

TABLE III—CHANGES IN INTERFACIAL TENSION BY CHANGES IN TEMPERATURE

(Tensions expressed in dynes per centimeter)

| Temperature °C. | Water-White Kerosene | Red Paraffin Oil | White Medicinal Oil | Highly Filtered Cylinder Oil | Paraffin Wax 55.55° C. |
|---|---|---|---|---|---|
| 4.4 ( 40° F.) | .. | .. | 55.6 | .. | .. |
| 25.0 ( 77° F.) | 48.0 | 42.5 | 54.7 | .. | .. |
| 37.8 (100° F.) | 46.5 | 41.8 | 52.1 | 54.5 | .. |
| 43.3 (110° F.) | .. | 41.5 | .. | .. | .. |
| 54.4 (130° F.) | .. | 41.0 | .. | .. | .. |
| 65.6 (150° F.) | .. | 40.8 | 49.6 | 52.9 | 49.8 |
| 76.7 (170° F.) | .. | 39.0 | .. | .. | .. |
| 79.4 (175° F.) | .. | .. | .. | .. | 47.2 |
| Average per ° C. | 0.115 | 0.065 | 0.099 | 0.058 | 0.187 |

Not much is known about the relations between the interfacial tension and the constitution of hydrocarbons. It can be stated as a general rule that straight-chain compounds have a higher tension than aromatic compounds. Unsaturated bonds in chain compounds apparently do not influence the tension. Low tensions of highly unsaturated chain compounds (such as dimethylbutadiene) were found to be caused by the adsorption of oxidation products, which are very rapidly formed from this class of compounds by exposure to light and air. No cycloparaffins or hydrogenated compounds of the aromatics with more than one ring have been examined, unfortunately, or the results of such examinations might have given some information about the constitution of the lubricant fractions of petroleum. It may be stated, however, that lubricating oils, purified as much as possible by adsorbents, contain hydrocarbons of different interfacial tensions towards water, and that those of lower

tension are attacked by fuming sulfuric acid and form substitution products with bromine, while those of higher tension are not acted upon by these reagents.

The interfacial tensions between a few hydrocarbons and water are given in Table V. For comparative purposes, the tensions of naphthalene and benzene in solutions are given.

## USE OF INTERFACIAL TENSION VALUES

Interfacial tension values have been found useful in problems connected with the theory and practice of lubrication, the making and breaking of emulsions, the treating of petroleum products with sulfuric acid and the washing of acid-treated oils, the improvement of crystallization of wax from distillates, the selection of solvents for various purposes, and in a number of other cases. The author believes that this short list can be considerably extended.

TABLE IV—CHANGES OF INTERFACIAL TENSIONS OIL TO WATER BY EXPOSURE OF OILS

(Tensions expressed in dynes per centimeter. Temperature, 25° C.)

| | Apparatus 1 | 2 |
|---|---|---|
| Water-white kerosene | 49.0 | 48.9 |
| Same, exposed to daylight 5 days | 46.4 | 46.2 |
| Same, exposed to daylight 45 days | 34.9 | 35.7 |
| Same, kept in dark place 18 days | 48.9 | 48.3 |
| Same, kept in dark place 62 days | 48.5 | 48.7 |
| Mineral seal oil | 49.7 | 49.5 |
| Same, exposed to daylight 56 days | 46.4 | 46.4 |
| White medicinal oil | 54.9 | .. |
| Same, exposed to daylight 14 days | 44.9 | .. |
| Same, exposed to daylight 40 days | 18.5 | .. |
| Filtered lubricating oil, 275 seconds viscosity | 49.4 | .. |
| Same, exposed to daylight 25 days | 43.0 | .. |
| Same, exposed to daylight 63 days | 35.7 | .. |
| Same, kept in dark place 48 days | 49.4 | .. |
| Turpentine, freshly distilled | 21.0 | 21.2 |
| Same, exposed to daylight 7 days | 14.1 | 14.8 |

## COMPARISON OF SURFACE AND INTERFACIAL TENSION VALUES

If the available surface tension values of petroleum products[9] are compared with corresponding interfacial tension values, it will be found that the former are much less characteristic than the latter, and are more influenced by other physical properties of the substances under examination. For instance, in the case of petroleum hydrocarbons the surface tension will be found gradually decreasing with increase of volatility, while the interfacial tension towards water is not influenced by the volatility. This decrease of the surface tensions is caused by the relatively great continuity of the phases hydrocarbon-hydrocarbon vapor, which continuity increases with increase of volatility and differs widely from the sharply defined hydrocarbon water phases in the case of interfacial tension.

To show the difference between surface and interfacial tension values, Table VI gives the changes in values of these factors in the case of three lubricating stocks while being filtered through fuller's earth. The relation between the quantities of earth, stock, and fractions was the same in every case.

TABLE V—INTERFACIAL TENSIONS BETWEEN HYDROCARBONS AND WATER

| | Temperature °C. | Dynes per Cm. |
|---|---|---|
| Paraffin wax | 65.6 (150° F.) | 49.8 |
| Pentane | 25 ( 77° F.) | 50.3 |
| Hexadecylene ("Cetene") | 25 | 50.1 |
| Benzene | 25 | 34.2 |
| Xylene | 25 | 35.0 |
| Pinene | 25 | 31.5 |
| White medicinal oil | 25 | 56.0 |
| White medicinal oil and 3 per cent benzene | 25 | 49.3 |
| White medicinal oil and 3 per cent naphthalene | 25 | 53.5 |

TABLE VI—COMPARISON OF CHANGES IN SURFACE TENSION AND INTERFACIAL TENSION AT 25° C. BY FILTRATION THROUGH FULLER'S EARTH

(Tensions expressed in dynes per centimeter)

| | | Stock 1 | | Stock 2 | | Stock 3 | |
|---|---|---|---|---|---|---|---|
| | | Surface | Interfacial | Surface | Interfacial | Surface | Interfacial |
| Stock | | 30.9 | 30.9 | 31.3 | 29.2 | 32.3 | 24.6 |
| Filtrate, fraction | 1 | 31.9 | 41.0 | 31.7 | 42.6 | 31.7 | 39.1 |
| | 2 | 31.5 | 39.3 | 31.7 | 42.5 | 32.5 | 38.3 |
| | 3 | 31.7 | 38.7 | 31.7 | 36.4 | 32.5 | 35.4 |
| | 4 | 32.9 | 36.3 | 32.5 | 32.7 | 32.3 | 30.7 |

The surface tension was determined by Jäger's method.[10]

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# Some Characteristics of the Hydrocarbons in Midcontinent Kerosene[1]

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*A closely fractionated kerosene cut from Midcontinent (Oklahoma) crude was separated into two fractions by use of liquid sulfur dioxide. The insoluble portion gave evidence of $C_nH_{2n}$ hydrocarbons, but no hydrocarbons of the paraffin series. The oils soluble in sulfur dioxide, from their specific gravity, index of refraction, carbon-hydrogen ratio, and boiling points, belong to the hydrogenated naphthalene series.*

IT IS a well-recognized fact that Midcontinent (Oklahoma) crude, even in the lower boiling point fractions, gives a product which is very different from products of the same boiling points produced from Pennsylvania crude. The automobile tourist who measures the value of gasoline solely by its Baumé gravity[2] can never be convinced that 58.0 gravity gasoline at St. Louis may have as good a distillation range as 62.0 gravity gasoline at Bradford, Pa.[2] It is also very commonly said that this difference in gravity is due to an admixture of naphthene (cyclohexane) derivatives with paraffin hydrocarbons in the Oklahoma crude.

It was thought worth while to make some tests to ascertain, if possible, the character of the hydrocarbons present in the Oklahoma crude. It had been frequently noted that it was very difficult by ordinary methods to secure a product which would be unattacked by 66° Bé. sulfuric acid (93.19 per cent $H_2SO_4$). This fact suggested the presence of aromatic compounds. Attempts to freeze out paraffin hydrocarbons from heavy gasoline and kerosene fractions were fruitless, even at temperatures as low as −50° C., causing considerable doubt as to the presence of compounds of this series in any but the lightest fraction of the petroleum. The method of Moore, Morrell, and Egloff[3] for separating the constituents of a special naphtha of specific gravity 0.7527 (56.5 Bé.) was tried. This naphtha, as well as all other oils investigated, was made by topping methods, which insure the presence only of compounds originally present in the crude oil. It had a boiling point range[4] of 100° to 160° C.

One thousand cubic centimeters were treated at −10° C. with liquid sulfur dioxide (in the ratio 2 parts oil to 1 part sulfur dioxide) and the sulfur dioxide was evaporated from the lower layer. After neutralizing with sodium hydroxide and washing with water about 30 cc. of a slightly fluorescent oil were obtained, which had a specific gravity of 0.8388 (37.2 Bé.) and the same boiling point range as the original

naphtha. This oil gave the formolite[5] reaction for aromatic compounds and was readily attacked by nitric and sulfuric acids.

Before going further with the work, qualitative tests were made on two other fractions, one of specific gravity 0.7927 (47.0 Bé.) and with a boiling point range of 146° to 210° C., the other of specific gravity 0.8132 (42.5 Bé.) and with a boiling point range of 192° to 240° C. With great surprise it was found that the quantity of $SO_2$-soluble constituents increased roughly in proportion to the increase in specific gravity and average boiling point. The specific gravity of these $SO_2$-soluble fractions also increased with the rise in boiling point. Because of the larger proportion of the $SO_2$-soluble compounds in the heavier cuts and because of the greater ease of securing a closely fractioned oil in considerable quantities, it was decided to carry on the investigation with this heavy fraction.

Several treatments of 1-liter quantities gave percentages of $SO_2$-soluble oil ranging from 4.6 to 6.0, with an average of 5.4 per cent. The procedure followed was to agitate the oil vigorously with one-third its volume of liquid sulfur dioxide at −10° C. or lower. After allowing to settle, the lower layer was removed and a second treatment made in exactly the same manner as the first. Sometimes a third treatment was made when the second yielded an appreciable quantity of soluble oil. After evaporating off the sulfur dioxide both the soluble oil and the insoluble oil were washed with large quantities of cold water, neutralized with strong caustic, and again washed with water. In every case it was found that the boiling points of the two fractions were unchanged. The specific gravity of the insoluble oil ranged from 0.8100 (43.2 Bé.) to 0.8081 (43.6 Bé.) and the specific gravity of the soluble oil from 0.9159 (23.0 Bé.) to 0.9094 (24.1 Bé.).

Where the sulfur in the original oil had been 0.046 per cent, the insoluble oil now contained 0.016 per cent, and the soluble oil 0.54 per cent. This soluble oil nitrated very readily with dilute nitric acid at the temperature of the steam bath, forming a red viscous liquid, which resisted all attempts to crystallize it. The product formed by action of concentrated nitric acid alone or in the presence of concentrated sulfuric

TABLE I—ANALYSIS OF SO₂-SOLUBLE FRACTIONS FROM MIDCONTINENT CRUDE

| Fraction | Distillation Range at 5 Mm. | Specific Gravity | $n_D^{20}$ | C | H | S | Molecular Weight | Formula Suggested | Calculated Analysis C | H | Calculated Molecular Weight |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 71 to 82 | 0.8697 | 1.4925 | 88.71 | 11.15 | 0.045 | 168 | $C_{12}H_{18}$ | 88.88 | 11.12 | 162 |
| II | 82 to 93 | 0.8866 | .... | 89.19 | 10.99 | 0.021 | 173 | $C_{14}H_{20}$ | 89.36 | 10.64 | 188 |
| III | 93 to 104 | 0.9117 | 1.5238 | 89.56 | 10.30 | 0.054 | 167 | $C_{13}H_{18}$ | 89.66 | 10.34 | 174 |
| IV | 104 to 115 | 0.9383 | 1.5448 | 90.27 | 9.49 | 0.062 | 177 | $C_{14}H_{18}$ | 90.32 | 9.68 | 186 |

TABLE II—ANALYSIS OF SO₂-INSOLUBLE FRACTIONS FROM MIDCONTINENT CRUDE

| Fraction | Distillation Range at 5 Mm. | Specific Gravity | $n_D^{20}$ | C | H | S | O (by Difference) | Molecular Weight | Suggested Formula | Calcd. Molecular Weight |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 71 to 82 | 0.8100 | .... | .... | .... | .... | .... | .... | .... | .... |
| II | 82 to 83 | 0.8109 | 1.4500 | 85.73 | 13.71 | 0.010 | 0.55 | 182 | $C_{13}H_{26}$ | 182 |
| III | 83 to 88 | 0.8118 | .... | 85.38 | 14.09 | 0.011 | 0.52 | 179 | $C_{13}H_{24}$ | 182 |
| IV | 88 to 93 | 0.8123 | .... | 85.27 | 13.85 | 0.012 | 0.87 | .... | .... | .... |
| V | 93 to 95 | 0.8125 | .... | 84.86 | 14.35 | 0.013 | 0.78 | 191 | $C_{14}H_{28}$ | 196 |
| VI | 95 to 103 | 0.8120 | 1.4517 | 85.46 | 14.21 | 0.010 | 0.32 | ... | .... | ... |

was essentially the same, but the reaction with concentrated nitric acid proceeded with explosive violence. It could only be controlled by keeping both acid and oil cooled by ice and salt and adding the acid very slowly.

It was thought that the presence of these sulfur compounds might be the cause of this violent reaction, and attempts were made to remove them by fractional distillation, by distilling with mercury, mercuric oxide, copper oxide, metallic sodium, and lead oxide. Finally, fuming sulfuric acid was used, but none of these methods materially reduced the sulfur content.

Several gallons of a specially processed low-sulfur oil were prepared in the hope that the SO₂-soluble fraction would be correspondingly low in sulfur. No attempt was made to determine the quantity of SO₂-soluble oil in the sample, because the treatment which it had received made it certain that some of these fractions had been removed. When it was found that the SO₂-soluble oil was very low in sulfur, enough was treated to give about 2500 cc. of the SO₂-soluble oil. This had a specific gravity of 0.941 (23.3 Bé.) and a boiling point range of 198° to 244° C.

This 2500 cc. of soluble oil was subjected to repeated fractional distillation at 5 mm. pressure. (It had been discovered in the preliminary work that some decomposition and some polymerization occurred when these fractions were distilled at atmospheric pressure.) In this way four main fractions were accumulated. Table I gives the results of an analysis of these fractions. Molecular weights were determined by the freezing point method, using recrystallized benzene.

The individual fractions were cooled down by a mixture of alcohol and carbon dioxide snow to ascertain their melting points. Practically the entire fraction solidified within a range of 2° C. Temperatures were taken by means of a toluene thermometer, and are not corrected: I, −70° C.; II, −65° C.; III, −48° C.; IV, −28° C. They are without doubt more accurate than the purity of the fractions.

Fraction II, when nitrated, gave, as in other experiments, a dark red, viscous liquid which could not be crystallized. (The reaction with concentrated acid was as violent as in preliminary experiments.) It was soluble in sodium hydroxide or sodium bicarbonate, being reprecipitated by acids. A nitrogen determination gave 9.55 per cent nitrogen, the calculated value for $C_{14}H_{18}(NO_2)_2$ being 10.05 per cent. Further nitration with fuming nitric acid caused little change in the appearance of the nitrated substance and added no more $NO_2$ radicals. Exposure to the air caused a gradual decomposition, evolving nitrous oxide and leaving a lustrous, resin-like body. Traces of acid catalyzed this decomposition. An ether solution, after being washed free of acid, remained perfectly stable for months. An attempt was made to reduce some of this nitrated substance by hydrogen sulfide and by action of hydrochloric acid on granulated tin. No amines could be recovered from the tarry mass left after either reduction.

It is almost impossible to get data from the literature on compounds similar to those met with in this work. Their odor very closely resembles the naphthalene oil cut from coal tar and it is believed that they are partly hydrogenated substituted naphthalenes. Their specific gravity, index of refraction, carbon-hydrogen ratio, and boiling points clearly eliminate the cyclohexane derivatives and the olefins. With the exception of Fraction I the benzene derivatives are likewise eliminated. A search through Beilstein, Engler-Höfer, Abegg, and *Chemical Abstracts* resulted in finding only a few references to compounds similar to those suggested, and the properties given for those are similar to the ones found in this laboratory. No other class of compounds which would include those studied here could be found. If the writer's assumptions were correct, I would be a substituted hexahydronaphthalene, II and III substituted tetrahydronaphthalenes, and IV a substituted dihydronaphthalene.

The SO₂-insoluble oil was also subjected to repeated fractional distillation under a pressure of 5 mm. These cuts were practically unaffected by 66° Bé. sulfuric acid, and had a very pleasant odor and a low sulfur content. Table II gives the analysis of these fractions.

The index of refraction, as well as the analysis of these compounds, indicates that they belong to the $C_nH_{2n}$ series and that paraffin hydrocarbons are largely, if not entirely, absent. A further evidence of the absence of paraffin hydrocarbons is found in the melting points, which were determined as described above: II, −43° C.; V, −29° C.; VI, −29° C. Their inactivity toward sulfuric acid makes it almost certain that they belong to the cyclohexane series.

ACKNOWLEDGMENT

## Trade Standards

A pamphlet entitled "Trade Standards Adopted by the Compressed Air Society" has just been published, embodying the result of extended study and research on the part of the executives and engineers associated with the members of that organization. It embraces the nomenclature and terminology relating to air compressors and their operations; a history of the development of speeds of air compressors; an explanation of capacities and pressures; instructions for the installation and care of air compressors with illustrations of devices suggested for cleaning the intake air; recommendation for the lubrication of air compressing machines and the cleaning of air receiver piping; a description of the low pressure nozzle test recommended by the society, and a partial list of applications of compressed air. Copies may be had from the members or by addressing the secretary of the society, C. H. Rohrbach, 50 Church St., New York, N. Y.

# Chemical Changes of Groundwood during Decay[1]

### By Mark W. Bray and T. M. Andrews

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IN EARLIER publications[2] of this laboratory some of the chemical changes which wood and wood pulp undergo during decay have been reported.

Johnsen's[3] investigations, together with those of Rose and Lisse[4] and of Acree[5] and others, have shown some of the chemical changes due to decay in woods.

The results of the chemical analyses set forth in these publications show only the relative percentages of the different constituents present in the sound and decayed materials. They do not show the loss in weight of the sound wood or pulp due to decay. By this method of presenting the results some of the constituents appear to increase, while in reality they either decrease or remain unattacked by the organisms.

Heretofore, the chemical studies of decay have been made on materials which were infected with mixtures of organisms consisting of wood-destroying fungi and molds.

In this article the authors show the chemical changes which groundwood undergoes when infected with specific organisms in pure culture, together with the loss in weight resulting from decay. With the data obtained from this latter determination it is less difficult to interpret the results of analysis, since the results may be based on equal weights of original sound material.

## Experimental Methods[6]

These experiments were carried out on fresh, clean groundwood, consisting of 70 per cent spruce and 30 per cent balsam. The pulp laps were cut into pieces 6.4 × 25.4 cm. (2.5 × 10 inches). These pieces were all oven-dried at 100° to 105° C. and weighed. One hundred-gram samples were then soaked in distilled water, folded, and placed on galvanized iron grids in 2-quart fruit jars, which served as culture chambers. The grids supported the pulp in the jar above the water (100 cc.) placed in the jar to maintain a constant humidity. The jars were then capped with a layer of cloth, a layer of cotton, then the top piece of the can lid, and finally with a layer of cloth over all. Two large rubber bands were used to fasten the cap in place. The jars were then sterilized by steaming in an autoclave at 100° C. for 1 hour on each of three successive days. After the last sterilization they were transferred immediately from the autoclave to the inoculating case, in which they were allowed to cool.

*The more important chemical changes, together with the losses in weight, which take place in groundwood as a result of infection with specific organisms in pure culture, have been studied.*

*From the data it has been shown that the brown rot organisms studied have a selective action on cellulose and act on the lignin only to hydrolyze off a part of its methoxyl groups. The loss in cellulose in the case of extreme decay was 54 per cent, with an accompanying loss of 3 per cent of lignin. The 2.8 per cent loss in methoxyl content practically accounts for the loss in weight of the lignin. The loss in weight and the chemical changes which the groundwood undergoes during a given time interval and under one set of conditions vary considerably with the nature of the organisms causing the decay.*

As the jars were inoculated they were capped as before described, removed from the culture case, and placed in storage in an inside basement room, the temperature of which was fairly constant (averaging 21° C.). The three jars of each set were opened at the end of 6, 9, and 12 months, respectively. One of the jars, containing Culture 4620-2, was allowed to stand for 3 years. The loss in weight due to the action of the organisms was determined at the end of the test for each culture. In order to determine whether or not the fungi remained pure and viable throughout the experiment, small pieces of the decayed pulp were planted upon malt agar plates.

The air-dry samples of groundwood were prepared for analysis by passing them through a power grinder. The grinder was set so that the material was reduced to a powdery condition of approximately 60 mesh.

The method of analysis employed was that used by Bray and Staidl.[7]

With the results of these analyses obtained at different intervals, it is possible to show some of the changes that groundwood undergoes during decay.

## Discussion of Results

Tables I and II give the values obtained from the chemical analysis of five samples of groundwood, which had been severally inoculated with wood-destroying organisms in pure culture. The samples were analyzed at different stages of decay and the results obtained were calculated to the oven-dry basis. For comparative purposes, the results were calculated on an equal weight of sample analyzed (Table I) and also on an equal weight of the original material (Table II). The latter method of calculation is based on the loss due to decay.

The organisms used for inoculation of the pulps were certain hymenomycetes, which cause brown rots, the names of which have been given except in cases where fruiting bodies have not been obtained and thus the organism was not positively identified. These are differentiated by culture number. Further work, however, is in progress on the identification of the unknown but virulent organisms. Although efforts were made to start the cultures under the same conditions, the moisture content of the groundwood ranged from 57 to 72 per cent, averaging 70 per cent.

Losses Due to Decay—The loss in weight of the groundwood during a given time interval varies considerably with the nature of the organism causing the decay. This may be due in part to the fact that the condition used in the experiments

Sets of three jars each were inoculated with a pure culture of a fungus that had been isolated from pulp or pulpwood in the following manner: Petri dish cultures of the fungus to be used were made on malt agar a week before inoculation of the pulps. The plate cultures were cut into pieces about 8 mm. square. One square was placed on the top of each of the three pieces of pulp in the jar.

[1] Presented before the Division of Cellulose Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Mahood and Cable, *Paper,* **25**, 11 (1920); Bray and Staidl, This Journal, **14**, 35 (1922).

[3] Johnsen and Lee, *Pulp Paper Mag. Can.,* **21**, 111 (1923).

[4] This Journal, **9**, 284 (1917).

[5] *Pulp Paper Mag. Can.,* **17**, 569 (1919).

[6] The experimental data upon which the discussion in this paper is based were presented in a manuscript which has been submitted for publication as a bulletin of the U. S. Department of Agriculture, entitled "Control of Decay in Pulp and Pulpwood," by Kress, Humphrey, Richards, Bray, and Staidl. The pathological work was carried out by C. A. Richards, assistant pathologist of the Bureau of Plant Industry, Madison, Wis.

[7] *Loc. cit.*

TABLE I—ANALYSIS OF GROUNDWOOD BASED ON EQUAL WEIGHTS OF SAMPLE ANALYZED
(Figures in per cent)

| Sample | Organism or Culture No. | Storage Time Months | Cold Water Soluble | Hot Water Soluble | 1% Alkali Soluble | Lignin | Cellulose | α-Cellulose | β-Cellulose | γ-Cellulose | Pentosan | Methoxyl | Copper No. | Ash |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2544 | Sound | 0 | 0.00 | 1.2 | 10.1 | 29.7 | 60.0 | 60.5 | 24.5 | 15.0 | 12.0 | 5.5 | 4.4 | 0.6 |
| 100 | 4620-2 | 6 | 11.1 | 17.95 | 54.9 | 38.0 | 36.7 | 19.6 | 67.2 | 13.2 | .. | .. | .. | .. |
| 102 | 4620-2 | 12 | 14.8 | 22.2 | 66.8 | 53.4 | 21.8 | .. | .. | .. | .. | .. | .. | 5.75 |
| 182 | 4620-2 | 36 | .. | 16.5 | 70.0 | 71.0 | 16.1 | ... | ... | ... | 6.8 | 7.2 | 23.0 | .. |
| 130 | Fomes roseus | 6 | 3.2 | 6.4 | 33.0 | 34.1 | 49.4 | 49.7 | 38.9 | 11.5 | .. | .. | .. | .. |
| 131 | Fomes roseus | 9 | 3.7 | 5.6 | 33.6 | 34.8 | 50.7 | . | . | . | .. | .. | .. | .. |
| 157 | Lentinus lepideus | 6 | 9.6 | 15.1 | 52.3 | 36.7 | 40.9 | 51.7 | 36.8 | 11.5 | .. | .. | .. | .. |
| 158 | Lentinus lepideus | 9 | 13.9 | 22.6 | 58.2 | 41.1 | 37.1 | ... | ... | ... | .. | .. | .. | .. |
| 106 | 4620-1 | 6 | 12.3 | 17.7 | 52.4 | 39.5 | 37.3 | 23.6 | 68.4 | 8.0 | .. | .. | .. | .. |
| 107 | 4620-1 | 9 | 16.6 | 22.8 | 62.2 | 43.1 | 27.2 | ... | ... | ... | .. | .. | .. | .. |
| 108 | 4620-1 | 2 | 14.9 | 21.2 | 62.0 | 46.5 | 27.6 | ... | ... | ... | .. | .. | .. | .. |
| 148 | Peniophora tabacina | 6 | 5.6 | 10.4 | 40.4 | 32.1 | 46.8 | 55.4 | 34.2 | 10.4 | .. | .. | .. | .. |

was more favorable for the growth of the organisms, causing the greatest loss.

The losses range from 10.3 to 27.12 per cent after the first 6-month period of infection. After 12 months' action of the organisms, Culture 4620-2 showed a loss of 49.5 per cent. Since this organism showed so large a loss after 1 year, it was allowed to act on groundwood for 3 years. This prolonged period of growth caused a loss of 62.4 per cent. The rate of loss of this organism during the first year of growth is practically a linear function; beyond this point the rate of growth is questionable.

CHEMICAL COMPOSITION—*Lignin and Cellulose.* One of the most important methods of determining the action of fungi on woods is through a study of the change in chemical composition based on equal weights of the sound material inoculated with specific fungi in pure culture. The rate of change in the percentage of lignin and cellulose is of special importance to the wood-using industries. Unfortunately, each of the organisms herein considered has shown a selective action on the cellulose with but slight action on the lignin. However, a further study of other organisms, including

for 1 year. A total of 3 years' storage gave no further loss. This loss is practically accounted for by the loss in the methoxyl content of the groundwood—viz., 2.8 per cent. This would indicate that a partial hydrolysis of the methoxyl groups of lignin takes place during decay. These results are substantiated by the observations of Fischer[10] and his co-workers in their report on the methoxyl content of decaying vegetation.

Samples 130 and 131 inoculated with *Fomes roseus* showed a slight increase in lignin content over that of the sound groundwood. (This increase, however, is very small and may be due to experimental error in the determination of loss in weight of sample.)

The greatest losses due to infection with these wood-destroying fungi are obtained in the cellulose content of the groundwood. The original sample contained 60 per cent cellulose. After 6 months' storage the cellulose content of Sample 100 infected with Culture 4620-2 had decreased to 26.8 per cent. After 1 year of storage the value was reduced to 10.9 per cent, and after 3 years only 6.05 per cent cellulose remained in the material.

TABLE II—ANALYSIS OF GROUNDWOOD BASED ON EQUAL WEIGHTS OF ORIGINAL SAMPLE
(Figures in per cent)

| Sample | Organism or Culture No. | Loss Due to Decay | Cold Water Soluble | Hot Water Soluble | 1% Alkali Soluble | Lignin | Cellulose | α-Cellulose | β-Cellulose | γ-Cellulose | Pentosan | Methoxyl | Copper No. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2544 | Sound | 0 | 0.0 | 1.2 | 10.1 | 29.7 | 60.0 | 36.3 | 14.7 | 9.0 | 12.0 | 5.5 | 4.4 |
| 100 | 4620-2 | 27.12 | 8.1 | 13.1 | 40.0 | 27.7 | 26.8 | 5.1 | 18.0 | 3.5 | .. | .. | .. |
| 102 | 4620-2 | 49.5 | 7.5 | 11.1 | 33.4 | 26.7 | 10.9 | .. | .. | .. | .. | .. | .. |
| 182 | 4620-2 | 62.4 | .. | 6.2 | 26.3 | 26.7 | 6.05 | .. | .. | .. | 2.56 | 2.7 | 8.65 |
| 130 | Fomes roseus | 10.3 | 2.9 | 5.7 | 29.6 | 30.6 | 44.3 | 22.0 | 17.2 | 5.1 | .. | .. | .. |
| 131 | Fomes roseus | 12.94 | 3.2 | 4.9 | 29.2 | 30.3 | 43.8 | .. | .. | .. | .. | .. | .. |
| 157 | Lentinus lepideus | 21.54 | 7.5 | 11.8 | 41.0 | 28.8 | 32.1 | 16.5 | 12.0 | 3.5 | .. | .. | .. |
| 158 | Lentinus lepideus | 30.31 | 9.7 | 15.7 | 40.6 | 28.6 | 25.8 | .. | .. | .. | .. | .. | .. |
| 106 | 4620-1 | 22.2 | 10.8 | 13.7 | 40.8 | 30.7 | 29.0 | 6.9 | 19.8 | 2.3 | .. | .. | .. |
| 107 | 4620-1 | 33.11 | 11.1 | 15.3 | 41.6 | 28.8 | 18.2 | .. | .. | .. | .. | .. | .. |
| 108 | 4620-1 | 38.63 | 9.3 | 13.0 | 38.0 | 28.5 | 16.9 | .. | .. | .. | .. | .. | .. |
| 148 | Peniophora tabacina | 13.5 | 4.8 | 9.0 | 34.9 | 27.7 | 40.5 | 22.5 | 13.9 | 4.2 | .. | .. | .. |

*Trametes pini* which is reported to act selectively on the lignin and leave the cellulose intact, is in progress.

Several investigators have shown that decayed wood contains a higher percentage of lignin than sound wood of the same species;[8] others have shown that wood that has been attacked by organisms which selectively act on the lignin contains more cellulose than the corresponding sound wood.[9] This is obviously not an actual increase in the amount of lignin, but is due to the fact that the percentage of lignin is based on the weight of decayed wood as analyzed, and not on the weight of sound wood which the sample represented. The data given in the tables show this apparent increase in lignin, varying with the nature and time of action of the organisms, ranging from 24 per cent to 41.3 per cent, when considered on an equal weight basis of the sample analyzed.

However, when these results are calculated on the basis of equal weights of the original sound groundwood, the value of the lignin either remains practically constant or a slight decrease is observed. Sample 101 infected with Culture 4620-2 showed a 3 per cent loss in lignin content after storage

This organism produced the most rapid changes in the cellulose content of the groundwood. Possibly this is because the conditions of the experiment were optimum for this particular brown rot. The rate of cellulose loss for the other organisms listed in the tables is not so great. However, possibly the losses would have been as great or even greater had the conditions of growth been optimum for these other organisms.

Most of the organisms thus far studied rapidly decrease not only the quantity of the cellulose but also its quality. This is shown by the decrease in the percentage of the α-cellulose content of the cellulose with increase of decay. With the rapid change in the cellulose content of the groundwood, the lignin remains practically intact except for the slight loss due to the hydrolysis of a part of the methoxyl groups. With this is view, it may be possible to prepare pure lignin for chemical investigation by means of the action of fungi on wood in place of treating it with strong mineral acids.

*Pentosans.* The loss in pentosans during decay agrees with the data obtained by Rose and Lisse[4] in their analysis of Douglas fir wood. The data show, however, that even in the cases of extreme decay a part of the pentosans remain

[8] Mahood and Cable, *loc. cit.*; Kress and Humphrey, *Paper Trade J.,* 71, 41 (1920); Johnsen and Hovey, *Paper,* 21, 46 (1918).

Johnsen and Lee, *Pulp Paper Mag. Can.,* 21, 112 (1923); Johnsen, *Ibid.,* 21, 383 (1923).

[10] Fischer, Schrader, and Friedrich, *Ges. Abhandl. Kenntnis Kohle,* 5, 530 (1920).

undecomposed. This would indicate that as long as any cellulose is left in the woods, pentosans will also be present.

COPPER NUMBER—The data obtained show a marked increase of reducing power with decrease in the cellulose content.

SOLUBILITY IN HOT WATER AND CAUSTIC ALKALI—The solubility of decayed groundwood in hot water and 1 per cent sodium hydroxide solution, calculated on equal weights of the original sample, increases to a maximum, then decreases rapidly as the cellulose content decreases. This point of maximum solubility is obtained when the cellulose content (calculated on the original sample) is approximately 25 per cent. This would indicate that the action of the organisms is first to produce alkali-soluble substances, which are destroyed by further action.

The solubility in 1 per cent caustic alkali solution, calculated on equal weights of the sample analyzed, continues to increase with decrease of cellulose content.

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# Quantitative Methods for the Analysis of Hemicellulose in Apple Wood[1,2]

By W. E. Tottingham and F. Gerhardt

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IN A previous article[3] consideration was given to the hydrolyzable fraction of apple wood, designated as hemicellulose, in relation to physiological aspects of fruiting. The present paper deals with certain results accrued from efforts to determine quantitatively the composition of this fraction. Where not designated otherwise, the wood was derived from branches one year old.

## SEPARATION OF EXTRACTIVE

Reference was made in the earlier paper to an extracted fraction, the constituents of which resembled those derived by mild acid hydrolysis. The best method of extraction as regards yield of extractive consisted of digestion in cold 1 per cent sodium hydroxide subsequent to removal of the calcium soluble in 1 per cent hydrochloric acid. Recovery of the dry extractive by precipitation in acidified alcohol varied from 5 per cent in apple wood to over 20 per cent in young plum branches. However, inasmuch as the yield of this fraction showed no correlation with physiological treatment of the trees, this phase of the investigation has been discontinued.

## REMOVAL OF STARCH

From the standpoint of convenience it would be more desirable to use takadiastase than saliva in preparing woody tissues for hydrolysis of the hemicellulose; yet it seemed desirable to compare results by enzymes from these two sources in the present case. After cessation of the usual starch reaction with iodine and filtration of the soluble products, the residue was redigested for 20 minutes with additional enzyme preparation. The results appear in Table I.

It appears that with the woody tissues diastase gives a smaller recovery of starch than does saliva. This difference

*The extract obtained in 1 per cent sodium hydroxide seems to have no physiological significance. In removing starch from the tissues precursory to acid hydrolysis, saliva is preferable over takadiastase.*

*Hydrolysis by dilute sulfuric acid appears to be preferable to the use of hydrochloric acid, as the former liberates a smaller proportion of reducing substances removable by clarification. Discrepancies in results previously reported can now be ascribed to the liberation of furfural from products of hydrolysis other than pentoses. The greater part of the apparent pentose content of unclarified products of hydrolysis consists of compounds removable by fermentation with yeast.*

*Excessive removal by basic lead acetate of products of acid hydrolysis with reducing power renders this clarifying agent unsuitable for use. The hydrolytic effects of boiling for 1 or 2 hours with 1 per cent sulfuric acid are limited largely to cleavage of pentose compounds, but the results give little promise of a general method for dissecting the hemicellulose. The destructive action of 4 per cent hydrochloric acid upon the products of hydrolysis causes its use in the determination of hemicellulose to be of highly questionable value.*

could hardly be due to aging of the enzyme preparation in this case, for it had been received from the producers only a few weeks before use. The results are suggestive of the difficulty encountered by Horton,[4] who ascribed inefficient activity of takadiastase to the persistence of dextrins produced in the preliminary phases of starch digestion. They led to preference for saliva in clearing woody tissues of starch.

## RELATION BETWEEN CONCENTRATION OF ACID AND RECOVERY OF HEMICELLULOSE

Samples of apple spur tissue weighing 10 grams each were freed from starch by diastatic digestion. Hydrolysis was then effected by digesting different samples 1 hour with 100 cc. of boiling sulfuric acid at various concentrations of acid. The extracts were filtered, neutralized, and subjected to determinations of reducing power and furfural yield before and after fermenting the hexoses.[5] Analyses were conducted in this case without clarification of the solutions. The results are given in Table II.

TABLE I—COMPARISON OF THE YIELDS OF STARCH BY DIASTATIC TREATMENT

| | Control, Boiled Only | DIGESTION BY SALIVA | | DIGESTION BY TAKADIASTASE | |
| --- | --- | --- | --- | --- | --- |
| KIND OF TISSUE | Per cent | Period 1 Per cent | Period 2 Per cent | Period 1 Per cent | Period 2 Per cent |
| Apple wood | 1.4 | 3.3 | 0.0 | 2.2 | 0.0 |
| Plum wood | 1.2 | 3.9 | 0.2 | 3.2 | 0.2 |
| Maize stalks | 1.1 | 3.3 | 0.1 | 3.4 | 0.1 |

TABLE II—RELATION BETWEEN CONCENTRATION OF ACID AND PRODUCTS OF HYDROLYSIS OF APPLE SPUR TISSUE

| | Concentration of Sulfuric Acid, Per cent | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 |
| *Reducing Power in Percentage Equivalents of Glucose* | | | | | | |
| Before fermentation | 19.0 | 18.5 | 22.8 | 27.6 | 32.5 | 38.0 |
| After fermentation | .. | 5.2 | .. | 5.8 | .. | 6.9 |
| *Furfural Yield in Percentage Equivalents of Pentose* | | | | | | |
| Before fermentation | .. | 11.4 | .. | 11.9 | .. | 16.9 |
| After fermentation | .. | 2.6 | .. | 2.9 | .. | 4.3 |

Inspection of the data shows that above the first interval of acid concentration the yield of reducing substances in-

[1] Received September 22, 1923.

[2] Published with the permission of the Director, Wisconsin Agricultural Experiment Station.

[3] Tottingham, Roberts, and Lepkovsky, *J. Biol. Chem.*, **45**, 407 (1921).

[4] *J. Agr. Sci.*, **11**, 240 (1921).

[5] E. B. Fred, of the Department of Bacteriology, supervised the addition of nutrient media and inoculation with a pure strain of Carlsberg yeast.

creases about 5 per cent with each successive increase of acid concentration. On the other hand, the liberation of non-fermentable reducing substances, and of furfural-yielding substances both before and after fermentation, increased relatively little with increasing concentration of the acid.

The results of the pentose determinations show that a large part of the furfural yield preceding fermentation is due to fermentable substances, these presumably being hexose in character. Spoehr[6] has previously stressed the necessity for removal of hexose compounds for accurate determination of pentosans. Special emphasis is placed upon the abnormal yields of furfural in proportion to pentose compounds here reported, as they offer at least partial explanation of the discrepancy between reducing power and other sugar values observed with products of hydrolysis in earlier work.[7] It appears probable that the values there attributed to xylose are entirely too high.

In this connection it should be recalled that with simple mixtures of arabinose and glucose Davis, Daish, and Sawyer[8] found no interference with the usual method for determining pentose when the proportion of glucose was not excessive. The writers prepared a solution containing 1 per cent glucose with 0.25 per cent xylose, and found no interference from the former in determining the latter sugar by the usual method based upon yield of furfural. These results support the view that their products of acid hydrolysis contain hexose components, possibly in conjugated forms, which yield furfural in the procedure for determining pentose compounds.

## Clarification of Products of Hydrolysis

Browne[9] regards the use of basic lead acetate for clarification as undesirable with sugar extracts. It seemed desirable, however, to compare it with the neutral salt for use upon the products of hydrolysis from apple wood. Spur tissue freed from starch was hydrolyzed in one instance by the action of boiling 2.5 per cent hydrochloric acid for 1 hour and in other cases by the use of 1 per cent sulfuric acid for different time periods. The filtered extracts were neutralized by sodium hydroxide, clarified by neutral lead acetate, and deleaded by sodium sulfate. Table III shows the analytical results.

Table III—Relation of Clarification to Yield of Reducing Substances from Hydrolysis of Hemicellulose

| Hydrolyzing Agent | Time of Hydrolysis Hours | Sample | Reducing Power in Percentage Equivalents of Glucose in Dry Tissue | |
| | | | Unclarified | Clarified by Neutral Lead Acetate |
| --- | --- | --- | --- | --- |
| HCl, 2.5 per cent | 1 | A | 14.9 | 5.0 |
| | | B | 15.0 | 8.0 |
| | | C | 15.3 | 9.4 |
| | | D | 14.9 | 5.3 |
| H₂SO₄, 1 per cent | 1 | E | 8.9 | 8.9 |
| | 2 | | 12.9 | 12.0 |
| | 3 | | 16.0 | 14.4 |
| | 4 | | 21.2 | 15.3 |

It is clear that hydrochloric acid liberates large proportions of precipitable reducing substances. The use of weak sulfuric acid, however, has little effect in this respect, except with prolonged action. Further data assembled in Table IV show that the action of basic lead acetate is more extensive than that of the neutral salt. With increase of hydrolytic effect the proportion of products precipitable by the former salt becomes excessive. The earlier failure to identify fructose among the products of hydrolysis of apple wood, together with a comparison of the results here with those of Bryan[10] derived from solutions of glucose and fructose, led to the belief that compounds other than simple sugars are involved in this effect of clarification. It seems

[6] Carnegie Inst. Pub., **287**, 36 (1919).
[7] J. Biol. Chem., **45**, 413 (1921).
[8] J. Agr. Sci., **6**, 410 (1914).
[9] "Handbook of Sugar Analysis," **1912**, p. 207.
[10] Browne, loc. cit. p. 215.

quite possible that products of partial hydrolysis of the hemicellulose, weakly acid in character, are here precipitated by the basic lead acetate. Inasmuch as it appears desirable to include these with the products defined by reducing power, the use of basic acetate for clarification is here deemed objectionable. Sulfuric acid also appears preferable to hydrochloric acid because of the smaller proportion of reducing substances produced by it which are precipitable by lead acetate.

Table IV—Clarifying Effects of Neutral and Basic Lead Acetates

| Hydrolyzing Agent | Time of Hydrolysis Hours | Sample | Reducing Power in Percentage Equivalents of Glucose in Dry Tissue | | |
| | | | | Clarified by | |
| | | | Unclarified | Neutral Acetate | Basic Acetate |
| --- | --- | --- | --- | --- | --- |
| H₂SO₄, 1 per cent | 3 | A | 14.0 | 13.4 | 10.9 |
| | | B | 10.9 | 10.3 | 7.9 |
| H₂SO₄, 4 per cent | 1 | C | .. | 20.4 | 13.9 |
| HCl, 2.5 per cent | | D | 34.5 | 26.9 | 9.2 |

## Selective Action of 1 Per cent Sulfuric Acid

That pentosans hydrolyze readily is well known.[11] By selective fermentation of the products of hydrolysis from treating spur tissues for 3 hours with boiling 1 per cent sulfuric acid (with clarification), it was found with a series of samples that an average of 85 per cent of the hydrolyzed material was of pentose character. In seeking a method to shorten the time requirement, the writers obtained the same yield of reducing substance by 4 per cent sulfuric acid acting 20 minutes as by 1 per cent acid for 1 hour, but did not determine whether or not the ratio of hexose to pentose products was the same in the two cases. The results of the same hydrolytic treatment varied so widely with different samples of tissue as to render doubtful the possibility of developing for general use any conditions of acid hydrolysis which would quantitatively recover only the pentose complexes.

## Destructive Action of 4 Per cent Hydrochloric Acid

The hydrolysate from the use of 4 per cent sulfuric acid, described previously[3] with reducing power equivalent to 70 per cent glucose, upon further hydrolysis with 4 per cent hydrochloric acid for 3 hours gave products equivalent to only 39.4 per cent glucose. Tests showed the presence in the final products of a small amount of levulinic acid and traces of furfuraldehyde. Further evidence of the destructive action of 4 per cent hydrochloric acid appears in the data of Table V. In these cases, with other properties remaining quite constant, the reducing power of the alcohol-soluble products of hydrolysis decreases as the yield increases. Table VI presents data in which 1 per cent sulfuric acid and 2.5 per cent hydrochloric acid give closely similar quantitative results, but the destructive action of 4 per cent hydrochloric acid is again apparent. These results render the use of the latter reagent, as employed by duSablon,[12] of extremely doubtful significance.

Table V—Comparison of Constants with Products of Different Hydrolytic Treatment of the Same Tissue
(Time of Hydrolysis, 2 Hours)

| Hydrolyzing Agent | Alcohol-Soluble Products Per cent | Constants of Alcohol-Soluble Fraction | | |
| | | Reducing Power, Sp. Rot. Degrees | Glucose Equivalent Per cent | Furfural Yield Pentose Equivalent Per cent |
| --- | --- | --- | --- | --- |
| H₂SO₄, 4 per cent | 12.2 | 20.0 | 67.8 | 51.8 |
| HCl, 4 per cent | 19.4 | 20.1 | 40.7 | 50.8 |

Table VI—Recovery of Reducing Substances from Varied Hydrolytic Treatment

| Hydrolyzing Agent | Time of Hydrolysis Hours | Sample | Reducing Power in Percentage Equivalents of Glucose Per cent |
| --- | --- | --- | --- |
| H₂SO₄, 1 per cent | 1 | A | 5.4 |
| | | B | 8.9 |
| HCl, 2.5 per cent | 1 | A | 5.0 |
| | | B | 9.4 |
| HCl, 4 per cent | 3 | A | 2.2 |
| | | B | 4.9 |

[11] Browne, loc. cit., pp. 547, 553.
[12] Rev. gén. botan., **16**, 341 (1904); **18**, 1, 82 (1906).

# The Gelatinization of Lignocellulose[1]

## II—Action of Dilute Sodium Hydroxide and Cuprammonium Solutions on the Pentosans

### By A. W. Schorger

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*The amount of pentosans removed from aspen wood by treatment with dilute sodium hydroxide solutions in the cold rapidly reaches a minimum, the extent of removal of the pentosans depending on the strength of the alkaline solution.*

*No adsorption of pentosans took place when aspen was ground in an alkaline solution of added pentosans.*

*When birch wood, given a preliminary extraction with concentrated ammonia, was treated with cuprammonium solution, the ratio of pentosan to orthoglucosan in the dissolved portion was approximately the same as in the Cross and Bevan cellulose. When treated with cuprammonium solution, the dissolved portion did not have the same composition as the residue with respect to pentosans and lignin.*

*No clean-cut proof exists that pentosans are chemically combined with orthoglucosan in wood cellulose, but the weight of experimental evidence is in favor of chemical combination as against the adsorption hypothesis.*

SINCE the discovery of the occurrence of pentosans in seed plants, there have been two schools of opinion regarding the state in which pentosans exist in the lignocelluloses and the celluloses therefrom. Most investigators have held that a portion of the pentosans are chemically combined with orthoglucosan,[2] while others, particularly in recent years, have considered them as held in a state of adsorption or solid solution. In view of the recent extensive review and speculations on wood cellulose by Wise[3] wherein the pentosans are considered as adsorbed, it is desirable to present briefly the literature from the opposite angle.

Wislicenus,[4] the chief exponent of the adsorption theory, has not precluded the possibility of chemical reactions such as esterification. His experimental work, upon which is based the theory that the cell wall grows by adsorption by a cellulose gel framework of colloids from the sap, is not particularly convincing if we consider it from a cytological standpoint. After the formation of the cell by division a layer of pectin is formed between it and its sister cell, this layer later becoming the middle lamella; layers of cellulose are then deposited, followed by lignification during the later stages. The fundamental syntheses take place within the protoplasm which is in intimate contact with the cell wall, and there is no reason to believe that any substances other than crystalloids can pass in quantity through the plasma membrane. The changes that the crystalloids undergo after leaving the plasma membrane are purely hypothetical.

Schulze and Tollens[5] found that all the pentoses were not removed from spent malt by a 6-hour digestion with 4 per cent sulfuric acid. The residue, after having been extracted with 5 per cent caustic soda, gave on extraction with cuprammonium solution a cellulose that still contained pentoses. The impossibility of separating the xylan from the cellulose led them to conclude that the two did not occur as a simple mixture but as a compound. A similar conclusion was reached by Schulze,[6] who found that the xylan in beech wood was not entirely destroyed by a 3-hour boiling with 1.5 per cent sulfuric acid followed by a 14-day treatment with F. Schulze's reagent (nitric acid and potassium chlorate).

Winterstein[7] found that the residue remaining after boiling beech wood with 5 per cent sulfuric acid for 3 hours still contained 10.16 per cent xylan. He concluded that the xylan is present in two forms, the one being removed by dilute acids and Schulze's reagent, the other resisting these agents; a part of the xylan is combined with the cellulose. In marked contrast the mannan of the conifers can be readily and quantitatively removed by hydrolysis with dilute acids.[8]

Heuser and Haug[9] found that the pentosan content of crude straw could not be reduced below 9.7 per cent xylan with boiling 6 per cent caustic soda. Commercial straw pulp obtained by alkaline digestion under pressure at 140° to 150° C. still contained 29 per cent xylan. More recently, Heuser and Boedeker[10] have asserted that all plant celluloses, when properly purified, are alike and have the empirical composition of cotton cellulose. Wood cellulose was practically freed from pentosans by repeated extraction with hot 6 per cent caustic soda or cold 17 per cent caustic soda, but with the simultaneous destruction of a considerable part of the cellulose. The view of these authors has been supported by Wise and Russell[11] on the ground of having obtained comparable yields of cellobiose octacetate from cotton and spruce cellulose after the latter had been treated with 17.5 per cent caustic soda to remove pentosans. In the writer's opinion the use of a boiling 6 per cent or a cold 17 per cent solution of caustic soda is too drastic a treatment upon which to base these conclusions; certainly, none of the cellulose esters prepared in the laboratory remain unaffected by them. It is to be understood that it is not yet known how the pentosans are held, an ether linkage being generally assumed. On cooking sulfite cellulose with calcium hydroxide or barium hydroxide under pressure, Schwalbe and Becker[12] found that the pentosan content could not be reduced below 5 per cent and advanced the opinion that pentosans are combined with the cellulose molecule.

The hemicelluloses, such as xylan, are, in general, soluble in cuprammonium solution. According to Reiss[13] some hemicelluloses are soluble, others not. Schulze[14] found that the hemicelluloses of various seeds were insoluble in cuprammonium solution; however, after boiling with dilute hydrochloric acid or treating with 10 per cent hydrochloric acid

[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] There is no suitable name for expressing a glucose anhydride grouping such as exists in cotton cellulose, and the term "orthoglucosan" is accordingly proposed; the name glucosan has long been used for an entirely different product.

[3] This Journal, **15**, 711 (1923).

[4] Wislicenus and Kleinstück, *Z. Chem. Ind. Kolloide*, **6**, 17, 87 (1910).

[5] *Ann.*, **271**, 55 (1892).

[6] *Z. physiol. Chem.*, **16**, 435 (1892).

[7] *Z. physiol. Chem.*, **17**, 381 (1893).

[8] Schorger, This Journal, **9**, 748 (1917).

[9] *Z. angew. Chem.*, **31**, 168 (1918).

[10] *Ibid.*, **34**, 461 (1921).

[11] This Journal, **14**, 285 (1922).

[12] *J. prakt. Chem.*, **100**, 37 (1919).

[13] *Landw. Jahrb.*, **18**, 747 (1889).

[14] *Z. physiol. Chem.*, **14**, 245, 266 (1890); **16**, 410 (1892); *Ber.*, **22**, 1194 (1889).

in the cold for 24 hours, they were readily soluble. This would indicate that hydrolysis was essential to solution. Fremy[15] as long ago as 1859 pointed out that vegetable ivory (phytelephas) dissolves readily in cuprammonium solution while the fibers of wood do not, the difference being accordingly unexplainable as regards the relative densities of the materials. Hoffmeister[16] found that by alternate treatment of lignocelluloses with acid and ammonia the cellulose became soluble in cuprammonium solution.

In an attempt to throw some light on the state in which pentosans occur in lignocelluloses, wood was treated with dilute sodium hydroxide solutions and cuprammonium solutions; in the former only the pentosans are soluble, in the latter both pentosans and cellulose. In order to obtain as thorough an extraction as possible, use was made of the ball mill whereby gelatinization was attained as described in a previous paper.[17] The insoluble residues remaining from treating aspen, three times in each case, with cold 1, 2, and 5 per cent sodium hydroxide contained 12.48, 9.23, and 6.71 per cent pentosans, respectively. The cell structure was completely destroyed by the method of grinding employed, leaving the particles in a swollen condition, thus offering with a minimum of chemical change a maximum surface for extraction. With each concentration of alkali the amount of pentosans removed rapidly reached a minimum and in no case was the removal of the pentosans approximately complete. If the alkali does not produce a chemical change in the wood, it is not apparent why a 5 per cent solution of caustic soda removes so much more xylan than a 1 per cent solution. It has long been recognized that xylan undergoes a change through extraction with caustic soda. Schmidt and Graumann[18] have recently stated that the xylan in beech wood is not affected by chlorine dioxide, but when isolated in the usual way by means of caustic soda it is attacked.

In the case of dilute alkali, having a definite solvent and chemical reaction with the xylan, it is not apparent how adsorption could play the same part as where a neutral solvent is employed. The case is not analogous to colloidal ferric hydroxide, from which, as is well known, it is impossible to remove all the alkali by washing with water. It is still less apparent how adsorption could play a large part in preventing the complete and rapid removal of xylan from wood by hydrolysis with acids, the xylan in this case being hydrolyzed to definitely crystalline products. Spoehr[19] considers as cellulose the carbohydrate residue resisting so mild a hydrolysis as heating on a water bath for 3 hours with 1 per cent hydrochloric acid. The writer has also ground aspen in an alkaline solution of xylan and found that no adsorption of pentosans took place. No great importance is attached to this fact per se, but it supports the contention that a portion of the pentosans is held in chemical combination; otherwise, all the pentosans would pass into solution, since under the experimental conditions employed there is every reason to believe that the sodium hydroxide comes into contact with all the pentosans. The latter condition may not be so readily attained with wood in its original irreversible condition.

Birch wood, on account of its high xylan content, was treated with cuprammonium solution (1) to determine if the solution exerted a highly preferential solvent action on the xylan, which should be the case if the xylan is not in chemical combination; and (2) to determine if, in the portion of the wood dissolved, the xylan had a constant relationship to orthoglucosan. When the wood was treated directly with cuprammonium solution a certain preferential solvent action

15 Compt. rend., 48, 277 (1859).
16 Landw. Jahrb., 17, 261 (1888).
17 This Journal, 15, 812 (1923).
18 Ber., 54, 1867 (1921).
19 Carnegie Inst. Pub., 287, 28 (1919)

was exerted on the pentosans that was to be expected owing to the presence of easily soluble pentosans; however, after two extractions the wood still contained 10 per cent pentosans. On the other hand, when the wood was first extracted with concentrated ammonia followed by cuprammonium solution, the dissolved portion showed a pentosan-orthoglucosan ratio fairly close to that existing in the Cross and Bevan cellulose. Whether this circumstance is fortuitous remains to be determined by further work, particularly on a number of species.

## EXTRACTION WITH DILUTE SODIUM HYDROXIDE

The material extracted was the comminuted wood of the aspen (Populus tremuloides) representing trees about 15 years old. It contained 22.94 per cent pentosans and 23.44 per cent lignin, as determined with 72 per cent sulfuric acid. The 25-gram sample (23.3975 grams of dry, ash-free substance) was ground in a ball mill with alkali for three periods of 48, 24, and 18 hours each. During the first grinding 1000 cc. of alkali were used. The amount of solution was reduced in subsequent grindings in proportion to the loss in weight; e. g., if the residue weighed 20 grams only 800 cc. of alkali were used. The ground material was placed on a fine muslin filter, the first runnings being returned to the funnel. The filtrate was opalescent, though it showed no change in appearance when passed through a filter paper. The gelatinous mass was washed with cold water until the filtrate was neutral to litmus, allowed to stand until it formed a coherent mass, and transferred to a large evaporating dish, the last portions of the wood on the filter cloth being removed by the careful use of a spatula and wash bottle. During drying, conducted at 40° C., the material was frequently crushed with a pestle so as to obtain a rather fine, granular mass before it had dried completely; if dried en masse the material is extremely hard and difficult to manipulate. The residue was then weighed to determine the loss by grinding, and portions were taken for the determination of pentosans, moisture, and ash. All results are corrected for moisture and ash, as well as for the amounts removed for the various analyses, in order that the figures for the three grindings may be comparable.

TABLE I—EXTRACTION OF ASPEN WITH DILUTE ALKALI

| Strength of NaOH Solution Per cent | Extraction No. | Wood Dissolved Grams | Wood Dissolved Per cent | Pentosan in Residue Per cent | Pentosan in Residue Per cent of Total Pentosans |
|---|---|---|---|---|---|
| 5 | 1 | 7.3218 | 31.29 | 8.62 | 25.82 |
|   | 2 | 0.7909 | 3.38 | 6.82 | 19.42 |
|   | 3 | 0.3928 | 1.68 | 6.71 | 18.62 |
| 2 | 1 | 6.5095 | 27.82 | 11.58 | 36.44 |
|   | 2 | 0.5891 | 2.52 | 9.67 | 29.37 |
|   | 3 | 0.4005 | 1.71 | 9.23 | 27.34 |
| 1 | 1 | 5.7645 | 24.64 | 16.01 | 52.60 |
|   | 2 | 0.8349 | 3.57 | 13.58 | 42.50 |
|   | 3 | 0.3962 | 1.69 | 12.48 | 38.14 |

The residues from the last grinding with 5, 2, and 1 per cent caustic soda solutions contained 20.36, 21.07, and 20.48 per cent of lignin, respectively, a uniformity unexpected and not easily explained.

Contrary to the general opinion, the pentosans were very appreciably soluble in 1 per cent caustic soda. With 5 per cent and 2 per cent caustic soda the amount of xylan removed rapidly approached a minimum after the second extraction; if the curves of Fig. 1 were extended they would be expected to be asymptotic.

## ADSORPTION OF PENTOSANS

To determine if pentosans are adsorbed by wood the following experiment was made: To 50 grams of aspen 500 cc. of 2 per cent ammonium hydroxide solution were added, allowed to stand 2 weeks, filtered, washed, and the residue air-dried. The latter was treated with 500 cc. of 5 per cent sodium hydroxide solution, allowed to stand 48 hours with frequent shaking, then filtered and washed with 5 per cent sodium

hydroxide solution until the filtrate amounted to 600 cc. The pentosan content of the solution was then determined. Twenty-five grams of aspen were then ground 48 hours with 500 cc. of 5 per cent sodium hydroxide solution and 500 cc. of the above filtrate containing 4.264 grams of pentosan, thereby increasing the pentosan content about 60 per cent. The gelatinized material was then washed and analyzed as usual. It contained 8.50 per cent pentosan in comparison with 8.62 per cent pentosan obtained in the absence of added pentosans. This shows that there was no adsorption of pentosans, though the gelatinous condition of the wood would presumably be favorable for it.

### Extraction with Cuprammonium Solution

The material used for treatment with cuprammonium was yellow birch (*Betula lutea*), a representative sample from a tree over 60 years old. The wood contained 27.86 per cent pentosans (or, by extraction of the phloroglucide with alcohol, 25.86 per cent pentosan and 2.21 per cent methylpentosan), and 61.9 per cent cellulose by the Cross and Bevan method, the latter in turn containing 28.3 per cent pentosans.
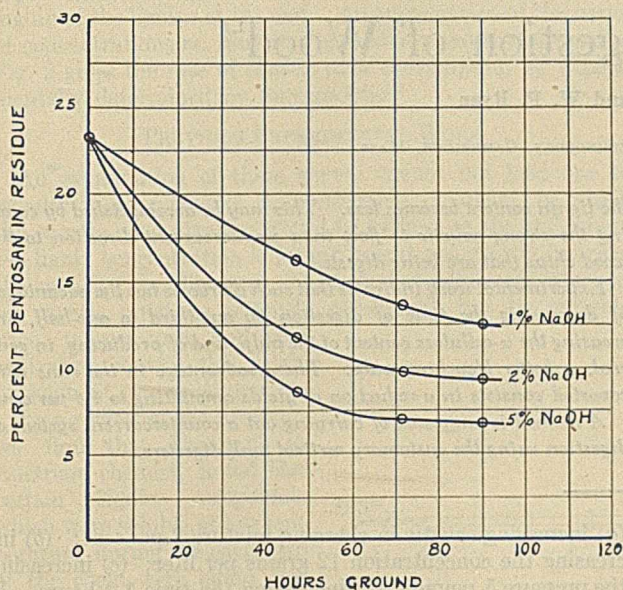


Fig. 1—Pentosan Content of Aspen after Extraction with Dilute Sodium Hydroxide

Previous to the use of cuprammonium solution it was of interest to determine the effect of concentrated ammonia alone. Yellow birch passing a 60-mesh sieve lost 10.9 per cent of its weight when treated with concentrated ammonia in the cold; the insoluble residue contained 25.8 per cent pentosan. Since the original wood contained 27.86 per cent pentosans, 17.49 per cent of the total pentosans were removed by the ammonia.

When 25 grams of birch were ground with 1 liter of concentrated ammonia for 24 hours, 14.49 per cent of the wood dissolved. The insoluble residue was filtered off and washed thoroughly. A pentosan determination was made on this residue and on a portion of the undiluted ammoniacal filtrate. A portion of the latter was also treated with an excess of crystalline copper hydroxide and allowed to stand with frequent shaking for 1 week to determine the effect on the pentosans. The solution was then filtered by pressure and the pentosans determined. The results are given below: *A* represents the pentosans calculated from the total phloroglucide precipitate, and *B*, after extracting the latter with alcohol.

TABLE II—Action of Ammonia on Birch

| | Pentosan | |
| | A % | B % |
| --- | --- | --- |
| Original wood | 27.86 | 25.86 |
| Residue from NH₄OH extraction | 21.51 | 21.21 |
| Ammonia solution | 4.98 | 4.86 |
| Cuprammonium solution | 1.81 | 1.39 |

In determining the pentosans in the cuprammonium solution, 200 cc. were used; most of the ammonia was removed by a vacuum at room temperature. The solution was then made up to 12 per cent hydrochloric acid, and after distilling down to 70 cc. the usual procedure for determining pentosans was followed. It will be noted that the addition of cupric hydroxide to the ammonia solution resulted in an appreciable loss of pentosans or furfural-producing substances; furthermore, the phloroglucide precipitate from the cuprammonium solution was soluble to the extent of 25.3 per cent in alcohol. It will also be seen that treatment with ammonia has destroyed to a considerable extent the so-called methylpentosans. The sum of the corrected pentosan values for the residue and the ammonia extract in *B* is in good agreement with that for the original wood, but in *A* there is a loss of 1.4 per cent. In the writer's opinion figures for methylpentosans as now determined are largely fictitious.

Previous extraction of the sample with concentrated ammonia in the cold removes easily soluble pentosans and reduces the amount of lignin in the cellulose subsequently removed by cuprammonium solution. The cellulose solution does not appear to undergo appreciable change on standing. In one experiment the birch was extracted with concentrated ammonia, well washed, and dried; 25 grams were then ground in 1000 cc. of cuprammonium solution prepared according to Gibson[20] for 24 hours. After allowing to settle, a portion of the solution *A* was filtered under pressure; for this purpose a 2.54-cm. (1-inch) threaded brass tube with a perforated brass cap was used, the latter containing a porcelain filter plate and a layer of asbestos. The cellulose solution mixed with fibrous kieselguhr was poured into the tube and an air pressure of 40 pounds applied. In this way a perfectly clear filtrate was obtained. It was impossible to filter the cellulose solution by suction. The cellulose in the filtrate was precipitated with hydrochloric acid and washed until the wash water gave no test for chlorides. The remainder of the cellulose solution *B*, after standing 12 days in a stoppered flask in a cool, dark place, was filtered and precipitated in the same way. The analyses of the two precipitates are given below.

TABLE III

| Cellulose | Lignin Per cent | Pentosan Per cent | Pentosan on Lignin-Free Basis Per cent |
| --- | --- | --- | --- |
| A | 5.61 | 27.09 | 28.70 |
| B | 5.70 | 26.40 | 27.99 |

The difference in pentosan content may be considered as within experimental error.

Birch wood, first extracted with concentrated ammonia, gave with cuprammonium solution in various experiments celluloses which on a lignin-free basis contained from 25 to 29 per cent of pentosans. In view of the various factors involved in the use of cuprammonium solution, this may be considered in fair agreement with the pentosan content (28.3 per cent) of the Cross and Bevan cellulose.

The writer has made numerous extractions with cuprammonium solution and has failed to obtain therefrom a cellulose constant in composition as regards the lignin and pentosan content. This is contrary to the statement of Cross and Bevan[21] that the soluble portion of the lignocelluloses has the same composition as the residue. In one experiment 40 grams of birch that had not been given a preliminary treat-

20 *J. Chem. Soc.* (London), **117**, 492 (1920).
21 "Cellulose," **1916**, p. 114.

ment of any kind beyond dry grinding were ground for 72 hours with 2 liters of cuprammonium solution. This product was centrifuged and subjected to the following treatments: A, solution obtained by centrifuging; B, cellulose precipitated from a portion of the centrifuged solution, washed with hot water; C, portion of centrifuged solution filtered through the brass tube; D, solution obtained by treating the sludge from the centrifuge with 1 liter of cuprammonium solution and let stand with frequent shaking for 5 days and centrifuging; E, sludge from treatment D. The centrifuged solutions were allowed to stand 24 hours and again centrifuged; they were still cloudy. The cellulose was precipitated as usual and washed with cold water unless otherwise specified. The analyses of the various celluloses are given in Table IV.

It is apparent that there is no uniformity in the precipitates in this table, and that a preferential solvent action was exercised on the pentosans. The lower lignin and pentosan content of B is readily explained by washing with hot water in which the pentosans, once dissolved, are appreciably soluble;

after washing with cold water the first washing with hot water was colored a decided yellow. There is no reason to expect that the pentosan in the cuprammonium solution is in chemical combination with orthoglucosan, though the optimum conditions for adsorption exist; as a matter of fact, the pentosan can be readily removed with dilute alkali and to an appreciable extent by prolonged treatment with hot water. The high pentosan contents of D and E indicate the great resistance of the pentosans to solution. The chlorine–sodium sulfite reaction for lignin was applied to the lignins isolated from A and D by means of 72 per cent sulfuric acid, the characteristic color reaction being obtained in both cases.

TABLE IV—CELLULOSES EXTRACTED FROM BIRCH BY CUPRAMMONIUM SOLUTION

| Precipitate | Lignin Per cent | Pentosan Per cent | Pentosan on Lignin-Free Basis Per cent |
|---|---|---|---|
| A | 13.58 | 38.82 | 44.92 |
| B | 9.77 | 36.91 | 40.91 |
| C | 13.97 | 33.07 | 38.44 |
| D | 12.84 | 17.68 | 20.28 |
| E | 34.11 | 10.01 | 15.32 |

# Countercurrent Digestion of Wood[1,2]

By R. T. Haslam and W. P. Ryan

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*In the soda process for the manufacture of wood pulp, the digester is charged at the start with caustic soda and wood chips. Thus strong caustic is brought in contact with wood when the concentration of lignin is large, leaving weak caustic to digest the small amounts of lignin remaining at the end of the digestion. This combination gives extremely rapid digestion of wood at the beginning and a very slow cleaning up of lignins at the end.*

*For rapidity of digestion the law of mass action indicates the advantage of using dilute caustic soda at the start when the lignin concentration is high, gradually increasing the strength of caustic as*

*the lignin content becomes less. This may be accomplished by causing the strong caustic to flow in a countercurrent direction to the wood chips that are being digested.*

*Experimental work indicates that such a process has the advantages of decreasing the time of digestion by one-third to one-half, increasing the α-cellulose content of the pulp, and of producing, in general, a better bleaching pulp. The disadvantage in the runs here reported consists in a reduction of yields amounting to 4.4 per cent.*

*A method is suggested of carrying out a countercurrent system of digestion using the customary vertical tank digesters.*

THE present soda process for the production of wood pulp is based on the patent granted Charles Watt and Hugh Burgess[3] in 1854, for, with the exception of the elimination of an intermediate chlorination practiced in the early days, few radical changes have been made. The digester, however, has been changed frequently, the tendency being always toward the large, vertical, stationary, direct heating type. The more important factors, such as charging mixture, concentration of caustic, pressure, temperature, and time of digestion, have been carefully studied, especially by Surface,[4] who recommends the following:

(1) Charging mixture............ 25 pounds NaOH per 100 pounds bone dry wood
(2) Concentration of liquor....... 70 grams NaOH per liter
(3) Pressure................... 100 pounds per square inch gage
(4) Temperature............... 338° F.
(5) Time of digestion........... 7 hours

Investigations by Sutermeister[5] show that a decrease of 1 per cent in the yield results from each of the following:

(a) increasing caustic in charging mixture 2 per cent; (b) increasing the concentration 12 grams per liter; (c) increasing the pressure 5 pounds; (d) increasing the time 1.2 hours. It is evident that the type of digester will have an important effect on operation, for on it will depend the character and amount of circulation of the cooking liquor. However, each mill using data in the literature as a guide can work out the operating conditions best suited to it. As the chemistry of the process has become better known, it has been possible to eliminate much of the trial and error method of earlier days.

It is generally believed that the action of caustic on the wood is one of alkaline hydrolysis, in which the lignocellulose is gradually broken down with the formation of acid products which combine with and neutralize the caustic.[6] If this is true, we would expect that for a definite weight of wood a definite amount of caustic would always be neutralized, and on a certain wood caustic neutralized at the end of digestion has been found to be 16.7 pounds out of 25 pounds charge per 100 pounds of bone dry wood. From this it would appear that we can regard the reaction as $A + B = C$, in which A represents the acid products resulting from hydrolysis, B the caustic, and C the sodium organic salts formed. By the mass law,
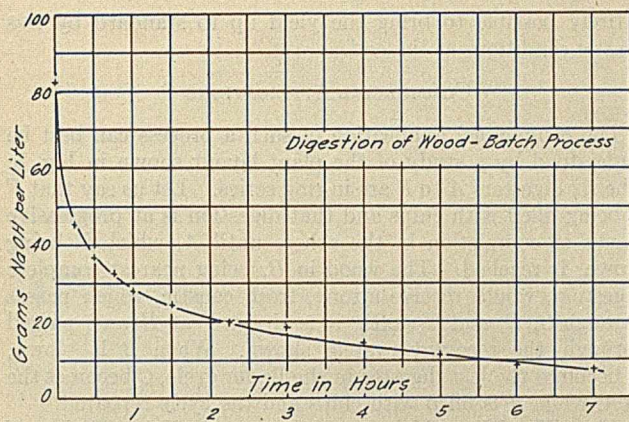
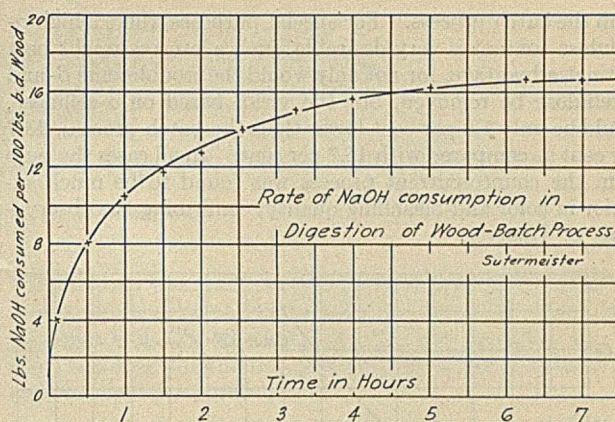$$\frac{A \times B}{C} = K$$

Fig. 1



Fig. 2

for any given conditions. It will be noted that in the usual batch process at the start the reacting substances are large while the product formed is small, whereas just the reverse is true at the end. We would, therefore, expect extremely rapid digestion of the wood at the start, and very slow cleaning up of the lignins at the end. An examination of the curve of concentrations *vs.* time in Fig. 1 shows the actual results. Fig. 2 gives the rate of caustic soda consumption as experimentally determined by Sutermeister.[5]

### Previous Experimental Work

An examination of these curves cannot but lead one to wonder if a process of countercurrent digestion, in which the caustic concentration would be highest at the end where the lignin concentration is lowest, might not greatly increase the capacity of a digester. The fact that cellulose is attacked by caustic must be seriously considered, but by suitable time, temperature, and concentration control this might be kept at a minimum.

In a review of the literature we find that Ungerer,[7] an Austrian chemist, noted that certain lignin compounds, which were soluble at low temperature during the early part of the cook, were again precipitated at the higher temperatures existing at the end of the digestion. In 1872 he secured a British patent, the chief object of which was to obtain a better bleaching pulp by removing the dissolved lignins by means of a countercurrent process. For that purpose he proposed to use nine digesters in series, the temperature of each being successively higher and the caustic being forced from one to the other until spent. There is nothing in the patent to indicate that he appreciated any other advantages that might result from the application of this principle. No record of the commercial application of his patent was found, which is not surprising when one considers the large

number of factors which he proposed to vary and the probable unreceptive attitude of the industry to such radical changes at that time.

In 1921 Clark and Cook[8] began experimental work to determine the effect of a countercurrent process on time of digestion and yield of pulp. For their purpose a small experimental digester shown in Fig. 3 was used. The digester consisted of a 5-foot section of 8-inch steel pipe, *A*, fitted with a removable flange cover and reducing coupling. The chips were charged through the cover, the caustic was added through the trap *G* at the same rate the solution was drawn off through *J*. Recirculation was effected by the centrifugal pump *D*. The solution was heated by burners about the pipe *E*, steam being used only to heat up the digester. The charge was blown through the cock *F* to a tank, where it was washed, sampled, and weighed. The pressure was reduced through *G* and *H*. Clark and Cook first ran a series of batch cooks, of which Fig. 1 is an example, and then a series of countercurrent cooks. The net result of their work showed that digestion could be completed in one-half the time required by the batch process, but that the yield averaged 8 per cent lower, the extremes being 4.1 and 13.0 per cent. Examination of the pulp showed that even with such a decrease in time overcooking had occurred. It was evident that considerable experience would be necessary to determine the exact end conditions in order to prevent a serious loss of cellulose.

Their work was continued the next year by Wagner, Sippel, and Miskelly,[9] who likewise found a time reduction of one-third to one-half over the batch process and a yield averaging 4.4 per cent lower. It is important to note that the $\alpha$-cellulose in the pulp from the countercurrent digestion averaged 91.7 per cent as compared with 86.9 per cent



Sketch of Apparatus

To Blow Tanks

Fig. 3

[7] British Patent 257 (1872).

[8] M. I. T. Undergraduate Thesis, **1921**.

[9] M. I. T. Thesis, **1922**.

from the batch process. For special purposes where a high $\alpha$-cellulose content is very desirable, such a process might be a distinct advantage, for not only would the troublesome $\beta$- and $\gamma$-cellulose be removed, but the yield, based on $\alpha$-cellulose, would be only 1.5 per cent lower than the batch process, 43.7 per cent as compared with 45.2 per cent. In all cases the pulp from the countercurrent process was found to be much superior in color and bleaching quality, confirming the observations of Ungerer.



FIG. 4

As examination of the curves in Fig. 4 shows that the concentration of caustic soda at the end of the countercurrent cook was much higher than at the beginning of the batch cook—in fact, accounting for a 2 per cent decrease in yield based on Sutermeister's[5] investigations. The actual decrease in yield in the cooks represented by the curves was 2.4 per cent, the $\alpha$-cellulose content of the countercurrent pulp was 5.9 per cent higher, and the Tingle[10] bromine figure 0.40 as compared with 0.27 for the batch process. It would appear

[10] THIS JOURNAL, **14**, 40 (1922).



FLOW SHEET
COUNTER CURRENT OPERATION
FIG. 5

entirely possible to bring the yield up to standard by less drastic conditions at the end.

### COMMERCIAL APPLICATIONS

The commercial application of such a process can best be understood by a study of the plant layout shown in Fig. 5. The six digesters $A$ to $F$ are in ring series. Let us say that $F$ is being filled with chips and that digestion is at progressive stages of completion in the others until $A$, which is being blown, is reached. The wood in $B$, being nearest complete digestion, would receive strong, fresh caustic, which passes through $C$, $D$, and $E$, until it is drained at $E$ and passed through the recovery system shown. When $B$ is blown, $F$ becomes the last digester in the liquor cycle, $C$ becomes the first, while $A$ is filled with chips and the cycle repeated.

The difficulties which beset the commercial adoption of such a process are apparent, especially to those familiar with the industry. It would be unwise to attempt plant operation without going through an intermediate stage in which a number of small digesters, such as the one shown, are used to determine more detailed information in regard to circulation and concentration of liquor, temperature, and time of digestion. Such experimentation would serve to train operators for the commercial unit and prevent costly mistakes through overcooking at large charges later on. The extra piping, storage tanks, and pumps required should not be excessive if well-balanced operation is maintained.

One objection which might be raised is the loss of caustic due to blowing a digester just charged with fresh liquor. If the tank system of washing pulp were used, this loss would indeed be serious, but it is thought that systems employing continuous filters of the drum type or continuous centrifugals would make possible the recovery of this caustic with very little dilution. The most serious question is that of yield, for even a 1 per cent decrease would represent a large yearly loss. It is encouraging to note that in the second investigation the average loss was decreased 50 per cent, and had the final treatment not been so drastic the yield would probably have been much better. It might conceivably pay to maintain a margin of safety by slightly undercooking the wood, the screening being returned to the digester to prevent excessive loss. As the bleaching quality of the pulp is much improved anyway, the increase in bleach consumption due to undercooking would be no detriment.

Experience has shown that wherever a batch process has been changed to a continuous process, almost invariably costs are reduced, and better quality and uniformity of product result because of the standardization of operation required. The increased capacity of the digester room, one of the most expensive units of a mill, the higher $\alpha$-cellulose content and better bleaching quality of the pulp, the more concentrated and uniform strength of black liquor to the evaporators, and the more complete utilization of soda are advantages which invite the industrial application of this process.

## Colloid Symposium Monograph

The papers and discussions presented at the First Annual Colloid Symposium, held at Madison, Wis., in June, 1923, have been published by the Department of Chemistry of the University of Wisconsin.

The monograph comprises 420 pages, and is one of the most important books on the subject of colloids ever published in this country. The twenty-two papers cover a wide range of theoretical considerations and applications to medicine and the industries. Copies may be obtained at cost of publication ($2.75 per copy, including postage) from the University Coöperative Co., Madison, Wis., to whom all remittances should be made. As the edition is limited, those contemplating purchase of copies should place orders promptly.

# Determination of Cellulose in Wood[1]

## Chlorination Method

### By G. J. Ritter and L. C. Fleck

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THIS study was suggested by some of the results given in Paper VII[2] of the series from this laboratory on the chemistry of wood. These results are found in Table I. They show the proportion of lignin remaining in three species of sawdust residues after varying periods of chlorination.

The samples in Paper VII were first extracted with a minimum boiling solution of alcohol-benzene in a Soxhlet apparatus, thoroughly washed with warm water in an alundum crucible connected with a suction pump. Four to five samples of each species were then alternately chlorinated and extracted with sodium sulfite, with the exception of Basswood Samples 3 and 4, which were not extracted at the end of the first 15-minute chlorination. It will be noticed in this case that scarcely any lignin (0.10 per cent) was removed by the second 15-minute treatment with chlorine. The intervals in which the tanbark oak and incense cedar sawdusts were in contact with chlorine were shortened to 10 and 5 minutes to ascertain the effect on removing lignin.

**Table I—Per cent of Lignin in Original and Partially Chlorinated Sawdust**

(Results based on oven-dry weight of original wood)

| Species | | Chlorination Period Minutes | Per cent Lignin |
|---|---|---|---|
| Basswood (original) | 1 | 0 | 20.70 |
| | 2 | 15 | 5.16 |
| | 3 | 15,[a] 15 | 5.06 |
| | 4 | 15, 15, 15 | 3.39 |
| Tanbark oak (original) | 1 | 0 | 23.70 |
| | 2 | 10 | 5.29 |
| | 3 | 10, 5 | 1.78 |
| | 4 | 10, 5, 5 | 1.38 |
| Incense cedar (original) | 1 | 0 | 37.73 |
| | 2 | 5 | 10.70 |
| | 3 | 5, 5 | 2.80 |
| | 4 | 5, 5, 5 | 1.00 |
| | 5 | 5, 5, 5, 5 | 0.75 |

*a* No sulfite extraction between first and second chlorinations.

The results on the three woods used indicate that chlorinations of 15 minutes' duration are no more effective than those of 5 minutes. With basswood 45 minutes, three 15-minute periods, reduced the lignin content from 20.7 to 3.39 per cent. Twenty minutes of actual chlorination, one 10 and two 5-minute periods, reduced the lignin from 23.7 to 1.38 per cent in tanbark oak. Four 5-minute periods reduced the lignin from 37.73 to 0.75 per cent in incense cedar. In the first wood two sulfite extractions were made; in the second, three; in the third, four. The actual chlorination period of the last two woods is less than one-half that in the first species, but the frequency of removing the "lignin chloride" is increased.

This study was made in order to determine (1) the efficiency of the short chlorination periods for removing lignin from cellulose and (2) whether the cellulose prepared by the short and long chlorination periods is the same as to quantity and chemical composition.

### Experimental

Sawdust (80–100 mesh) was extracted with minimum boiling alcohol-benzene solution for 4 hours, thoroughly washed with hot water, and sucked dry in an alundum crucible connected to a suction pump. The cellulose was then determined in each of the species in Table II by using the following two chlorination periods: 20, 15, 15, 10, 10, and 5, 5, 5, 5, etc. In the table the first series of chlorinations is indicated as the *long* and the second as the *short* periods. Any material difference in the cellulose prepared by the two methods should be found in one or more of the following constants: total cellulose, pentosans in cellulose, lignin in cellulose, α-, β-, and γ-cellulose in cellulose. The samples prepared were accordingly analyzed, with the results found in Table II.

### Discussion of Results

CELLULOSE IN WOOD—In the determination of cellulose a difference of 0.50 per cent for duplicate samples is found to be within the experimental error. In the case of eastern hemlock (heartwood) an increase of 1.41 per cent in favor of the short method is found. An increase of 0.91 per cent in favor of the short method is also found in black locust (heartwood). The difference in yields of cellulose with eastern hemlock (sapwood) and catalpa (sapwood) is approximately 0.50 per cent. This difference in cellulose content may be due to one or a combination of three causes:

1—It is possible that hydrochloric acid formed during the chlorination hydrolyzes some of the cellulose to sugar and it is dissolved during the washing process.
2—A larger percentage of the less resistant pentosans may be removed in one process than in the other.
3—A more complete removal of lignin may be accomplished in one case than in the other.

The second and third factors were investigated as shown by Table II.

PENTOSAN IN CELLULOSE—In eastern hemlock cellulose the pentosan content is slightly higher in that prepared by the short than by the long chlorination method; in black locust and catalpa cellulose the opposite is true. The greatest difference in the pentosan content of cellulose prepared by the two methods is 1.74 per cent in the black locust. In general, the influence of pentosans on the character of the cellulose prepared by the two methods is uniform.

**Table II—Comparison of Cellulose Prepared by Short and Long Chlorination Periods**

(Percentages based on oven-dry weight of materials)

| Species | | Method of Chlorination | Chlorination Periods Minutes | Cellulose in Wood | Pentosans in Cellulose | Lignin in Cellulose | α-Cellulose in Cellulose | β-Cellulose in Cellulose | γ-Cellulose in Cellulose |
|---|---|---|---|---|---|---|---|---|---|
| Eastern hemlock | (sapwood) | Short | 5, 5, 5, 5, 2 | 54.23 | 6.98 | 1.50 | 49.7 | 31.7 | 18.6 |
| | | Long | 20, 15, 5, 15, 10 | 54.76 | 6.15 | 1.30 | 45.3 | 33.8 | 20.9 |
| | (heartwood) | Short | 5, 5, 5, 5, 2 | 54.18 | 7.04 | 1.60 | 46.3 | 23.8 | 29.9 |
| | | Long | 20, 15, 15, 10, 5 | 52.77 | 6.10 | 1.50 | 48.1 | 22.6 | 29.3 |
| Black locust (heartwood) | | Short | 5, 5, 5, 3 | 52.82 | 23.02 | 1.27 | 71.3 | 18.7 | 10.0 |
| | | Long | 20, 15, 15, 10 | 51.91 | 24.76 | 1.32 | 45.0 | 32.0 | 23.0 |
| Catalpa (heartwood) | | Short | 5, 5, 5, 5 | 55.33 | 21.68 | 0.95 | 73.7 | 7.6 | 24.7 |
| | | Long | 20, 15, 15, 10 | 55.79 | 22.90 | 1.15 | 71.4 | 17.8 | 10.7 |

LIGNIN IN CELLULOSE—The lignin content of the cellulose prepared by the two methods agrees within the experimental error. This is to be expected, for in either case the chlorination was carried on until the sodium sulfite solution used for extracting the chlorinated product showed no discoloration.

α-, β-, AND γ-CELLULOSE IN CELLULOSE—The only marked difference between the effect of the two methods on α-cellulose is shown in black locust. β-Cellulose is considerably lower in black locust and catalpa cellulose prepared by the short chlorination method. From the limited amount of data available it appears that short-chlorinated cellulose is more stable than that prepared by the long method.

A comparison of the results obtained from the short and long chlorination methods indicates that the reaction between chlorine and lignin is fairly rapid. The substance "lignin chloride," soluble in sodium sulfite, must be removed from the surface of the wood particles. The "lignin chloride" seems impermeable to chlorine, for prolonged contact of the gas with the chlorinated sawdust has little effect in further removing lignin. This statement is based on the data of (1) the last samples of basswood, tanbark oak, and incense cedar

(Table I), in which two, three, and four sulfite extractions were made, respectively, and (2) the cellulose prepared by the short and long methods (Table II) in which the number of extractions are equal. Prolonged chlorination does, however, break down the α-cellulose.

## CONCLUSION

In preparing pulp for paper commercially, it is found that from 40 to 45 per cent of the wood is utilized. Approximately 60 per cent should be utilized, for that amount of cellulose can be isolated from the wood by the chlorination method. Thus, 25 per cent of the paper-making material is lost in commercial operations. It is this lost cellulosic material that the progressive paper manufacturer is striving to recover by modifying his pulping process. There are two objections to the chlorination method—the number of steps involved and the cost of the chlorine. If the amount of chlorine can be reduced in a commercial operation in the same proportion as reported in this paper, one of the objections against introducing the chlorination process for preparing pulp commercially will have been overcome.

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# The Solubility of Sulfur in Rubber[1]

By W. J. Kelly and K. B. Ayers

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*The question as to whether or not rubber adsorbs sulfur has been discussed quite extensively in the literature. In the following work it is proved by a study of the distribution of sulfur between rubber and another phase that the system obeys Henry's law and hence the sulfur is dissolved in and not adsorbed by the rubber. Figures are given showing the solubility at different temperatures and degrees of vulcanization. The bearing of this on theories of vulcanization is indicated and the possibility of using the laws of chemical kinetics to study the reaction between sulfur and rubber is pointed out.*

IN THE discussions of the theories of vulcanization which have been published in the past several years, many references are made to the fact that the first step in the process was either the solution of sulfur in or its adsorption by the rubber. No definite work to show which of these processes actually took place was done until Skellon[2] published his experiments on the migration of sulfur in rubber. As a result of this work Skellon concluded that the rubber dissolved the sulfur and hence did not adsorb it. Venable and Green[3] also made some similar experiments, but went further and determined the maximum amount of sulfur which the rubber would take up under certain conditions. Both these methods had one thing in common. The sulfur was allowed to diffuse into the rubber—in Skellon's work from another piece of rubber containing a large excess of sulfur, and in Venable and Green's experiments from the elementary sulfur itself. Both authorities conclude from their work that the rubber dissolves the sulfur.

The conditions of the experiments do not permit the definite conclusions that the sulfur is not adsorbed, because in both cases the sulfur might have diffused through the vapor phase and been adsorbed by the rubber. The best way to determine whether sulfur is dissolved or adsorbed by the rubber is to study the distribution of the sulfur between rubber and a known solvent for the sulfur in which the rubber is insoluble. In this way if an equilibrium exists between the two phases it can be approached from both sides. If the

ratios of the concentrations in the two phases are constants, the system obeys Henry's law and the sulfur is dissolved by the rubber. Thus by plotting the corresponding values of the concentrations a straight line passing through the origin would be obtained. Even if the sulfur were dissolved in the rubber it would be possible to have a curved line passing through the origin if the molecular weight of the sulfur in the rubber were different from that in the other phase. Assuming for the moment that in the liquid phase sulfur were present as $S_8$ and in the rubber as $S_4$, we should have the reaction expressed by the equation

$$S_8 \rightleftharpoons 2S_4$$

taking place at the interface, and instead of expressing Henry's law as

$$\frac{C_1}{C_2} = K \qquad (1)$$

we should have to write

$$\frac{C_1^2}{C_2} = K \qquad (2)$$

and the result would be a curve of the second degree. In this case it would be difficult to distinguish between solubility and adsorption without resorting to other means, as the adsorption isotherm is expressed by the equation

$$\frac{X}{M} = K\left(C^{1/n}\right) \qquad (3)$$

which, if $n = 2$ or 0.5, gives exactly the same curve as Equation 2.

For the experiments to be described in this paper n-butyl alcohol was chosen as the liquid, and it was found that when

[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.
[2] *India Rubber J.*, **46**, 251 (1913).
[3] THIS JOURNAL, **14**, 319 (1922).

the corresponding concentrations were plotted the result was a straight line passing through the origin. Thus Equation 1 is applicable to this system, and it must be concluded that the sulfur is actually dissolved in the rubber and not adsorbed by it. Taken in conjunction with the work of Endres[4] the proof of solubility is complete.

### EXPERIMENTAL

Two methods were employed in this work and the equilibrium was approached from both sides. In the first method the sulfur was mixed with the rubber and the mixture placed in amyl alcohol and allowed to come to equilibrium. Portions of the solution were then removed and the concentration of the sulfur was determined. The total amount of sulfur in the alcohol could then be calculated, and this subtracted from the amount originally present in the rubber gave the concentration of the sulfur in the rubber. In the second method different amounts of rubber were placed in a definite volume of saturated solution of sulfur in butyl alcohol, and after equilibrium had been reached the solution was again analyzed. The sulfur lost from the solution was taken up by the rubber and its concentration could be easily calculated. These experiments were all carried out in a thermostat controllable to ± 0.01° C.

### FIRST METHOD

PROCEDURE—To determine the amount of sulfur in the alcohol a known weight was taken and evaporated to dryness on the steam bath. The residue was then oxidized with nitric acid saturated with bromine and potassium chlorate and the sulfur precipitated and weighed as barium sulfate.

RESULTS—The results of these experiments are given in the tables and figures.

TABLE I—SULFUR ORIGINALLY PRESENT IN RUBBER
(Samples in amyl alcohol at 40° C.)

| Per cent Sulfur in Rubber Originally | Weight Rubber and Sulfur G. | Amyl Alcohol G. | $C_1{}^a$ | Total Sulfur Present G. | Total Sulfur in Amyl G. | Sulfur Rubber G. | $C_2{}^b$ | $K = \dfrac{C_2}{C_1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.42 | { 19.3 | 40.0 | 0.395 | 0.0806 | 0.0158 | 0.0648 | 3.36 | 8.50 |
|      | { 20.0 | 39.7 | 0.394 | 0.0840 | 0.0156 | 0.0684 | 3.42 | 8.68 |
| 0.80 |       |      |       |        |        |        |      |      |
| 0.80 | { 7.05 | 39.8 | 0.466 | 0.0564 | 0.0186 | 0.0378 | 5.36 | 11.5 |
|      | { 7.20 | 40.0 | 0.455 | 0.0576 | 0.0176 | 0.0400 | 5.56 | 12.5 |
| 0.95 | { 5.0  | 40.0 | 0.497 | 0.0475 | 0.0190 | 0.0285 | 5.70 | 11.5 |
|      | { 5.18 | 39.6 | 0.499 | 0.0493 | 0.0195 | 0.0298 | 5.92 | 11.8 |
| 1.21 | 5.03 | 39.8 | 0.681 | 0.0610 | 0.0243 | 0.0367 | 7.29 | 10.7 |
| 1.41 | 5.02 | 39.8 | 0.783 | 0.0708 | 0.0282 | 0.0426 | 8.50 | 10.7 |

$^a$ $C_1$ = mg. sulfur per gram alcohol.
$^b$ $C_2$ = mg. sulfur per gram rubber.

In the experiment reported in Table I the sulfur was originally present in the rubber and was partially removed by the alcohol, and in Table II the equilibrium was approached from the opposite direction. These results are plotted in Fig. 1, the lines I and II corresponding to the data in Tables I and II, respectively. It is obvious that the points all fall fairly well on a straight line passing through the origin, and hence the conditions of Henry's law as stated in Equation 1 are fulfilled.

TABLE II—SULFUR ORIGINALLY PRESENT IN BUTYL ALCOHOL
(Different weights of rubber added to 100 cc. of butyl alcohol saturated with sulfur at 30° C. 25-cc. samples for analysis)

| Rubber G. | $C_1{}^a$ | $C_2{}^b$ | $K = \dfrac{C_2}{C_1}$ |
|---|---|---|---|
| 2 | 1.68 | 8.4 | 5.0 |
| 4 | 1.49 | 7.9 | 5.3 |
| 6 | 1.36 | 7.2 | 5.3 |
| 8 | 1.23 | 6.7 | 5.4 |
| 10 | 1.09 | 6.4 | 5.9 |
| 12 | 1.06 | 5.5 | 5.2 |
| 14 | 0.98 | 5.2 | 5.3 |

$^a$ $C_1$ = mg. sulfur per gram alcohol.
$^b$ $C_2$ = mg. sulfur per gram rubber.

[4] India Rubber World, 68, 635 (1923).

According to Henry's law, if one of the phases is saturated the other is also, and hence the intersection of the equilibrium line with the coördinate corresponding to saturation of the alcohol will give the solubility of sulfur in rubber at the temperature employed. For butyl alcohol at 30° C. the value at saturation is 1.87 mg. per gram, and hence the solubility of sulfur in rubber is 10.1 mg. per gram. The solubility of the sulfur in amyl alcohol at 40° C. was not determined, as immediately after the data in Table I were obtained amyl alcohol was discarded in favor of n-butyl alcohol, which was used in all the later experiments.
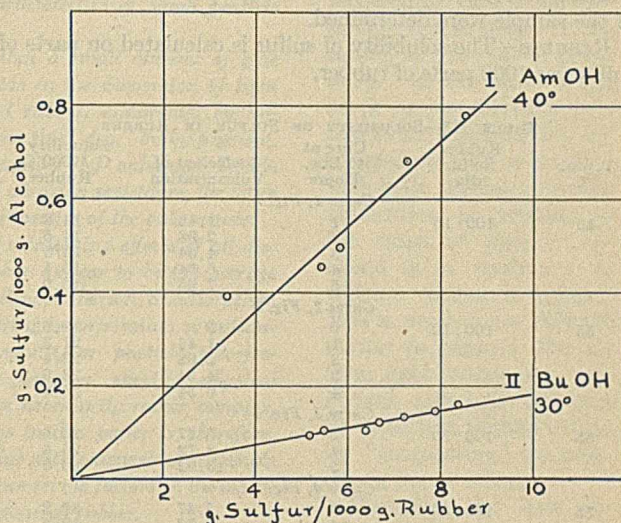


FIG. 1—DISTRIBUTION OF SULFUR BETWEEN RUBBER AND BUTYL AND AMYL ALCOHOLS

Since this method is too cumbersome for the determination of the solubility of sulfur in a large number of samples, it was used only to establish the fact that the rubber dissolves and does not adsorb the sulfur.

### SECOND METHOD

As was stated above, if the alcohol is saturated with sulfur and equilibrium has been established between the sulfur in the alcohol and that in the rubber, then the rubber is also saturated with respect to the sulfur. Hence, it is only necessary to leave a strip of rubber in contact with a saturated solution of sulfur in the alcohol for a sufficient length of time to establish equilibrium and then remove and analyze the rubber for sulfur. This method was followed in the experiments to be described and good results were obtained at 40° and 55° C. At higher temperatures other complications arose which could not be eliminated, and these will be discussed later.

PROCEDURE—Slabs of rubber, vulcanized or unvulcanized, approximately 2 mm. thick and weighing about 2 grams, were first extracted with acetone and then suspended in a saturated solution of sulfur in butyl alcohol. The solution was contained in an aluminium vessel equipped with a cover and having a stirrer on which the samples were hung. The rubber was kept near the top of the solution and an excess of sulfur was always present. The surface of the rubber sample was kept free of solid sulfur by employing a deep vessel with the butyl alcohol about 15 cm. (6 inches) deep. If the solution is stirred slowly it will be kept saturated throughout without causing the solid sulfur to be agitated sufficiently to come in contact with the rubber. If any solid sulfur adheres to the rubber the determination is spoiled, as it cannot be completely removed. In this way several samples could be suspended in the same solution as each piece of rubber formed its own system with

the solution. After the samples were in the solution long enough for equilibrium to be established, they were removed and placed directly in weighing bottles and weighed. They were then vacuum-dried and weighed again in order to determine the amount of butyl alcohol in them and thus make a correction for the sulfur in this amount of alcohol. The rubber was then extracted with acetone and the sulfur thus obtained was oxidized, precipitated, and weighed as barium sulfate. The acetone extraction was made so that the sulfur taken up by the rubber from the alcoholic solution could be separated from the sulfur combined with the rubber, for which a correction would have to be made if the total sulfur of the sample were determined.

Results—The solubility of sulfur is calculated on parts of sulfur per 1000 parts of rubber.

Table III—Solubility of Sulfur in Rubber

| Temp. °C. | Rubber Sulfur Mix | Cure at 40 Lbs. Hours | Coefficient of Vulcanization | Solubility G./1000 G. Rubber |
|---|---|---|---|---|
| | | *Curve 1, Fig. 2* | | |
| 40 | 100:10 | 1 | 1.46 | 14.8 |
| | | 2 | 2.98 | 14.5 |
| | | 3 | 4.34 | 15.3 |
| | | 4 | 6.54 | 16.1 |
| | | 5 | 7.95 | 16.9 |
| | | *Curve 2, Fig. 2* | | |
| 55 | 100:10 | 0 | 0 | 19.6 |
| | | 1 | 1.46 | 21.3 |
| | | 2 | 2.98 | 22.4 |
| | | 3 | 4.34 | 23.9 |
| | | 4 | 6.54 | 25.6 |
| | | *Curve 3, Fig. 2* | | |
| 55 | 100:30 | 3 | 5.47 | 23.6 |
| | | 4 | 8.72 | 26.4 |
| | | 5 | 13.92 | 30.0 |
| | | *Curve 4, Fig. 2* | | |
| 75 | 100:30 | 3 | 5.47 | 32.2 |
| | | 4 | 8.72 | 42.5 |
| | | 5 | 13.92 | 54.2 |
| | | 6 | 16.91 | 59.0 |

The figures for 75° C. are included in the table for one mixing and are plotted in Fig. 2, Curve 4, although there is some doubt as to their accuracy. By the method employed it is not possible to obtain reliable results at the higher temperatures because the rubber depolymerizes or is oxidized and becomes soluble in the butyl alcohol. This complicates the analysis of the samples to such an extent that no confidence can be placed in the results at present. It is hoped that these difficulties may be overcome and reliable figures obtained for the solubility of sulfur in rubber at higher temperatures.
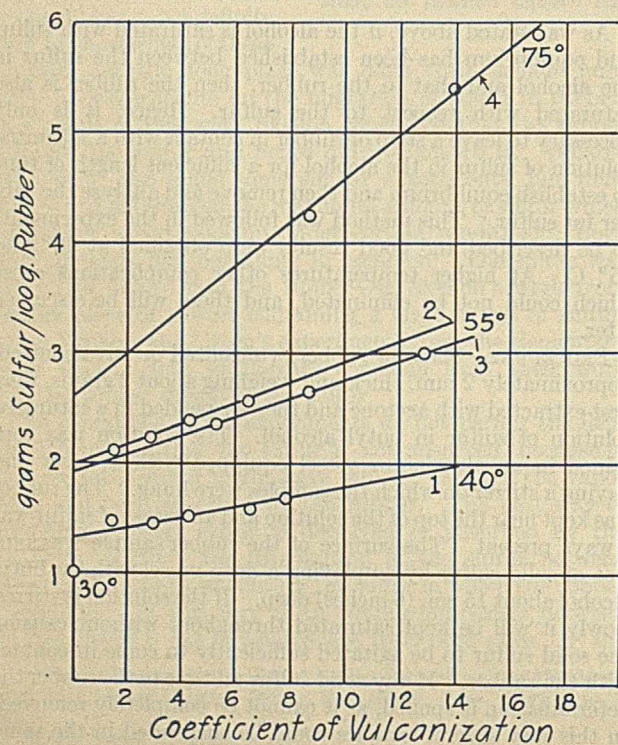
Working according to Venable and Green's method it is not possible to determine the solubility of the sulfur on account of the extreme slowness of diffusion when the coefficient of vulcanization is more than about 7. The results recorded here, however, prove that the solubility of sulfur increases linearly with the coefficient up to a value of the latter of 17, or up to the point where about 35 per cent of the double bonds of the rubber are saturated with sulfur.

There is a slight difference in Curves 2 and 3, which is possibly due to experimental error. However, it may also be due to differences in degree of aggregation of the rubber, in which case the mixing which is disaggregated more should dissolve more sulfur. In these two stocks the one for which the points on Curve 2 were obtained contained less sulfur originally and hence would vulcanize more slowly. This would result in a more disaggregated rubber and thus the solubility of the sulfur should be greater. This explanation is offered only tentatively until sufficient data are at hand to prove it.

The value for the solubility of sulfur in rubber changes very slightly at room temperature as the cure is prolonged. At 30° C. it is about 1 part per 100 of rubber, and hence if a stock is vulcanized so that it contains not over 1 per cent of true free sulfur it cannot bloom out.

## Conclusion

The fact that rubber dissolves and does not adsorb the sulfur has a direct bearing on the theories of vulcanization. In the first place it is not possible for one substance to dissolve and at the same time adsorb a second substance. Thus there is only one way to have sulfur adsorbed by the rubber and that is to convert it to the form which is insoluble in the rubber. This might happen in rubber through the reactions between sulfur and the resins, proteins, or accelerators. It has, however, been shown by Twiss[5] that there is no difference in the rate at which $S_\mu$ and $S_\lambda$ vulcanize, and also that when a stock containing only the insoluble form is vulcanized, all the free sulfur is soluble in acetone after vulcanization. This is also in agreement with the results obtained by Endres,[4] who showed that the rhombic or soluble form is the most stable of the forms of free sulfur in rubber. Hence, instead of insoluble sulfur being formed in rubber, the opposite takes place and the insoluble form is converted to the soluble.

Thus the sulfur-rubber mixture, being a solution, must be homogeneous with respect to these two substances at all concentrations of sulfur below the saturation point, and as this point is rather high at vulcanizing temperatures it should be possible to apply the laws of chemical kinetics to the system, and thus obtain some insight into the mechanism of the reaction.

[5] *J. Soc. Chem. Ind.*, **36**, 787 (1917)



Fig. 2—Solubility of Sulfur in Rubber

## Thomas T. Read Honored

Thomas T. Read, supervising mining engineer of the Bureau of Mines, Department of the Interior, has been awarded a gold medal and a commemorative diploma by the Government of Brazil. Dr. Read was the representative of the Department of the Interior with the United States commission to the celebration of the 100th anniversary of the independence of Brazil at Rio de Janeiro last year, and was also the special delegate of the American Institute of Mining and Metallurgical Engineers to the Federated American Engineering Congress held in connection with the celebration.

# The Influence of Glue on the Reinforcing Effect of Light Magnesium Carbonate in Rubber[1,2]

By H. W. Greider

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A NUMBER of the pigments used in rubber, and particularly several of the "reinforcing pigment" group, are quite bulky—i. e., they enclose mechanically relatively large volumes of air, and the ratio of the apparent density of the loosely packed powder to the absolute density of the individual pigment particles is quite low. Young[3] has recently given some figures for this ratio for a number of rubber pigments. The values, recalculated into metric units and reproduced in Table I, obviously apply only to the particular qualities of commercial fillers examined by him, but illustrate this property.

The figures given are, with the exception of that for china clay, smaller than those for inert fillers, such as whiting and barytes, and show that magnesium carbonate and lampblack are more bulky than gas black and zinc oxide.

*Certain rubber pigments, notably gas black, lampblack, and light magnesium carbonate, are difficult to incorporate in rubber, and this seems to be associated with their characteristics of small particle size and extreme bulkiness.*

*Data have been obtained showing that a small amount of glue previously incorporated in the mix aids in the dispersion of light magnesium carbonate in unvulcanized rubber, apparently by improving the wetting power of the rubber for this "dry," bulky pigment. The improved dispersion is accompanied by enhanced tensile strength, resilient energy capacity, and abrasion resistance, the latter a composite index of the mechanical properties of the vulcanizate.*

*The principal factors governing the reinforcing effects of all discrete compounding ingredients in rubber appear to be (1) average particle size (specific surface), (2) wetting, adhesion, or adsorption, etc., (3) flocculation of the pigment during incorporation or vulcanization, (4) particle shape, (5) uniformity, or particle size-frequency distribution. The relations between specific physical properties and the foregoing factors are necessarily rather complex, and the consideration of these relations in this paper is, therefore, largely speculative. The behavior of glue with magnesium carbonate is discussed with reference to its influence on the factors in the mechanism of pigment reinforcement in vulcanized rubber.*

*Other means of improving the dispersion of bulky pigments in rubber mixes, including softeners, plastic materials such as mineral rubber, and organic accelerators such as ethylidene aniline, which function also as "softeners," are considered.*

adjusting themselves to either cubical (loose) or tetrahedral (close or normal) piling, such as might be assumed in the case of larger units. In the case of gas black or lampblack a portion of the mechanically entrapped air may be expelled with little difficulty by the application of pressure to the mass of pigment enclosed in a container to which a vacuum is applied. It is a much more difficult matter to remove the air from light magnesium carbonate, although this can be done to a limited extent by "compacting" the powder between rollers.

Probably the best example of the structure in a mass of finely divided pigment is furnished by magnesium carbonate, which can readily be compressed to form a block of apparently solid magnesia, which has quite marked strength and rigidity and yet contains approximately eight times the volume of air corresponding to the actual volume of magnesium carbonate present. The observed rigidity must be explained by attraction forces between individual particles which cause them to form clumps or aggregates. These aggregates, in turn, are attracted to other aggregates to form pellets, and the net result is an exceedingly open, yet relatively rigid and strong network structure. The forces between the particles which thus cause bulkiness are, apparently, the same forces which induce flocculation when the pigment is suspended in a liquid medium, except that in this case air replaces the liquid. The force of flocculation is one which is different for each pigment and for each liquid in which it is suspended. With increasing subdivision of the pigment the degree of flocculation in any given liquid (and also the bulkiness of the dry powder in air) is increased, because the surface forces between the particles are increased by the corresponding increase in the specific surface.

The bulkiness of certain rubber pigments, and especially of gas black and light magnesium carbonate, is a source of some trouble to the rubber compounder, because of the difficulty in obtaining a reasonably complete and uniform dispersion of these pigments in a rubber mixing on the mill. If all the entrapped air is not expelled by careful incorporation, an objectionable microporosity may result, and a considerable proportion of the pigment may be present in the vulcanized compound, not as individual dispersed particles or flocculates of particles, but as undispersed aggregates or lumps of pigment. Bulky pigments, termed "dry" by the practical compounder, have a tendency to form compressed

### TABLE I

| POWDER | Specific Gravity | Weight Kg. per Cu. M. | Approx. Weight Kg. per Cu. M. Calcd. from Specific Gravity | Ratio Apparent to True Density |
|---|---|---|---|---|
| Magnesium carbonate | 2.3 to 2.4 | 160 | 2400 | 0.067 |
| Lampblack | 1.8 to 1.9 | 128 | 1890 | 0.068 |
| Zinc oxide | 5.5 to 5.6 | 480 | 5600 | 0.086 |
| Gas black | 1.8 to 1.9 | 208 | 1890 | 0.110 |
| China clay | 2.5 | 870 | 2500 | 0.350 |

Bulkiness in a pigment has often been considered an indication of extremely small particle size, since, in general, coarse pigments do not form bulky masses. It must now be evident that some other factor is also involved, for it will be noted that the bulkiness of gas black given above is less than that for zinc oxide and magnesium carbonate, although it has much smaller particle size. It seems probable that in the cases of gas black, magnesium carbonate, and lampblack, the characteristic of bulkiness is due, not alone to small particle size, but to a structure existing in the mass of particles. That a structure exists is not difficult to prove, but as to its mechanics we cannot be so sure. It seems obvious that in a loose mass of bulky pigment there is no possibility of the particles

flakes between the rolls of the mill. When these flakes are subsequently taken up by the compound in the process of incorporation, it is extremely doubtful whether their dispersion is as complete as that of the portion of the pigment which does not flake. If the dispersion is not complete, a part of the true reinforcing power of the pigment is thus lost. Although this difficulty might be overcome by very slow addition of the pigment, this would not be a practicable solution because of the greater time required and the excessive mastication of the rubber. The rubber industry has, therefore, been interested in any device by which such dry, bulky pigments could be more uniformly dispersed in rubber, to take full advantage of their reinforcing properties, and a number of patents covering methods for improved incorporation of pigments have been granted.

Hartong[4] has claimed the method of incorporating various materials in rubber (including aluminium hydrate, glue and other gel-forming emulsoids, zinc oxide, and other insoluble, noncolloidal compounding ingredients, etc.) by the process of suspending or dissolving them in water, or other carrier liquid, in a fine state of subdivision, mixing the suspension or emulsoid gel with rubber, and subsequently removing the volatile carrier liquid or solvent by evaporation. A later patent[5] by the same inventor deals with the incorporation of finely divided compounding ingredients (gas black in particular) together with a gel-forming protein, such as animal glue. The gas black is thoroughly mixed with a glue gel which has first been emulsified with a small proportion of pine oil, and the whole is then incorporated into the rubber mix. The heat developed by milling removes part of the water; the remainder is removed by drying the mix, and the small proportion of pine oil (or glycerol, turpentine, asphaltic oil, etc.) remains in the compound. The dispersion of the gas black is claimed to be considerably improved by this method. North[6] has subsequently patented an improvement on Hartong's method, just described, which consists in emulsifying the glue gel with a volatile liquid, such as benzene, instead of the nonvolatile pine oil, before mixing



Fig. 1

the gas black with the glue solution. These two inventors both claim improved dispersion of the gas black by incorporation of the pigment mixed with a glue gel, with a corresponding improvement in the tensile strength and wearing qualities of the vulcanized product.

4 U. S. Patent 1,301,693 (1919).
5 U. S. Patent 1,396,837 (1921).
6 U. S. Patent 1,399,789 (1921).

Glue itself behaves as a reinforcing pigment, as has been shown by Wiegand[7] and by a stress-strain curve published by Cranor,[8] but is not so powerful in its effects on tensile strength and toughness as gas black or magnesium carbonate. It may be supposed, however, that where used in the proportions specified in the Hartong and North patents (50 pounds of glue to 100 pounds of carbon black) there is a pronounced additive reinforcing effect due to the glue, as well as to the influence of the glue gel on the initial dispersion of the black.

No data have so far been published showing the influence of glue on the behavior of gas black and other bulky pigments in rubber, with respect to completeness of dispersion and the more important physical properties of the vulcanized compounds. The purpose of the experiments described in this paper was to study the influence of small amounts of glue on the dispersion and reinforcing effect of light magnesium carbonate, the "type" of bulky and difficultly incorporated compounding ingredients. It has been suspected for some time that the ordinary methods of incorporation do not give the most complete possible dispersion or realize the greatest possible reinforcing effect obtainable with this pigment. Twiss[9] has recently suggested that certain pigments used in rubber may have a mutually beneficial effect on their dispersion in the mass, and considers that the customary association of zinc oxide and gas black may unconsciously be based upon such an effect, owing to the excellent results obtained in a practical way with mixtures of these two pigments.

### Experimental Procedure

The proportion of glue used in these experiments was 1 per cent by weight of the rubber in the compound, or about 0.75 volume per cent, an amount so small as to give hardly any measurable reinforcement of the vulcanizate on its own account; so that if an enhancement of the tensile strength and other physical properties of the compounds were observed, it might fairly be attributed to improved dispersion of the magnesium carbonate. Preliminary experiments with 5 per cent of glue (3.75 volumes) showed that the added reinforcement, both stiffening and increased tensile strength, was considerably greater than could be accounted for on the basis of improved dispersion alone, and this proportion of glue had a marked effect in reducing the time of cure, so that a part of the improvement was, without doubt, due to the acceleration and not to the physical behavior of the compounding ingredients.

Owing to the fact that magnesium carbonate has such an exceedingly high absorbing capacity for water, it was found unsatisfactory to incorporate the magnesium carbonate in the form of a paste mixture with a glue gel, because of the difficulty in evaporating this large excess of water from the compound. It was thought that the glue might exert a beneficial effect regardless of whether it was incorporated in such a form, and the method adopted in these experiments was, therefore, to mix the glue in the process of breaking down the raw rubber, adding it as a previously prepared dry compound of 50 per cent glue and 50 per cent smoked sheet.[10] The light magnesium carbonate (technical grade[11]) and other

7 *Can. Chem. J.*, **4**, 167 (1920).
8 *India Rubber World*, **68**, 429 (1923).
9 *India Rubber J.*, **65**, 697 (1923).
10 The 50:50 rubber-glue compound for this experimental work was kindly furnished by the Rex-Hide Rubber Co., East Brady, Pa.
11 The specifications for technical light magnesium carbonate, suitable for use in rubber compounding, require: hygroscopic moisture, not over 1.5 per cent; total ignition loss, between 54.5 and 56.8 per cent; free lime, none; heavy metals, none; insoluble in HCl (silica, etc.), not more than 0.5 per cent; iron oxide and alumina, not over 0.5 per cent; lime as calcium carbonate, not over 1.0 per cent. Where tested by the wet-screening method 100 per cent of the material should pass through a screen having 128 meshes per centimeter (commonly designated 325 mesh).

compounding ingredients were then incorporated in the usual way in this 99:1 rubber-glue compound. The basic mixing used was a 50:50 pale crepe–smoked sheet compound, containing 5 per cent of sulfur and 5 per cent of zinc oxide, and accelerated with 1 per cent of hexamethylenetetramine. The curing and physical properties of this test compound have been described in a previous paper.[12] The physical tests upon the compounds—tensile strength, ultimate elongation, rigidity (tensile stress at 300 per cent elongation), resilient energy capacity, and abrasion resistance—were made according to the methods outlined in that contribution.



Influence of Glue on the Abrasion Resistance of Rubber Compounded with Magnesium Carbonate
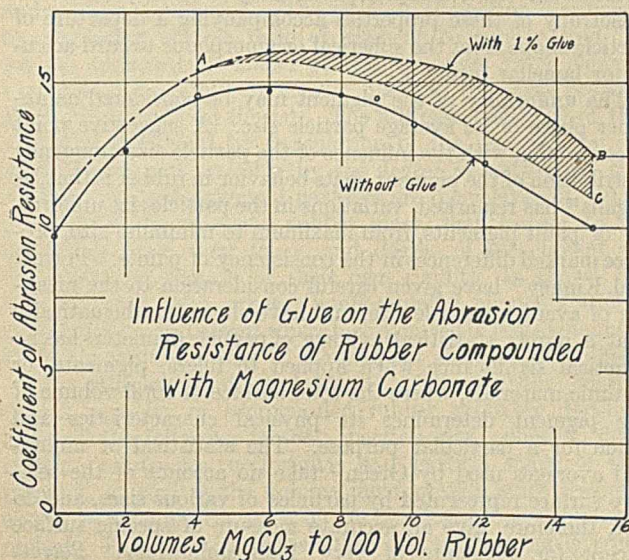
Fig. 2

Compounds were prepared containing 0, 4, 6, 8, 10, 12, and 15 volumes of magnesium carbonate in the basic mix described (but containing 1 per cent of glue), and comparison of these compounds was made with a similar series[12] containing no glue. It may be noted that even this small proportion of glue had the effect of reducing the time of cure to the selected optimum (slightly below maximum tensile strength) about 10 minutes on an 85-minute cure. In curing the compounds, conditions of maximum distortion (heavy overflow from mold under pressure) were maintained in order to minimize the "grain" effects[13] in the vulcanizate resulting both from strains in the rubber phase and orientation of the pigment particles.

### DISCUSSION OF RESULTS

The physical properties of rubber compounded with magnesium carbonate, without glue, are recorded in Table II. The influence of glue on these properties is shown in Table III. In Fig. 1 the tensile strength and resilient energy values are compared graphically. With respect to tensile strength, it will be noted that this property is only slightly greater for compounds containing six volumes or less. Without glue the tensile maximum occurs at 6 to 8 volumes of magnesium carbonate per 100 volumes of rubber, and falls off steadily with further increments in the compound. With glue, however, the tensile strength continues to rise with increasing proportions of the filler and does not reach its maximum until 10 to 12 volumes have been incorporated, after which it falls off quite sharply. Except possibly in the case of the 10 and 12-volume compounds, the increase in rigidity appears to be only that which should be expected from the presence of the glue, as shown in the basic mix sample.

12 This Journal, **15**, 504 (1923).
13 *Ibid.*, **15**, 259 (1923).

With the resilient energy values a quite similar pair of curves is obtained. The values are always higher with glue and do not fall off after 8 volumes have been incorporated, but continue to increase, reaching a maximum at 10 to 12 volumes, as with the tensile strength figures. It may be noted particularly that the effect of the glue is not only to increase the tensile strength and resilient energy capacity, but very considerably to broaden the effective compounding range of this pigment for its maximum reinforcing effect.

Table II—Data on Light Magnesium Carbonate (without Glue)

| Volumes Light MgCO₃ to 100 Volumes Rubber | Tensile Strength Kg./Sq. Cm. | Ultimate Elongation, Per cent | Total Resilient Energy, Kg. Cm./Cc. | Tensile Stress at 300 Per cent Elongation Kg./Sq. Cm. (Rigidity) | Coefficient of Abrasion Resistance | Abrasion Resistance Per cent of Basic Mix Resistance |
|---|---|---|---|---|---|---|
| 0a | 227 | 710 | 372 | 21.1 | 9.7 | 100 |
| 2 | 232 | 670 | 393 | 29.9 | 12.6 | 130 |
| 4 | 255 | 670 | 452 | 39.4 | 14.5 | 150 |
| 6 | 268 | 640 | 536 | 54.6 | 14.7 | 152 |
| 8 | 264 | 600 | 557 | 65.1 | 14.6 | 151 |
| 9 | 261 | 595 | 549 | 70.3 | 14.5 | 150 |
| 10 | 260 | 590 | 546 | 74.0 | 13.5 | 139 |
| 12 | 258 | 580 | 532 | 86.1 | 12.2 | 126 |
| 15 | 238 | 530 | 495 | 103.7 | 10.1 | 104 |

a Basic mix.

A better indication of the improved physical properties obtained is given by measurements of a composite index of these properties, abrasion resistance, recorded in the curves of Fig. 2. The abrasion resistance is in every case greater than that of a similar compound containing no glue. The area *ABC* may be taken as representing the improvement in the dispersion of the pigment. Evidently, proportions of magnesium carbonate less than 6 volumes per 100 of rubber are sufficiently well dispersed so that glue does not greatly aid, but with larger proportions the effect is quite marked. With abrasion resistance as the criterion of toughening effect the range for maximum reinforcement has evidently been extended from 4–9 volumes to 4–12 volumes. The increase in abrasion resistance is most marked for the 12-volume compound, and with larger proportions the aggregative tendency of the pigment appears to be so great that the small quantity of glue present is insufficient to effect its complete dispersion in the mass. It may be remarked here, as has been emphasized in the previous paper,[12] that this method of making abrasion tests apparently gives results slightly too high for pure gum and lightly compounded stocks, as compared with more rigid compounds (referred to their probable service performance), owing to the absence of any considerable load between the abrasive surface (granular carborundum) and the rubber in carrying out the test.

Table III—Data on Light Magnesium Carbonate (with 1 Per cent Glue)

| Volumes Light MgCO₃ to 100 Volumes Rubber | Tensile Strength Kg./Sq. Cm. | Ultimate Elongation, Per cent | Total Resilient Energy, Kg. Cm./Cc. | Tensile Stress at 300 Per cent Elongation, Kg./Sq. Cm. (Rigidity) | Coefficient of Abrasion Resistance | Abrasion Resistance Per cent of Basic Mix Resistance |
|---|---|---|---|---|---|---|
| 0a | 234 | 695 | 388 | 24.6 | 10.8 | 100 |
| 4 | 267 | 660 | 519 | 43.1 | 15.5 | 144 |
| 6 | 277 | 640 | 565 | 56.3 | 16.7 | 154 |
| 8 | 288 | 620 | 582 | 68.6 | 16.0 | 148 |
| 10 | 296 | 600 | 641 | 88.0 | 15.8 | 146 |
| 12 | 296 | 590 | 650 | 96.8 | 15.5 | 144 |
| 15 | 274 | 550 | 590 | 105.5 | 12.5 | 116 |

a Basic mix.

In considering the tensile strength and resilient energy figures, it might possibly be supposed that the enhancement given by the glue is due to a "grain" effect, in spite of the distortion of the compound in the early stages of the cure,

since Vogt and Evans[14] have shown that both glue and magnesium carbonate impart anisotropy of physical properties to rubber in which they are compounded. Such reasoning cannot, however, apply to the abrasion results obtained with circular rings, since these values represent an average of the physical properties in all directions in the compound.

## FACTORS GOVERNING REINFORCING EFFECTS OF PIGMENTS

The behavior of glue, as shown in the data above, may best be discussed in the light of its influence on the factors controlling the reinforcing effects of all pigments in vulcanized rubber. For any given pigment the quantity factor determining the degree of reinforcement is, of course, the volume ratio between the pigment and rubber phases. In the light of recent investigations it appears that the other principal factors include the following physical properties of the pigments: (1) average particle size (specific surface); (2) wetting of the pigment by the rubber, or adhesion, surface tension, etc.; (3) flocculation of the pigment subsequent to its dispersion in the rubber matrix—i. e., during vulcanization; and (4) particle shape of the pigment. It seems quite possible also that the uniformity, or particle size–frequency distribution, of the pigment, may be an additional factor of some importance, although there are as yet no published investigations bearing on this characteristic in relation to the behavior of the pigment in rubber.

The work of Wiegand[15] has demonstrated conclusively the relation of particle size to reinforcing effect for a number of rubber pigments, and this investigator suggested comparative vulcanization tests as a means of estimating particle size. Data have also been published by Schippel,[16] by North,[17] and by Green,[18] which have some bearing on this question. From the standpoint of ease of incorporation and completeness of initial dispersion, there can hardly be any doubt that ready wetting of the pigment by the rubber is advantageous. Schippel's work on the volume increase of compounded rubber under strain has also shown the importance of this factor in maintaining permanent adhesion between the rubber matrix and the surface of each dispersed particle, and this observation has been confirmed microscopically by Green. Green's researches on the flocculation of pigments in paints and in rubber have thrown considerable light on the influence of flocculation of the pigment particles on the consistency of paints and the stiffness (rigidity) of vulcanized rubber. Sulman[19] has postulated that the force of flocculation resides in the interface between the solid and liquid phases and that flocculation is due to incompleteness of wetting of the pigment by the continuous phase, which view, that wetting and flocculation are reciprocal functions, is supported by Green. The term "completeness of wetting" must, however, be carefully defined if this theory is to be accepted, since it is conceivable that the pigment may be completely dispersed and the surface of every particle wet by the liquid (rubber) phase, and that flocculation may ensue, nevertheless, owing to the fact that the intensity of wetting, or adhesion, is insufficient to prevent it. Flocculation of the pigment need not imply that the surfaces of the particles are not in complete contact with the rubber matrix at every point, but only that the particles have drawn together in groups or clumps. One should distinguish carefully between completeness of wetting and *intensity* of wetting. In the case of rubber it must also be borne in mind that the

wetting or adhesion of the pigment in the unvulcanized mass (initial dispersion) may bear little relation to the degree of attachment between the particles and the rubber after vulcanization. This seems to be the case with lithopone and colloidal barium sulfate, which, although they are readily taken up by unvulcanized rubber, appear to have little adhesion to it after vulcanization.

Vogt and Evans[14] have demonstrated the very marked influence of the particle shape of pigments on the physical properties of compounded rubber (for tensile strength, permanent set, Poisson's ratio, volume increase under strain, and stress-strain relationships), particularly with respect to the anisotropy of these properties accompanying a departure of particle shape from the spherical or amorphous toward acicular or lamellar form.

The uniformity of the pigment may be considered as another phase of its average particle size. A suggestive point in connection with the influence of the particle size–frequency distribution of the pigment on its behavior in rubber is that, as Ingalls[20] has remarked, variations in the particle size uniformity of paint pigments, from maximum to minimum size, produce marked differences in the consistency of paints. Perrott and Kinney[21] have given careful consideration to the meaning of average particle size, and have shown mathematically that a purely statistical average of particle diameters has no practical significance when applied to fillers, pigments, or ceramic materials, where the total surface or total volume of the pigment determines its physical characteristics and value for a particular purpose. The statistical or numerical averages used by Green[22] take no account of the relative surface represented by particles of various sizes, and do not, therefore, give an accurate measure of specific surface except for pigments of very high uniformity. Perrott and Kinney have developed formulas for effective average particle diameter in terms of the number, length, surface, and volume (or weight) of the particles. The value for effective average diameter obtained by substituting for numerical frequency of occurrence the percentage of the total surface represented by particles of the respective sizes, is represented by

$$d_{av} = \frac{y_s d}{100} = \frac{\Sigma n d^3}{\Sigma n d^2}$$

where $y_s$ is the percentage of total surface represented by particles of diameter $d$, and $n$ is the relative number of particles of diameter $d$. The effective average diameter thus obtained is inversely related to the specific surface of the pigment, in accordance with the formula: $\rho\, S\mu = 6$, where $\rho$ = density of the pigment, $S$ = surface per unit weight, and $\mu$ = diameter in microns (harmonic mean of the three dimensions). This method of determining the effective average particle size is designed to give proper weight to the surface developed by each size group in the pigment, and therefore involves considerations of its uniformity. If a pigment has a low degree of uniformity, so that a considerable part of its weight (or volume) is not effective in developing particle surface, it may be expected that its reinforcing effect in rubber (at least from the standpoint of stiffening) will not be so great as that of a similar pigment of the same average size, but of greater uniformity, because of the differences in flocculation tendencies. It may be anticipated, also, that the initial dispersion of a pigment of relatively uniform particle size will be better than that of a nonuniform pigment. It seems probable that in the cases of a number of commonly used rubber pigments a portion of the pigment incorporated is relatively ineffective in reinforcement.

[14] THIS JOURNAL, **15**, 1015 (1923).

[15] *Can. Chem. J.*, **4**, 160 (1920); THIS JOURNAL, **13**, 118 (1921).

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

[17] *India Rubber World*, **63**, 98 (1920).

[18] THIS JOURNAL, **13**, 1130 (1921); *Chem. Met. Eng.*, **28**, 53 (1923). *J. Franklin Inst.*, **192**, 637 (1921).

[19] *Bull. Inst. Mining Met.*, **182** (1919), preprint; *J. Soc. Chem. Ind.*, **39**, 27A (1920).

[20] Paint Mfrs. Assoc. U. S., *Circ.* **135**.

[21] *J. Am. Ceram. Soc.*, **6**, 417 (1923).

[22] *J. Franklin Inst.*, **192**, 637 (1921).

#### PIGMENT CHARACTERISTICS AND PHYSICAL PROPERTIES OF COMPOUNDED RUBBER

Now, although a general classification of the factors in the reinforcement of rubber can be made in terms of the physical properties of the pigments, it is not quite such a simple matter to dissociate the influence of each factor from that of the others, with respect to definite physical properties of the vulcanized products. It appears, however, that for any given toughening pigment the tensile strength is largely influenced by the volume of pigment incorporated, its particle size (specific surface as developed in the initial dispersion), and wetting or adhesion. The ultimate elongation is reduced by increasing volume ratio of pigment to rubber, and, in general, pigments of smaller particle size give lower elongation than is imparted by coarser fillers in the same proportions (within certain limits). The stiffness (rigidity) of the rubber is influenced by flocculation of the pigment, by its particle size, and probably by the degree of wetting by the rubber. Since the pigment particles are themselves of much greater rigidity than the rubber mass, they impart to it, depending upon their shape and degree of attachment to the matrix, a portion of their own rigidity, as shown by the fact that even coarse, nonflocculated pigments stiffen rubber to a limited extent where incorporated in large amounts. Probably the uniformity of the pigment also has some effect on the stiffness of the vulcanizate. The resilient energy (work) capacity of compounded rubber probably depends upon all the following factors: particle size, adhesion, flocculation tendencies, uniformity, and particle shape of the pigment, as well as the volume incorporated, since resilient energy is a composite index of the physical properties above named. It may be supposed that the same thing is true, in a different degree, for the property of abrasion resistance. The importance of a high degree of attachment between the particles and the rubber after vulcanization, in its influence on physical properties, is clearly indicated by the fact that lithopone and colloidal barium sulfate, although of very small particle size and satisfactory uniformity, do not increase tensile strength, resilient energy, or abrasion resistance, and influence rigidity much less than would be expected from their particle size, because they lack high adhesion in the vulcanizate.

#### EXPLANATION OF BEHAVIOR OF GLUE WITH LIGHT MAGNESIUM CARBONATE

The explanation offered for the observed effects of glue, in enhancing the toughening effect of light magnesium carbonate, is that it effects an improved initial dispersion of the pigment due to increased wetting of the particles by the rubber. In milling the pigment, especially with the larger volume proportions, the increased ease of incorporation and lessened formation of flakes between the rolls are quite noticeable. An improved initial dispersion implies a smaller effective particle size and an increased specific surface. The improved wetting in the unvulcanized mass may, quite probably, be associated with an enhanced degree of adhesion between the particles and the rubber after vulcanization. Since no marked increase in rigidity has been noted, it seems improbable that the glue has any great effect on the tendency of the magnesia to form flocculates during vulcanization. Improved dispersion of the pigment means a smaller number of aggregates of particles, which, in turn, implies a superior uniformity of particle size of the pigment as it exists in the vulcanized product. There would, of course, be no effect upon particle shape except in so far as the dispersion of aggregates would make the average shape more nearly approach that of the (average) ultimate particle.

#### OTHER MEANS OF IMPROVING THE DISPERSION OF PIGMENTS

The results obtained with glue make it appear probable that other substances have a similar effect in improving the dispersion of bulky pigments and thus enhancing their toughening effect. It is well known, for instance, that softeners, which increase the "tackiness" and wetting power of the unvulcanized rubber, facilitate the incorporation of "dry" pigments, implying also that their dispersion on the mass is correspondingly improved. Most softeners, however, if used in proportions sufficient to increase greatly the ease of incorporation of the pigment, have a disaggregating effect on the rubber due to their solution in or swelling power for rubber, so that the lowering in tensile strength and other mechanical properties which results is more than enough to offset any beneficial effect from the improved dispersion of the pigment. An exception to this, however, is mineral rubber (blown asphalt), which, although it has no marked effect on the stress-strain curve, does increase tensile strength up to 7 volumes per 100 of rubber. It may be expected, therefore, that small amounts of mineral rubber will improve the dispersion of magnesium carbonate and gas black and enhance the physical properties of the compounds. The use of mineral rubber has not been studied in this investigation, but it seems to merit additional experimentation. Another possibility lies in the fact that certain accelerators, of the type of aniline, ethylidene aniline, etc., perform a double function in the mix, since they also act to a certain extent as softeners. It seems probable that such accelerators, if added in the breaking down of the rubber, will improve the dispersion of pigments subsequently incorporated, and that their disaggregating effect will then be largely offset by the increase in tensile strength resulting from their effect in shortening the time of cure. Some extremely interesting and valuable compounding data might be obtained by studying the influence of each reinforcing pigment, in varying proportions, upon the reinforcing effects of others.

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# A Simple Distinction between Citric and Tartaric Acids[1]

### By Hoyt Stevens

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This test from the methods book of an analyst for a large drug house has proved to be a quick and dependable distinction between these two acids which are used in large quantities in the business.

About 0.2 gram of the sample is placed on a small spatula and held in a flame until it ignites. Then the spatula is removed and the ignition observed.

In case of tartaric acid, the burning mass draws up into a dry ball and burns with a *blue* flame, the ball shrinking in size until only a small residue of carbon is left on the spatula.

The citric acid, when ignited, spreads out on the spatula, remaining in a liquid state while burning with a *yellow* flame. It burns in this manner until all is consumed excepting a brownish black residue spread out on the spatula. The burning is accompanied with considerable spattering.

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# Granular Carbon Resistor Furnaces[1]

## By M. M. Austin

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TWO types of granular carbon furnaces are described in which some of the disadvantages of such furnaces have been overcome and their construction simplified. This discussion is given in the hope that those who have suitable transformer equipment for operating such furnaces may construct them at small cost and use them with satisfaction in alloy or other research work requiring temperatures of 1600° to 1700° C.
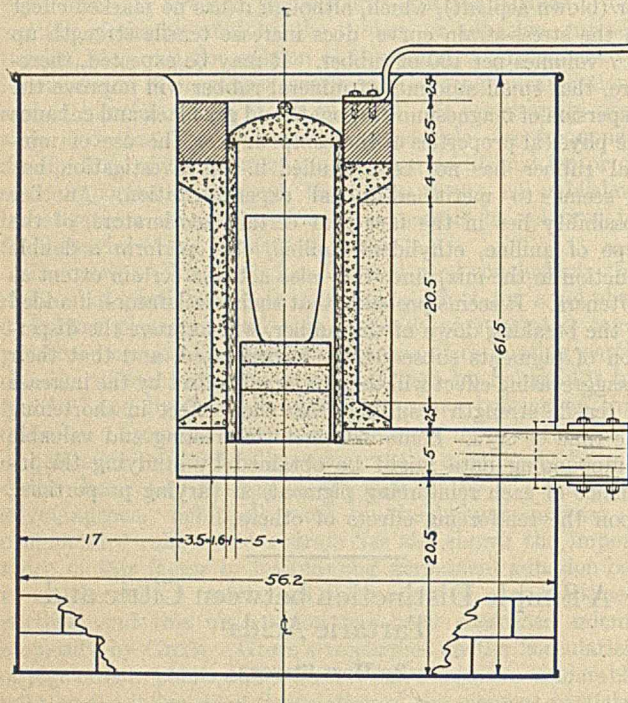


FIG. 1—VERTICAL GRANULAR CARBON FURNACE

The furnace illustrated in Fig. 1 is designed to give a uniformly heated space 10 cm. in diameter and 15 cm. deep. The current requirement is 200 to 400 amperes at 30 to 70 volts. The following material is required for its construction: heavy can, graphite slab, buss bar copper, high temperature alundum cement, alundum tube, cast-iron ring, wood form, crushed arc carbon passing 6-mesh and held on 30-mesh screen, and fire brick.

The lower electrode is bricked in as shown in Fig. 1, leaving a central cylindrical opening 22.3 cm. in diameter and 35.5 cm. deep. The wood form is put in place, making sure that it is centrally located with respect to the depression cut in the lower electrode, and a layer of very stiff alundum is rammed in about it to a depth of 25.5 cm. This cement can be put in so dry that the form can be removed immediately and the top and bottom of the lining shaped as indicated. This lining must be made of a very refractory material. Fire brick and ordinary refractory cements will not stand the temperatures encountered at this point. Before putting the inner tube, resistor material, and iron ring in place, the furnace should be dried out as thoroughly as possible. Small

amounts of the resistor material should be put in at one time and worked down with a small rod. The inner tube must be centered so as to give a uniform section of carbon about it. The sectioned refractory support permits of the crucible being placed in the zone of maximum temperature.

The horizontal type of furnace illustrated in Fig. 2 is designed to give a heating space 13 cm. in diameter and 15 cm. deep, with 200 to 700 amperes at 20 to 40 volts. It is simpler in construction and slightly less uniform in heating. It is built in a metal box, each end of which is sheeted with transite 1.3 cm. thick. Holes are cut to receive the electrodes, which are 10 cm. square and 30.5 cm. long. The strap iron yoke and the electrodes are insulated from the metal box by this transite sheeting and by transite washers on the inside. A 30-cm. layer of brick is laid in the bottom and the bricking is continued up the sides to the top, leaving a central trough 11.5 cm. wide which is enlarged to an opening 26 cm. square at the center. The bricking above and below the electrode so as to give a large surface of contact with the resistor is shown in the detail, Fig. 2. A second detail, Fig. 2, shows a particularly rugged type of copper connecter which will carry the necessary current without water cooling. The central portion of the furnace is faced with high temperature alundum cement so that it will keep its shape at the high temperatures encountered there. It can be put in place by hand without using a form. About 4 cm. should be allowed for resistor on each side and a somewhat larger space between the electrodes and the inner tube.

To operate smoothly these furnaces must be repacked frequently, and it is therefore necessary that this be easily accomplished. Positive pressure between the electrodes and the granular carbon is also important.

A convenient procedure to follow in operating a furnace of this sort is to warm it up gradually, together with a new crucible, for 2 hours in the morning. It will then be hot and ready for use early in the afternoon.
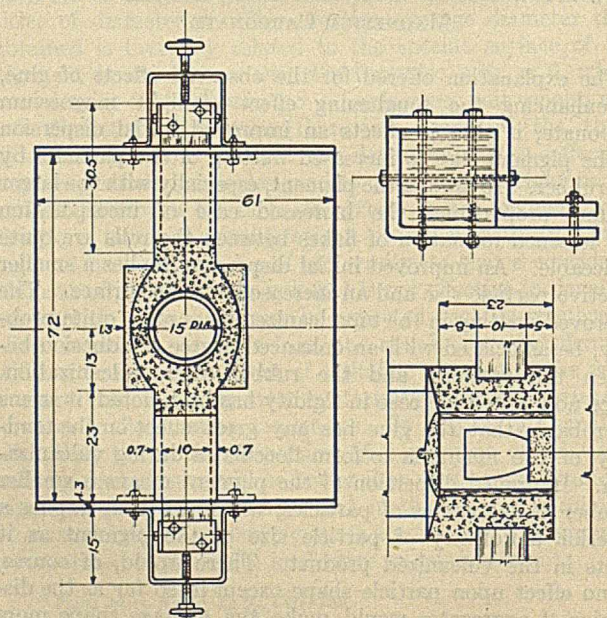


FIG. 2—HORIZONTAL GRANULAR CARBON FURNACE

It is hoped that the current and voltage data given above will be of considerable assistance to others in building furnaces of somewhat modified design. Ease of repacking, heavy electrode connections, positive pressure on the electrodes, and solid construction in general are emphasized.

# Action of Trypsin upon Diverse Leathers[1,2]

### By Arthur W. Thomas and Frank L. Seymour-Jones

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IT HAS been shown that the proteolytic enzyme, trypsin, catalyzes the hydrolysis of collagen[1,*] at a hydrogen-ion concentration pH = 5.9, and at the temperature of 40° C. Since the chemistry of the mechanism by which collagen combines with various substances to form leather is still almost entirely speculative, it seemed possible that interesting results might be obtained by subjecting collagen, tanned in various ways, to the action of trypsin. Not only would this help in elucidating the theory of tanning, but it might also give some idea of the mechanism of tryptic hydrolysis.

The primary difficulty in the study of the hydrolysis by trypsin of collagen which has been treated with various tanning agents lies in the fact that most of the substances used for tanning—e. g., heavy metal salts and formaldehyde—are very definite enzyme poisons. Nevertheless, it seemed at least possible that by thorough washing of the treated hide powder all soluble and ionized matter could be removed, leaving merely the insoluble combination of collagen and tanning agent. There then seemed no reason why a more complex compound, such as that of the collagen tanning agent, should not be hydrolyzed by trypsin, just as collagen alone is hydrolyzed. It is to be remembered that these various tanned collagen compounds are in general characterized by the fact that, unlike collagen alone, they are not attacked by boiling water to yield gelatin, although some—e. g., vegetable-tanned collagen—are not entirely unchanged by hot water. There is further the possibility that the trypsin might hydrolyze the tanned collagen sufficiently to liberate enough of the tanning agent to inhibit the further action of the trypsin by "poisoning" it—i. e., presumably by combining with or precipitating it.

Yet the possibilities of throwing light on (a) the point of attack of the trypsin in the collagen molecule, and (b) the nature of the combination in each tannage, seemed such that they warranted the employment of this method of attack.

## MATERIALS USED

Standard hide powder was chosen as the source of collagen. The trypsin was a high-grade commercial product which was

*It is shown that trypsin is capable of hydrolyzing collagen which has been treated with various agents, such as gallotannin, quinone, formaldehyde, and copper sulfate. Where the tanning agent combines only with the carboxyl groups of the collagen, as with copper, hydrolysis is as great as with untanned collagen, and does not depend on the amount of tanning agent present. Where the tanning agent, such as formaldehyde and quinone, combines with the amino groups of the collagen, the amount of hydrolysis depends on (a) the nature of the linkage—i. e., the type of tannage, and (b) the amount of tanning agent combined with the collagen. Chrome collagen is not hydrolyzed by trypsin.*

tested on a casein substrate, according to the condition laid down by Sherman and Neun[2]—namely, 2 mg. of trypsin acting on a casein substrate at pH = 8 at 40.00° C. for half an hour. Under these conditions 2 mg. of the enzyme gave 17.7 mg. of soluble nitrogen. This represents a trypsin strength approximately one-third that of the strongest high-grade commercial preparation used by Sherman and Neun. As much as 20 mg. of the enzyme tested under the conditions requisite for pepsin activity gave no soluble nitrogen whatever.

The acidity was controlled by a buffer solution, the hydrogen-ion concentration being determined electrometrically.

## METHOD

Fine siftings (100 mesh) of hide powder were tanned in solutions of basic chromium sulfate, quinone, formaldehyde, copper sulfate, and gallotannin, washed and dried as described in detail below. About 0.5 gram of tanned hide powder was placed in a 10-cc. centrifuge tube with a conical bottom, graduated in tenths of a cubic centimeter. Ten cubic centimeters of the buffer solution at pH = 5.9 containing 0.5 per cent trypsin were added. The tubes were then corked and fastened to a shake machine, rotating at 8 r. p. m. in a water thermostat at 40.00° C. After rotation for 20 minutes, the tubes were removed and centrifuged for 20 minutes at 1200 "times gravity." Control tubes in which the trypsin was omitted were run parallel with the digestions and the percentage of hydrolysis determined by comparison of the volumes.

The accuracy obtained in this method of measurement is limited entirely by that in reading the level in the tubes. With the centrifuge and the fine sifted hide powder it was possible to obtain a well-defined boundary, and the percentage digestions so obtained are accurate to ±2 per cent. Considering the insoluble nature of the substrate, the method is probably the most accurate available, while being reasonably rapid. It is distinctly preferable to filtering off the undigested hide powder and determining that dissolved by an estimation of nitrogen in the filtrate, a procedure which is objectionable and inaccurate for several reasons. Only small quantities of liquid are available. It is difficult to filter off the undigested hide powder satisfactorily and to obtain a clear filtrate; the degradation products of hydrolysis are in part molecularly and in part colloidally dispersed, and any filtration will merely effect an arbitrary separation dependent upon the size of the filter pores. More particu-

larly, part of the nitrogenous matter in solution will be absorbed by the undigested hide powder, and a true aliquot will be impossible.

### Chrome-Tanned Hide Powder

A chrome liquor of approximate composition $Cr(OH)SO_4$ was made up from chromium sulfate and sodium hydroxide to give 1.04 per cent chromium. Ten grams of 100-mesh hide powder were tanned in 200 cc. of this liquor ($A$), and 10 grams further in 200 cc. of the stock liquor diluted 1:4 with water—i. e., 0.21 per cent chromium ($B$), for 22 hours on the shake machine. The tanned powders were thoroughly washed with distilled water until no test for $Cr^{+++}$ could be obtained, then were dried at 75° C.

Hydrolysis was then carried out as described above, the results being given in Table I.

TABLE I—Digestion of Chrome Leathers

| Chromed Hide Powder | Per cent Hydrolyzed | |
|---|---|---|
| | Trypsin | Control |
| $A$ | 3.6 | 0.0 |
| $B$ | 6.9 | 0.0 |

Further sets of hide powder were tanned in basic chromium sulfate solutions of various concentrations, but when the tanned powder was subsequently treated at pH = 5.0, some of the chromium was stripped from the leather. Even with this, only the lightest tanned powder showed any digestion with trypsin. It was not found possible to prepare chrome liquors for tannage at pH = 5.9, since the chromium began to precipitate out at this hydrogen-ion concentration.

It appears from this that where hide powder is completely chrome-tanned, it is not hydrolyzed by trypsin. Whether this is due to the poisoning action of the chromium on the trypsin, or to the chromium masking the linkage which is attacked by trypsin, is not definitely established. In any case, the theory of chrome tannage[3] is at present in so uncertain a condition that no light can yet be thrown on the action of trypsin in this particular reaction.

### Quinone-Tanned Hide Powder

About 10 grams of 100-mesh hide powder were drummed up for 24 hours in each of three solutions of 1.0 ($a$), 0.5 ($b$) and 0.25 per cent ($c$) quinone, respectively, at pH = 5.9, then allowed to stand for 48 hours, thoroughly washed to remove all uncombined quinone, and dried out at 40° C. Hide powder tanned in a 0.1 per cent quinone solution was discarded because it was obviously undertanned. These tanned powders were analyzed, giving the results shown in Table IIa.

TABLE IIa—Composition of Quinone-Tanned Leathers

| Quinone Collagen | Water | Hide Substance ($N \times 5.62$) | Quinone (by Difference) |
|---|---|---|---|
| $a$ | 8.6 | 84.1 | 7.3 |
| $b$ | 8.8 | 86.7 | 4.5 |
| $c$ | 9.2 | 89.6 | 1.2 |

Half-gram lots of these three tanned hide powders together with some untanned hide powder for comparison were digested with trypsin as described before. Subsequently, the residual liquors were poured off, fresh trypsin and buffer solution added, and a further digestion period of 20 minutes was given.

TABLE IIb—Digestion of Quinone Leathers

| Quinone Collagen | Per cent Hydrolysis | | | |
|---|---|---|---|---|
| | 1st 20 Minutes | | 2nd 20 Minutes | |
| | Trypsin | Control | Trypsin | Control |
| $a$ | 34 | 0 | 61 | 0 |
| $b$ | 50 | 0 | 69 | 0 |
| $c$ | 68 | 0 | 79 | 0 |
| Raw collagen | 86 | 13 | 91 | 23 |

Considerable quantities of quinone and hydroquinone were liberated during hydrolysis, showing that the quinone

collagen was decomposed. Neither quinone nor hydroquinone appears to destroy the trypsin. The group at which the collagen normally hydrolyzes with water appears to have been so changed by the tannage that hydrolysis no longer occurs. With trypsin some masking of the attacked group is shown by the lessened hydrolysis, which degree of hydrolysis varies with the amount of quinone used in tanning—i. e., in combination with the collagen.

Quinone tannage was discovered by Meunier[4] in 1908. His view[3] of the process is that it takes place by oxidation of the collagen and reduction of the quinone. Representing the collagen as $R—NH_2$, we may have either

$$R—NH_2 + 2C_6H_4O_2 \rightarrow R—N\underset{O}{\overset{O}{\diagup\diagdown}}C_6H_4 + C_6H_4(OH)_2 \quad (a)$$

$$2R—NH_2 + 3C_6H_4O_2 \rightarrow \underset{R—N—O}{\overset{R—N—O}{\underset{|}{}}}C_6H_4 + 2C_6H_4(OH)_2 \quad (b)$$
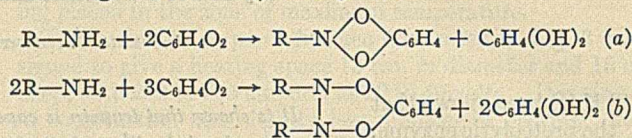
These reactions are exactly like those between quinone and aromatic amines. Support is lent to this view by the fact that hydroquinone is found in the solution after tannage.

Fahrion,[5] on the other hand, presumes a preliminary oxidation of the collagen, followed by combination with the quinone.

$$2R—NH_2 + O \rightarrow R—NH—HN—R + H_2O \quad (a)$$

$$R—NH—HN—R + C_6H_4O_2 \rightarrow \underset{R—NH—O}{\overset{R—NH—O}{}}C_6H_4 \quad (b)$$
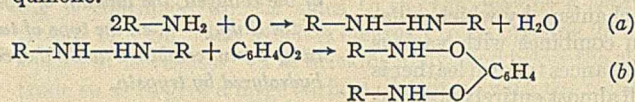
This view does not explain the presence of hydroquinone in the residual liquor, unless it be supposed that the oxygen necessary for the first reaction is furnished by reduction of the quinone.

Whichever view of the mechanism of the tannage is accepted, it is the amino group which is linked through oxygen to the benzene ring. The quinone-tanned collagen is readily hydrolyzable by trypsin, although not quite so rapidly as the untanned hide powder. The combination therefore exerts only a slight retarding effect.

### Formaldehyde-Tanned Hide Powder

About 10 grams of 100-mesh hide powder were drummed for 24 hours in each of four solutions of ($a$) 1.90, ($b$) 0.95, ($c$) 0.38, ($d$) 0.19 per cent formaldehyde at pH = 5.9, then allowed to stand for 21 days, filtered, thoroughly washed, dried at 40° C., and powdered. Half-gram lots of these tanned hide powders were digested with trypsin, as described before.

TABLE III—Composition and Digestion of Formaldehyde Leathers

| Sample | Water Per cent | Hide Substance Per cent | Formaldehyde (by Difference) Per cent | Per cent Hydrolysis | |
|---|---|---|---|---|---|
| | | | | Trypsin | Control |
| $a$ | 7.1 | 87.8 | 5.1 | 6 | 5 |
| $b$ | 7.0 | 88.8 | 4.2 | 8 | 14 |
| $c$ | 6.4 | 90.3 | 3.3 | 18 | 3 |
| $d$ | 8.2 | 89.0 | 2.8 | 35 | 0 |
| Raw collagen | .. | .. | .. | 86 | 13 |

The results shown in Table III, particularly in the controls, are somewhat irregular. Formaldehyde was found to be present in all the residual liquors after digestion, and its destructive action on the trypsin may well account for the comparatively small hydrolysis in the more heavily tanned powders.

Tannage with formaldehyde is of the type most generally acknowledged to be purely chemical in nature. It is usually represented as

$$R\underset{COOH}{\overset{NH_2}{}} \text{ or } R\underset{COO}{\overset{NH_3}{}} + HCHO \rightarrow R\underset{COOH}{\overset{N = CH_2}{}} + H_2O$$
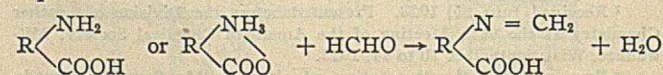
Tannage is only possible[6] on the alkaline side of the isoelectric point of collagen. It may be taken that the formaldehyde masks the amino groups while freeing the carboxyl

groups in the collagen molecule. The formaldehyde-tanned collagen is hydrolyzable by trypsin, although to a lower degree than the untanned hide powder. This particular combination therefore exerts a fairly considerable retarding effect.

### Copper Collagenate

Ten-gram lots of 100-mesh hide powder were drummed for 24 hours in 200 cc. of (*a*) 2.5 and (*b*, *c*) 5 per cent copper sulfate solution made up in a buffer of pH = 5.9, then allowed to stand for 24 hours, filtered, thoroughly washed, dried, and powdered. Powdering was not very satisfactory, since the tanned powder dried in hard fibrous lumps, not at all friable. Hide powders treated in more dilute copper sulfate solutions were discarded, since they gelatinized on drying. Tryptic digestion was carried out as before, the results being given in Table IV with the composition of the copper collagenate samples.

**Table IV—Composition and Digestion of Copper-Collagen Compounds**

| Sample | Water Per cent | Hide Substance Per cent | Copper Per cent | Per cent Hydrolysis Trypsin | Control |
|---|---|---|---|---|---|
| *a* | 9.8 | 89.5 | 0.13 | 87 | 21 |
| *b* | 9.6 | 89.5 | 0.61 | 89 | 19 |
| *c** | 7.6 | 91.2 | 0.67 | 79 | 26 |
| Raw collagen | .. | .. | .. | 86 | 13 |

* Sample *c* was tanned at a different time and was not so finely powdered as Sample *b*.

Copper was present in the residual liquors, but almost entirely in an un-ionized form. It is remarkable to note that hydrolysis is as great with the treated as with the untreated powder, and in the controls the copper treatment actually seems to activate the hydrolysis.

No work appears to have been done on copper tanning, and it is indeed very doubtful whether this treatment can be spoken of as a true tannage. The treated hide powder, when wet, feels like wet raw hide powder, and not like wet tanned hide powder, whether the tannage be vegetable, chrome, quinone, or formaldehyde. It may be supposed that we have here merely the formation of a salt between an amphoteric electrolyte, on the alkaline side of its isoelectric point, and a metallic cation, in accord with Loeb's work.[7]

Representing the collagen, as before, as $R\begin{smallmatrix}NH_2\\COOH\end{smallmatrix}$, the combinations would be:

$$2H_2N—R—COOH + CuSO_4 \rightarrow (H_2N—R—COO)_2Cu + H_2SO_4$$
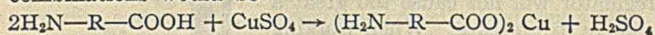
Here it is to be noted that the copper combines with the carboxyl group, leaving the amino group free. The copper-tanned hide powder is hydrolyzable by trypsin or water to a degree as great as the untanned hide powder. This combination therefore appears to exert no retarding effect whatever on the hydrolysis.

### Vegetable-Tanned Hide Powder

For purposes of comparison, 10 grams of 100-mesh hide powder were tanned in 200 cc. of 5 per cent gallotannin solution at pH = 5.9 for 48 hours, then thoroughly washed, dried out at 40° C., and powdered. Analysis of the product gave 5.44 per cent water, 72.23 per cent hide substance, and 22.33 per cent tannin (by difference). This was digested with trypsin as before. The tanned hide powder gave 48 per cent hydrolysis with trypsin and 19 per cent in the blank. The residual liquors from the trypsin gave a very faint positive gelatin-salt test for tannin.

There are innumerable theories of vegetable tanning, chemical, physical, and colloidal, but until more is known of the chemical nature of tannins and collagen it would be idle to speculate on exactly what type of combination occurs. Accepting Fischer's view of gallotannin as of the nature of a pentadigalloylglucose, it would seem reasonable to suppose that combination is largely with the basic groups of the colla-

gen molecule. Considering the foregoing experiment in conjunction with those on the other types of tannage, this view would seem to be upheld.

### Conclusion

In the preceding experiments two instances were found where tannage is believed to consist in combination with the amino group—e. g., with quinone and formaldehyde, and one instance where tannage probably consists in combination with the carboxyl group—e. g., with copper sulfate—where the tanned collagen was hydrolyzable by trypsin. In yet another instance, that of chrome tannage, which is sometimes believed to consist in a union of chromium with the carboxyl group, the product was not hydrolyzable by trypsin. In view of the first three instances cited, it would follow that chrome tannage must consist of some other kind of combination, and is obviously a more complicated process in its nature.

It appears also that where combination of the tanning agent occurs with the carboxyl group of the collagen, both tryptic and ordinary hydrolysis are as great as with untanned hide powder, such being the case with the copper tannage. Where combination of the tanning agent occurs with the amino group, it appears to depend on the nature of the linkage what degree of hydrolysis will be obtained. Naturally, the greater the amount of tanning agent combined, the less the hydrolysis.

These results of the action of trypsin on tanned collagen suggest a fertile field for further investigation on the mode of action of trypsin and possibly also on the nature of tanning. The possibility of combinations of the tanning agent with some of the polypeptide (—NH.CO—) linkage has not been considered, as the theory of tannage has not yet reached the stage where this would be profitable. Nevertheless, it is a possibility to be borne in mind in future work, particularly as it is at these linkages where hydrolysis probably occurs.

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4—Meunier, *Collegium*, **1908**, 195; *Mon. sci.*, [4] **23**, 91 (1909).
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## Journal of Chemical Education

A new journal devoted to the interests of teachers of chemistry has been founded by the Section of Chemical Education of the American Chemical Society. This journal is to be known as the *Journal of Chemical Education*, the first number of which has been mailed. It has been made possible by the hearty coöperation of members of this section under the active leadership of Neil E. Gordon, its secretary. Dr. Gordon, the editor-in-chief, will be assisted by the following able departmental editors:

H. C. Sherman, Columbia University, New York, N. Y.
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Contributing editors from about thirty States are aiding in the success of the project.

It is planned that each issue of the *Journal of Chemical Education* will contain twenty-four pages, 6 x 9 inches. The journal will issue on the fifteenth of each month, with the exception of July and August when no issue will be forthcoming. The subscription price is $2.00 per year. Subscriptions should be sent to *Journal of Chemical Education*, University of Maryland, College Park, Md.

# An Automatic Pressure Regulator[1]

By Louis E. Dawson

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IN MAKING some measurements of rates of filtration it was desirable to maintain the pressure constantly at 500 mm. less than atmospheric pressure over a period of an hour or more, by automatic means. Several attempts were made to devise an arrangement which would hold the pressure constantly at a certain value and would not require personal supervision.

The apparatus described herein very satisfactorily maintained a steady pressure for a period of days with a maximum variation of only 2 or 3 mm. of mercury when operating under 500 mm. vacuum. This variation, which occurred only for a fraction of a second, was due to admission of air by the regulator. With differences in atmospheric pressure no adjustment of the apparatus is necessary when the pressure is measured with a mercury manometer which has one end open to the atmosphere and the other end connected with the system. This holds true only when atmospheric pressure is being used—that is, when the effective pressure desired is the difference between the atmospheric pressure and a second pressure mechanically produced. The regulator, as described here for systems under pressure less than that of the atmospheric, may be used for pressures greater than atmospheric pressure by making a slight modification.

The regulator consists essentially of a form of trap or baffle connected by means of two vertical tubes of different diameters and lengths with a reservoir of mercury exposed to the atmosphere. Its action depends upon the passage of a certain quantity of air through the tubes of smaller diameter when enough mercury in the reservoir to uncover the lower end of the smaller tube has been forced through both tubes into the trap. The passage of this air alters the pressure, and further passage of air is stopped when the mercury in the reservoir rises, owing to its return through the larger tube, and closes the end of the smaller tube.

The trap prevents the mercury from being carried over into the evacuated system when a quantity of air is permitted by the regulator to enter the system. It should be so constructed that the mercury, violently sucked up with the admitted air, is rapidly returned to cover the top of the two tubes. It may be made from a test tube, a, about 3 cm. in diameter and 18 cm. long, with an L-shaped side tube, b, 2.5 cm. in diameter with one arm 4 cm. and the other 7 cm. long, sealed in about 3 cm. from the closed end of the test tube and with the long arm of b turned facing the opposite direction to that faced by the open end of the test tube. To the free end of b is sealed a 6 or 8-mm. tube, c, by which the regulator is connected to the system which it is desired to maintain at constant pressure.

Into the open end of the test tube part of the trap is fitted a rubber stopper having two holes. Through one hole is passed a glass tube, d, 10 mm. inside diameter and 47.5 cm. long, while through the other hole is passed a smaller glass tube, e, 3 mm. inside diameter and 46 cm. long, with the opposite end, f, flared open to about 10 mm. diameter. Without this flared end the regulator is less sensitive and therefore allows greater fluctuation.

The free ends of the two tubes, d and e, dip into mercury held in a reservoir, g, 4 cm. in diameter and 11 cm. long, made

with the closed end sealed to a small bent tube 6 or 8 mm. in diameter, to which a small separatory funnel, h, of about 100-cc. capacity is connected by means of a rubber tube, i. By means of this separatory funnel the height of the mercury in the main reservoir g may be adjusted. The lower end of the tube d should not be too close to the bottom of the reservoir g. The various members of the regulator are supported by means of clamps on a ring stand.

When adjusting the regulator, the vacuum is slowly built up in the system to be evacuated and enough mercury to cover the ends of both tubes d and e is allowed to flow over into the main reservoir g from the separatory funnel h until the mercury in both tubes d and e has risen into the trap a and a manometer indicates the desired pressure. Then the separatory funnel is lowered and the mercury level in g is brought down to the lower end of the small tube e, when air is sucked up through this tube and the mercury returns to the reservoir g through the large tube d and closes the end of the small tube e. When the pressure subsequently becomes reduced, the end of e is uncovered, air is again allowed to pass in, and the cycle continues, allowing the proper mercury level to be set.

The regulator should be connected to a suction flask with a capacity of 2 or more liters, as a reservoir to furnish capacity so that the small quantity of air admitted through the regulator will not cause too great a change in pressure. When working with a large vacuum pump of high capacity, such as is used for supplying vacuum to buildings containing several laboratories, it is necessary to have the valve to the system only partly open, or to insert a small capillary tube to furnish friction; otherwise, with the dimensions used for the tubing and trap, the suction of air through the regulator will come at too rapid intervals. By choosing tubes d and e with larger dimensions, a regulator suitable for use with pumps of large capacity may be made.

If it is desired to work with pressures other than 500 mm. vacuum, the lengths of the tubes connecting the reservoir with the trap will need to be altered to meet the special conditions. They should be such as to allow about 3 to 5 cm. of mercury to be in the trap above the top ends of the tubes d and e. This prevents too violent spurting of the mercury into the trap. Moreover, for pressures beyond the range of the capacity of the small tube, e, used here, as also with systems having much greater pump capacity, the diameter of the tubes should be changed accordingly; that is, when a much lower vacuum on the same pump or when a
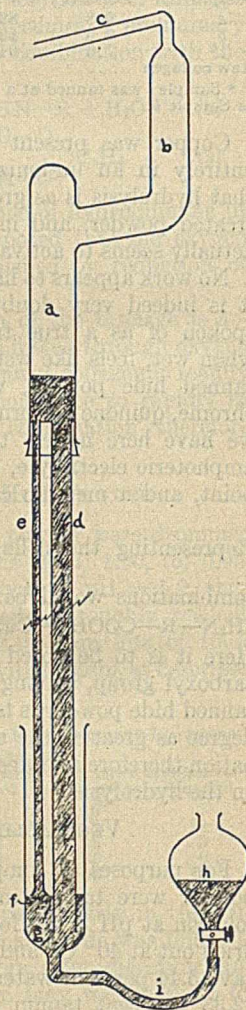
pump of higher capacity is used, more air must be admitted to the system in the same interval of time, so that tubes *d* and *e* of greater diameters may be necessary in order to give a regulator of the same degree of sensitivity.

When working with systems under pressures greater than atmospheric, the following slight modification of the regulator described should be made: Tube *c* is left open to the air, while the reservoir *g* is closed with a rubber stopper hav-

ing three holes, two of which hold tubes *d* and *e* and the third a tube 6 or 8 mm. in diameter, which is also connected by rubber tubing to the system under pressure. When this is in operation it allows excess air to escape automatically into the atmosphere from the system. The diameters of tubes *d* and *e* should be chosen according to the sensitivity desired and the pressure pump capacity and the pressure desired in the system under control.

# Surface Tension of Gelatin Solutions[1,2]

By Clarke E. Davis, Henry M. Salisbury, and M. T. Harvey

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*The Morgan method has been used to determine the drop weights of gelatin solutions. These determinations are made with apparent ease in concentrations up to nearly 10 per cent when the temperature has been raised above the transition point given heretofore as 38° C. Further evidence of this transition point at 38° C. is found in drop weight measurements.*

*Increasing concentration causes decrease in the drop weight.*

*With increasing temperature the drop weight increases in more concentrated solutions, but finally shows decrease until the transition point is reached above which all concentrations show no appreciable change in drop weight.*

*With increasing pH there is a tendency for all concentrations to reach a minimum at the neutral point.*

*The drop weight changes slightly with age of the solution.*

---

**V**ERY few measurements of the surface tension of gelatin solutions have ever been made, and the few that are recorded cover such a limited range of working conditions that it was deemed advisable to measure the surface tension of gelatin solutions under varying conditions.

Quincke[3] records the surface tension of one concentration. This measurement is undoubtedly in error, because the specific gravity of the gelatin solution at 20° C. is given as 1.0000, which is in error.

Density measurements have been made by Davis and Oakes.[4] Zlobicki[5] measured changes in surface tension of gelatin solutions with temperature, making only a limited number of measurements, and reached a concentration of only 2 per cent gelatin. Bancroft[6] says, referring to Zlobicki's work, "addition of 0.5 to 0.8 gram gelatin to 100 cc. water causes a marked decrease in the surface tension of water, while addition of further amounts has practically no effect. In the same connection, Alexander[7] says, "0.5 to 0.8 gram of gelatin to 100 cc. of water causes a marked lowering of the surface tension of water although further addition does not increase the effect."

Consideration of Fig. 2 shows that increasing concentration of gelatin causes a continuous and appreciable decrease in the surface tension of water.

Sheppard and Sweet[8] measured the interfacial tension between gelatin solutions and toluene, but have made no measurements of gelatin solutions in contact with air.

The present paper covers an investigation of the variation of surface tension with (1) concentration, (2) temperature, (3) pH, and (4) age of solution.

## EXPERIMENTAL

APPARATUS—The apparatus used was the Morgan drop weight apparatus,[9] with the exception that a manometer tube was included in the suction line to give an accurate control during the formation and falling of the drop of liquid. Cottonseed oil was used in this tube because of its low weight and low vapor pressure. The amount of suction used at the time when the drop fell was 0.47 mm. of mercury.

METHOD OF MAKING DETERMINATIONS—The determinations were made in the usual manner[10] by collecting and weighing a given number of drops, and from these the drop weight of the solution in milligrams was calculated. The apparatus
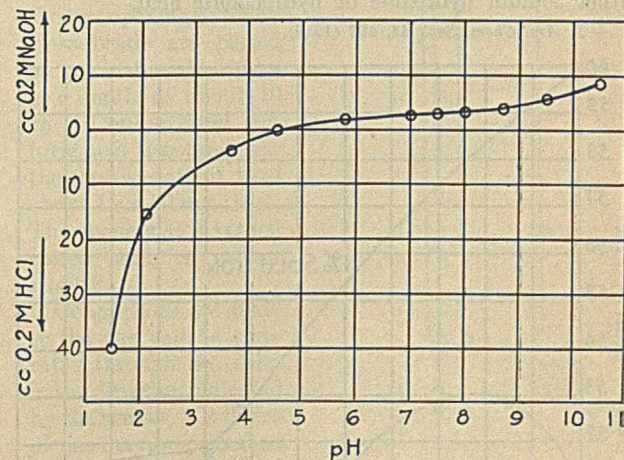


FIG. 1—TITRATION CURVE FOR OSSEIN GELATIN NO. 1. 1 PER CENT SOLUTION

was thoroughly cleaned and dried before each determination. During the determination a constant temperature was maintained by use of a water thermostat.

[3] *Ann. Physik,* **10**, 507 (1903).

[4] *J. Am. Chem. Soc.,* **44**, 464 (1922).

[5] *Bull. acad. sci. Cracovie,* 488 (1906).

[6] "Applied Colloid Chemistry," 1921, p. 189.

[7] "Glue and Gelatin," 1923, p. 138.

[8] *J. Am. Chem. Soc.,* **44**, 2797 (1922).

[9] *J. Am. Chem. Soc.,* **32**, 349 (1911).

[10] Morgan and co-workers, *J. Am. Chem. Soc.,* **30** (1908); **33** (1911); **35** (1913), a series of some twenty papers.

The results in this paper are left in their original form as drop weights, for it is agreed that the Morgan method gives results which are experimentally accurate but it is not agreed as to just what correction, if any, should be made to calculate the surface tension; hence it is left to the discretion of the critic as to what correction formula should be used.
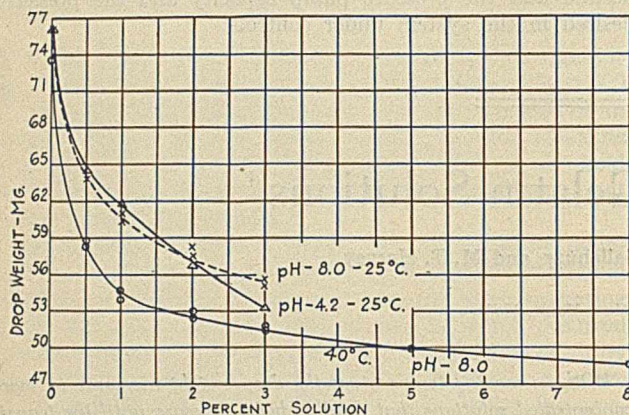


Fig. 2—Variation of Drop Weight with Strength of Solution Ossein Gelatin No. 1. pH = 4.2 and 8.0. 25° and 40° C.

Harkins and Brown[11] present an elaborate formula for this:

DROP WEIGHTS OF KNOWN LIQUIDS
*Conductivity Water*

| Temperature °C. | Weight Mg. |
|---|---|
| 25 | 76.35 |
| 40 | 73.65 |
| *Benzene (Thiophene-free)* | |
| 25 | 28.96 |

The diameter of the tip used was approximately 5.2 mm.

METHOD OF MAKING GELATIN SOLUTIONS—Gelatin solutions were always made according to the same procedure. Sufficient gelatin was weighed out and added to distilled water to give a certain percentage of gelatin in the finished solution. The solution was made by heating with stirring on an electric hot plate. Care was used to see that the solution came to definite temperatures after given periods of heating. The solution reached 75° C. in 20 minutes. It was then removed from the hot plate and adjusted to the desired pH by adding either sodium hydroxide or hydrochloric acid.

[11] *J. Am. Chem. Soc.*, **41**, 499 (1919).
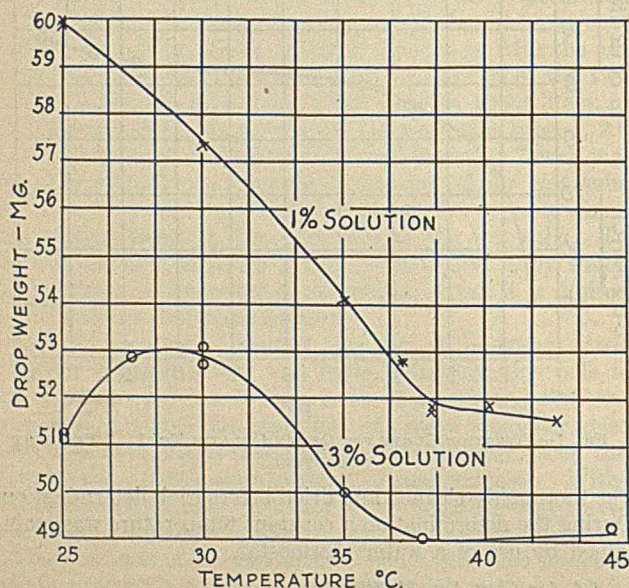


Fig. 3—Variation of Drop Weight with Temperature of 1 and 3 Per Cent Solutions of Ossein Gelatin No. 1. pH = 8.0

The amount of either of these necessary was predetermined by running a titration curve of the gelatin under examination. A typical curve of this sort is shown in Fig. 1. The solution was then filtered and finally brought to the temperature at which the determination was to be made by placing it in the thermostat. Uniformity of procedure in making the solution was absolutely necessary in order to obtain results of value, as both the sol and gel forms were present.[12] Any deviation in the heating causes changes to take place in the character of the gelatin.

HYDROGEN-ION DETERMINATIONS—These were made by means of the Clark and Lubs series of indicators[13] and by means of the hydrogen electrode using the method as described by Beans and Oakes.[14]

## RESULTS

VARIATION OF DROP WEIGHT WITH CONCENTRATION— Fig. 2 shows the relationship of drop weight to per cent gelatin in solution using ossein gelatin. In the upper curves the determinations were made at 25° C. The solutions were made at pH 4.2 and 8.0. These curves follow each other closely, showing a marked decrease in drop weight with an increase in the percentage of gelatin. It was impossible to carry these determinations to a higher percentage of gelatin at 25° C., owing to the formation of a jelly. This decrease in drop weight was found to hold in about the same relation at several other pH values examined. The lower curve shows the effect of raising the temperature to 40° C. There was a marked lowering of the drop weight in comparison with the 25° C. curve and determinations were made up to 8 per cent gelatin. There were indications that the percentage could have been carried even further, no jelly formation taking place because the temperature was high enough to insure the complete transition from the gel to sol form.[4]

VARIATION OF DROP WEIGHT WITH TEMPERATURE—Fig. 3 shows the relationship between drop weight and temperature, using two concentrations—namely, 1 and 3 per cent solutions. Examination of the curve for the 1 per cent solution shows a marked decrease in drop weight until the temperature reaches 38° C., at which point the direction of the curve changes abruptly and becomes practically a straight

[12] Davis, Oakes, and Brown, *J. Am. Chem. Soc.*, **43**, 1526 (1921).
[13] Clark and Lubs, *J. Bact.*, **2**, 1, 109, 119 (1917).
[14] *J. Am. Chem. Soc.*, **42**, 2116 (1920).
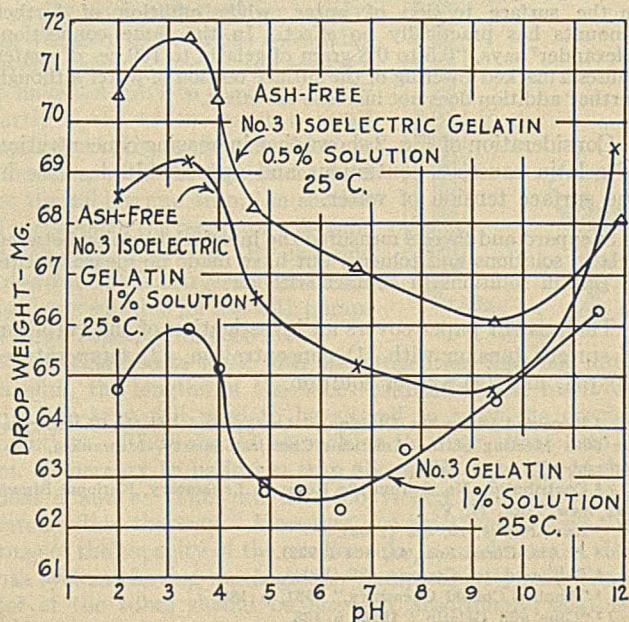


Fig. 4—Hide Gelatin Used

line showing no further change in the drop weight. The curve for 3 per cent solution likewise shows a decided change in direction of the curve at 38° C. above which the drop weight value is practically constant.
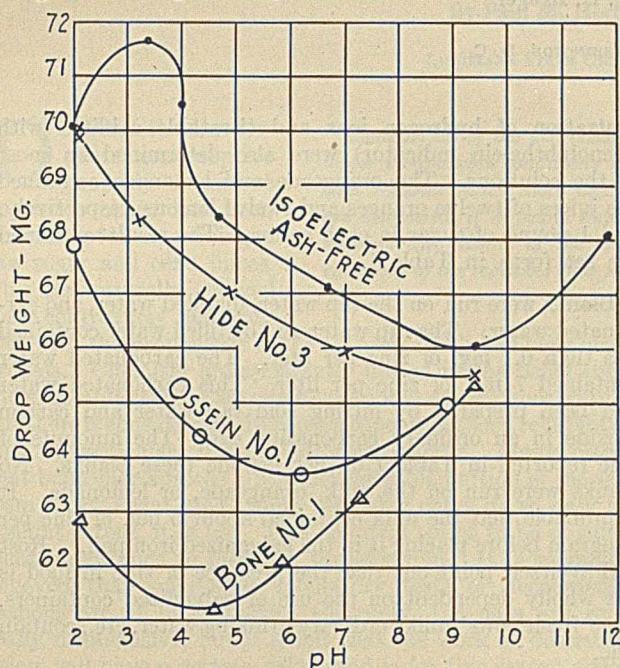


FIG. 5—VARIATION OF DROP WEIGHT WITH pH OF 0.5 PER CENT SOLUTIONS AT 25° C.

Further evidence is here found for the existence of the transition point heretofore claimed as 38° C.[4]

In the 3 per cent solution there is a decided maximum around 30° C. Some evidence of this maximum also shows at this point in the 1 per cent solution.

PREPARATION OF ISOELECTRIC GELATIN—Isoelectric gelatin was prepared by the method described by Loeb.[15]

VARIATION OF ISOELECTRIC GELATIN WITH pH—Fig. 4 shows the relationship of isoelectric gelatin with pH at 25° C. The isoelectric gelatin was made from hide gelatin No. 3. The curves show the relationship of the original gelatin with that of the isoelectric gelatin. The isoelectric gelatin can, of course, only be called isoelectric at pH 4.7. When it is adjusted to pH values other than 4.7 it must be called ash-free.

[15] *J. Am. Chem. Soc.*, **44**, 213 (1922).
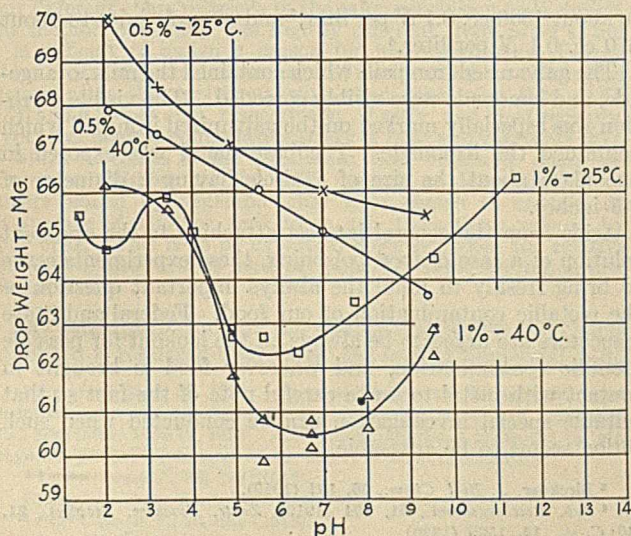


FIG. 6—VARIATION OF DROP WEIGHT AND pH OF HIDE GELATIN No. 3. 0.5 AND 1 PER CENT SOLUTIONS. 25° AND 40° C.

It is to be noted that the original gelatin with its impurities lowers the surface tension more than the ash-free gelatin, and that the 1 per cent ash-free gelatin lowers the drop weight more than the 0.5 per cent solution, which agrees with the information shown in the curves giving the relation between concentration and drop weight.

VARIATION OF DROP WEIGHT WITH pH—Figs. 5 and 6 show the variation of drop weight with pH at concentrations of 0.5 and 1 per cent.
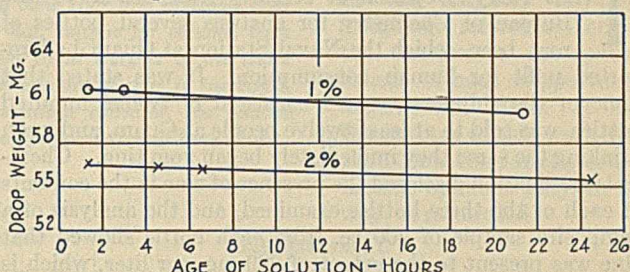


FIG. 7—VARIATION OF DROP WEIGHT WITH AGE OF No. 1 GELATIN (BONE). pH = 4.2. 25° C.

VARIATION OF DROP WEIGHT WITH AGE OF SOLUTION—Drop weight measurements were made on 1 and 2 per cent solutions of bone gelatin at a pH of 4.2 at 25° C. over a period of 24 hours, as shown in Fig. 7. Both solutions showed a slight decrease in the drop weight with age, and the curves themselves are approximately parallel.

# Apparatus for Drying Gases[1]

## By V. T. Jackson

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THE piece of apparatus shown in the sketch has been found useful in drying gases. The small openings should be made from glass tubing having an internal diameter of 7 mm. The other dimensions are indicated in the sketch.

A layer of glass wool about 1 cm. thick is placed in the bottom of the barrel so as to cover the two openings. Small glass beads are placed on top of the glass wool to a depth of about 10 cm. Concentrated sulfuric acid is poured over the beads until it rises about 1 cm. above them. The opening at *A* is then closed with a rubber stopper.

Connections are made so the gas can be aspirated through the drier in the direction indicated by the arrows. Bubbles of gas may be passed at the rate of fifty a minute. Two or more driers may be connected in series if it is desired to pass the gas faster. The stopcock provides a means of withdrawing the spent acid without removing the drier from the train of apparatus.

This apparatus has also been used to remove carbon dioxide from the air by using a 50 per cent solution of potassium hydroxide.



[1] Received January 12, 1924.
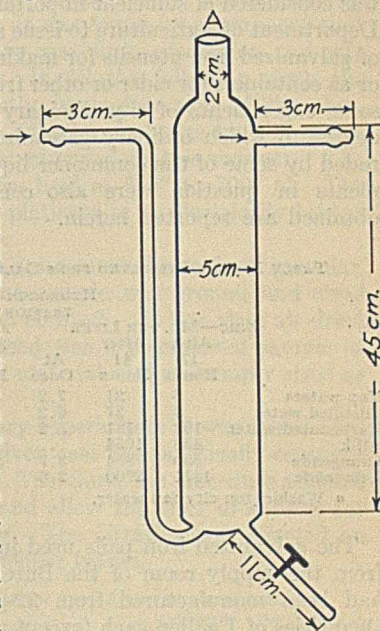
# Contamination of Beverages and Other Food with Zinc[1]

By J. W. Sale and C. H. Badger

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

THE Navy Department recently transmitted to the Bureau of Chemistry for analysis several bottles of root beer, which the Naval Station at Guam had reported unfit for human consumption. It was stated that some of the shipment, which consisted of twelve hundred bottles, was sold to at least twelve people at Guam, and upon drinking the same they immediately began vomiting. Chemical examination disclosed the presence of zinc in the contents of each of the three bottles examined, and the analysis of a composite sample of 200 cc. from each bottle showed that zinc was present to the extent of 229 mg. per liter, which is equivalent to 3.3 grains of zinc chloride per bottle containing 15 fluid ounces.

At about the time the examination of the root beer was completed, four thousand galvanized iron buckets were distributed as premiums in the District of Columbia by a chain of grocery stores. A short time previous a case of mass poisoning by zinc at a large institution near London had been reported in the literature,[2] from which it appeared that over two hundred persons developed typical symptoms of zinc poisoning immediately after a meal consisting of bread, margarine, stewed apples, and tea. Subsequent investigation showed that the apples had been cooked in galvanized iron baskets placed in iron steamers, and that the fruit acids had dissolved the zinc from the baskets. It seems quite probable that some of the buckets being distributed in the District of Columbia and elsewhere would be used for holding semisolid or liquid food, such as cider, lemonade, etc. The matter was considered of sufficient importance for the United States Department of Agriculture to issue a warning against the use of galvanized iron utensils for making preservatives or jellies or as containers for cider or other fruit juices, and to conduct some experiments of a preliminary nature to ascertain the degree to which ordinary galvanized iron buckets are corroded by some of the commoner liquid foods. The experiments in question were also conducted and the results obtained are reported herein.

Table I—ZINC DISSOLVED FROM GALVANIZED IRON PAILS

| | ZINC—MG. PER LITER | | HYDROGEN-ION CONCENTRATION EXPRESSED AS pH | | | ACIDITY Cc. 0.1 N ACID PER LITER | |
|---|---|---|---|---|---|---|---|
| | After 17 Hours | After 41 Hours | At Once | After 17 Hours | After 41 Hours | After 17 Hours | After 41 Hours |
| Tap water[a] | 5 | 21 | 7.2 | 8.4 | 8.8 | 0 | 0 |
| Distilled water | 9 | 27 | 6.2 | 7.5 | 8.2 | 1 | 0 |
| Carbonated water | 193 | 181 | 5.2 | 6.4 | 6.9 | 348 | 96 |
| Milk | 438 | 1054 | ... | ... | ... | ... | 1109 |
| Orangeade | 530 | 854 | 3.7 | ... | ... | 397 | 533 |
| Lemonade | 1411 | 2700 | 2.6 | ... | ... | 493 | 366 |

a Washington city tap water.

The galvanized iron pails used in this test were obtained from the supply room of the Bureau of Chemistry. They had been manufactured from 22-gage galvanized sheets. Quantities of 1 gallon each (except milk) of Washington city tap water, distilled water, carbonated water, milk, orangeade, and lemonade were placed in the galvanized iron pails. The quantity of sweet milk used was 1 quart. Samples were examined for zinc at the end of 17 and 41 hours. The concentration of hydrogen ions and titratable acidity (with phenolphthalein indicator) were also determined on most of the solutions. The orangeade and lemonade contained the juices of twelve oranges and twelve lemons, respectively, and 1 pound of sugar in each gallon. The results obtained are set forth in Table I.

Blanks were run on the tap water, distilled water, and carbonated water. The tap water and distilled water contained less than 0.1 mg. of zinc per liter. The carbonated water contained 7 mg. of zinc per liter. This carbonated water had been prepared by mixing cold tap water and carbon dioxide in an ordinary carbonating egg. The amounts of zinc reported in Table I do not include these blanks. No blanks were run on the milk, orangeade, or lemonade. It is probable that the milk contained about 5 mg. of zinc per kilogram before placing it in the galvanized iron pail.[3] Rost and Weitzel[4] point out that the presence of zinc in food is not wholly dependent on the use of galvanized containers, since fresh cows' milk, ordinary drinking water, etc., contain zinc.

It will be noted from Table I that the quantity of zinc found after 17 hours increases directly with the concentration of hydrogen ions and with the titratable acidity. The concentration of hydrogen ions and the titratable acidity in general decrease, except in the case of the acidity of orangeade, after 41 hours, with lapse of time due, no doubt, chiefly to the mechanical loss of carbon dioxide in the case of the carbonated water and to the corrosive action of the other liquids on the metal of the container. The acidity of the orangeade after 41 hours had increased from 397 to 533 cc. of 0.1 N acid per liter. This may be explained by the fermentation of the liquid and the formation of carbon dioxide, the experiments being conducted in midsummer. A determination of the volatile and nonvolatile acid of the orangeade after 41 hours showed that the volatile acidity amounted to 244 cc. and the nonvolatile acidity to 289 cc. 0.1 N acid per liter. It is of some interest in this connection to note that the total acidity of Concord grape juice amounts to about 1330 cc. 0.1 N per liter,[5] and of apple juice to about 670 cc. 0.1 N per liter.[6]

The galvanized iron pails which contained the milk, orangeade, and lemonade were visibly corroded. The visible corrosion was especially marked on the galvanized iron pail which contained the lemonade. The base metal was exposed in one place about the size of a circle having a diameter of 2.5 inches.

Aside from the general interest attaching to the apparent solution of a case of food poisoning, these experiments serve to bring freshly to mind the always important question of the metallic contamination of our food. Federal and State inspectors are urged to be always on the lookout for possible metallic contamination, and wherever food is brought in contact with metal to make careful note of the fact so that suitable special investigation can 'be conducted when such action seems to be advisable.

[1] Presented before the Division of Agricultural and Food Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

[2] Lancet, 204, 214 (1923); abstracted in Analyst, 48, 184 (1923).

[3] Birckner, J. Biol. Chem., 38, 191 (1919).

[4] Arb. Reichsgeshamt., 51, 494 (1919); Zentr. Biochem. Biophys., 21, 440; C. A., 14, 1569 (1920).

[5] U. S. Dept. Agr., Bull. 656.

[6] From unpublished data in Bureau of Chemistry.

# Comparative Ash Adsorption of Vegetable and Bone Chars[1]

By Paul M. Horton and P. T. Sengson

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**D**URING the last few years the adsorptive property of various vegetable chars has been made use of in the refining of raw sugar and cane juices. This has naturally evolved some controversy and conflict with the proponents of the old and established bone char process. Chemists are apparently united in the belief that the vegetable carbons are much superior in decolorizing power, but there is considerable discussion concerning cost, reliability, and, in particular, the ash-adsorbing power. Many claim that bone char adsorbs a very considerable portion of the ash from a raw sugar melt, while vegetable chars do so only to a slight extent, if at all. This one item seems to be of sufficient importance to merit an investigation. It is generally believed that small-scale laboratory tests of decolorizing carbons are of little worth. Certainly, the data are generally inconclusive, but it is felt that the work as described below will have a certain value, and is for this reason given in some detail.

*Comparison of the ash adsorbed by bone char and vegetable char under comparable conditions shows that, volume for volume, bone char removes much more ash. When equal weights of the chars are compared, it is found that as the amount of char is increased, keeping the volume of the testing solution constant, the relative efficiency of the vegetable char seems to approach that of bone char.*

In the majority of the foregoing references only the conclusions are published, without supporting experimental data. It is the purpose of this work to show how the various conflicting opinions may, in a way, be reconciled.

## Previous Work

In 1916, Wijnberg[2] found that after norit had been in use for some length of time a quantity of inorganic salts accumulated in the char, a finding in agreement with the results of other investigators. In 1918, Zerban and Taggart[3] investigated the ash adsorption from cane juice using rice-hull carbon. As an average of four experiments it was found that 4.8 per cent of the total ash in the juice was removed. When the char was introduced into the sirup, the ash adsorption was much greater. At about this time Weinrich[4] printed his version of the subject, in which he denied that any vegetable carbon is capable of removing ash from solution. This conclusion seems to be based on results obtained with vegetable carbons known thirty years ago. On the other hand, Sauer[5] shows that norit will adsorb many other substances in addition to the usual coloring matters, among which are colloidal gums, silica, and soluble salts such as the calcium and potassium salts of the various organic acids. The analytical methods used by Sauer will be discussed later. Furthermore, Horne[6] in a study of four different chars proceeds to the same conclusion as Weinrich. His method of testing was slightly different from Sauer's, but it is difficult to assign a reason for his experimental figures. From a raw sugar melt showing 0.35 per cent ash he obtained a filtrate after the treatment with char containing 0.36, 0.37, 0.34, and 0.39 per cent, respectively. Lastly, and most recently, Avot[7] has made a comparative study of bone and vegetable char, in which he comes to the conclusion that vegetable chars do remove ash almost to the same extent as does bone char. Sugars refined by vegetable char were shown to contain on an average of 0.05 per cent more ash than those refined by bone char. This is to be expected, however, when the relative amounts of the carbons used per pound of sugar are taken into consideration.

Any attempt to compare the various statements and claims published is rendered difficult by the lack of numerical data.

## Experimental

In determining the ash adsorbed by norit, Sauer proceeded as follows: Impure sugar was melted to a sirup having a Brix of 50.° To any quantity of this sirup was added 5 per cent of the char based on the total solids, and the mixture was heated to 90° C. for about 2 minutes. After filtration the amount of mineral matter removed was figured (1) from the analysis and purity of the sirup before and after treatment with the char, and (2) by determining the ash content of the char before and after its use in the impure sugar solution. In the experiments carried out by Horne the chars were heated with a raw sugar melt at 80° C. for 40 minutes. The ash content of the sirups was found by direct incineration. Equal volumes of the various chars were used. Method 2 of Sauer seems to be the most rapid and logical. It was found to be accurate and the ash adsorbed is not washed out by the wash solution when removing the adhering sirup.

In the present work it was decided to use a final molasses solution as the standard. It was found by experiment that a solution of 15° Brix gave maximum adsorption and was not too viscous to filter. In all the following work the ash was determined directly by incineration of the char, previously washed free of adhering molasses by hot water. The adsorbed ash was not removed in this manner. The temperature of ignition was held at 650° to 700° C. The ignition was carried out in platinum in an electrically heated muffle furnace.

The bone char used was a commercial sample of granular, acid-washed material. The sample was ground and sized to through 60 mesh and on 80 mesh. It was then air-dried and bottled. The norit used was a commercial sample of the powdered, acid-washed material, and was simply sized as above and bottled.

By a series of preliminary experiments it was found that adsorption of ash in any given case was practically complete after 40 minutes' boiling. Therefore, the procedure adopted was to reflux for 1 hour and allow the char to subside for 30 minutes and then filter. The filtration was effected on an ashless filter held in a Büchner funnel.

[1] Received June 28, 1923. Presented before the Division of Sugar Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923. Abstracted from thesis presented by Mr. Sengson in partial requirement for the degree of M.Sc. in chemistry.

[2] *Intern. Sugar J.*, **18**, 194 (1916).
[3] Louisiana State Expt. Sta., *Bull.* **161**.
[4] *Intern. Sugar J.*, **20**, 424 (1918).
[5] *Ibid.*, **20**, 24 (1918).
[6] This Journal, **14**, 1134 (1922).
[7] *Intern. Sugar J.*, **25**, 196 (1923).

**Effect of Concentration upon Adsorption of Ash**

| Weight of Char Grams | °Brix of Solution | Ash in Original Char Per cent | Ash after Adsorption Per cent | Per cent Ash Adsorbed Per cent Char |
|---|---|---|---|---|
| 1.5784 | 10 | 89.12 | 90.12 | 1.00 |
| 1.6362 | 15 | 89.12 | 92.59 | 3.47 |
| 1.6502 | 20 | 89.12 | 92.91 | 3.79 |

The foregoing experiment was made with bone char and shows the effect of concentration upon the amount of ash adsorbed. The use of a 15° Brix solution gives maximum ash adsorption, and a solution more concentrated than this simply increases the difficulties and offers no advantages.

Whereas it is a well-known fact that the amounts of bone char and vegetable char used in the refinery are not the same, and for this reason no comparison of the amounts of ash adsorbed can be made, it is equally true that if equal quantities of the two chars are used there is no reason to believe that the amounts of ash adsorbed will be the same. For this reason it is desirable to determine the relative ash adsorption using equal weights of the two chars and then to repeat using equal volumes.

Definite volumes of bone char—namely, 5 cc., 10 cc., 15 cc., and 20 cc.—were measured in a graduated cylinder and the corresponding weights taken. Each sample was added to 500 cc. of 15° Brix solution of final molasses and refluxed for 1 hour. The ash was determined in the char as previously described.

ASH ADSORBED BY EQUAL VOLUMES OF BONE CHAR OR NORIT

| Volume Cc. | Weight Grams | Ash in Air-Dry Char (or Norit) Per cent | Ash after Testing Per cent | Ash Adsorbed — Per cent Char (or Norit) | G./Cc. |
|---|---|---|---|---|---|
| | | | Bone char | | |
| 5 | 3.917 | 83.41 | 84.40 | 0.99 | 0.0077 |
| 10 | 7.835 | 83.41 | 84.45 | 1.04 | 0.0083 |
| 15 | 11.751 | 83.41 | 84.46 | 1.05 | 0.0082 |
| 20 | 15.668 | 83.41 | 84.46 | 1.05 | 0.0082 |
| | | | Norit | | |
| 5 | 1.072 | 7.57 | 8.02 | 0.45 | 0.0010 |
| 10 | 2.144 | 7.57 | 8.10 | 0.53 | 0.0011 |
| 15 | 3.216 | 7.57 | 8.24 | 0.67 | 0.0015 |
| 20 | 4.287 | 7.57 | 8.33 | 0.76 | 0.0016 |

It is apparent from the foregoing figures that on a volume basis bone char is approximately five times as efficient as norit in removing ash from solution. This figure is taken from the results using 20 cc. of char, as the ash adsorbed per cubic centimeter seems to have become constant at this ratio.

This series was repeated using equal weights of the chars.

ASH ADSORBED BY EQUAL WEIGHTS OF BONE CHAR OR NORIT

| Weight Grams | Ash in Air-Dry Char (or Norit) Per cent | Ash after Testing Per cent | Ash Adsorbed — Per cent Char (or Norit) | G./G. |
|---|---|---|---|---|
| | | Bone Char | | |
| 2 | 83.41 | 84.39 | 0.98 | 0.0098 |
| 4 | 83.41 | 84.38 | 0.97 | 0.0097 |
| 6 | 83.41 | 84.38 | 0.97 | 0.0097 |
| 8 | 83.41 | 84.37 | 0.96 | 0.0096 |
| | | Norit | | |
| 2 | 7.57 | 8.17 | 0.60 | 0.0060 |
| 4 | 7.57 | 8.30 | 0.73 | 0.0073 |
| 6 | 7.57 | 8.39 | 0.82 | 0.0082 |
| 8 | 7.57 | 8.48 | 0.91 | 0.0091 |

## DISCUSSION OF RESULTS

The interpretation of the preceding determinations will depend somewhat on the viewpoint. The values obtained may be considered to show that norit will adsorb as much ash as bone char under conditions favorable to the latter. Taken as a whole, however, over the entire range of concentration the results are decidedly in favor of bone char. It will be observed that, although the percentage of ash adsorbed by the bone char is constant and independent of the weight of char used, the percentage of ash increases, in the case of norit, as the weight of char is increased, using a fixed amount of solution. In 500 cc. of a 15° Brix molasses solution, the total solids approximate 80 grams. In a range of from 2.5 to 10 per cent of char on total solids, bone char adsorbs a constant (0.97 per cent) amount of ash. In the same range norit increases in adsorptive power from 0.60 to 0.91 per cent. From the adsorption curves it will be found that 10 grams of norit will remove the same amount of ash as 10 grams of bone char. This fact, if of any significance at all, seems to show that the ash adsorbed per unit weight of char is a function of the total amount of insoluble ash present in the char. Horne has shown that, in the case of bone char, the carbon present is the decolorizing agent and the mineral skeleton removes the ash. It

has been suggested that on this basis 11 grams of norit containing 0.832 gram ash should show the same unit adsorption as 1 gram of bone char containing 0.834 gram ash. By extrapolating the data it is found that such is the case. Ten grams each of norit and bone char adsorb from 500 cc. of solution nearly 0.098 gram of ash. The relative efficiency of norit compared with bone char over the range of 2.5 to 12.5 per cent of char to total solids is shown by the following table:

RELATIVE EFFICIENCY OF BONE CHAR AND NORIT

| Per cent Char to Total Solids | Weight per 500 Cc. Solution Grams | | Efficiency of Norit Per cent |
|---|---|---|---|
| 2.5 | 2 | (0.60/0.98) × 100 = | 61.2 |
| 5.0 | 4 | (0.73/0.97) × 100 = | 75.3 |
| 7.5 | 6 | (0.82/0.97) × 100 = | 85.5 |
| 10.0 | 8 | (0.91/0.96) × 100 = | 94.8 |
| 12.5 (extrapolated) | 10 | (0.98/0.96) × 100 = | 102.0 |
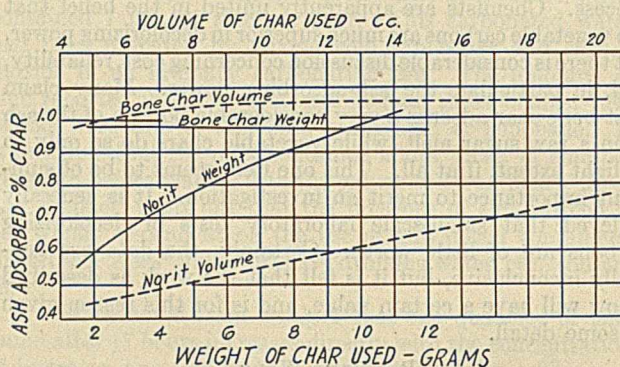


It will be observed that by choosing the conditions of the test, norit may be shown to be from 61 to 102 per cent as efficient as bone char in adsorbing ash from sugar solutions. Evidently, the methods of testing are at fault, and too much credence must not be placed on the results of a laboratory test of competing chars.

Note.—These results are not intended to show the relative value of the two products, which were chosen simply as representative substances, but are given to indicate the variation of analytical ratings when the conditions of testing are varied.

The norit was used as it is supplied to the sugarhouses, and since it contains 1.5 per cent of water-soluble ash, the results obtained may be given an entirely different interpretation if the ash adsorbed is figured on the insoluble ash rather than on the total ash in the char. However, in light of present knowledge of the nature of ash-forming constituents, no method of distinguishing between the ash adsorbed by the char, and the ash lost to the solution from the char, is available. It is the total change in the inorganic constituents of cane juice that gives a basis for evaluating the char. Hence a carbon containing soluble ash is penalized to that extent. It is understood, however, that only factory trials will actually show the true value of a given carbon. Work in progress in this laboratory will attempt to extend the information on this subject.

## CONCLUSION

The results obtained in the foregoing experiments show that: (1) increasing the time of heating of char in solution also increases the amount of ash adsorbed, (2) adsorption is greater when dealing with higher concentrations of sugar solution than with rather dilute solutions, (3) volume for volume bone black will remove more ash than norit under the same conditions, and (4) weight for weight norit under certain conditions is just as effective as bone char, though in general the bone char is the more efficient. These statements are not to be taken as final generalizations, but merely as tentative suggestions subject to modification.

It is thought that the diverging opinions found in print may be due to several causes: (1) ignition of char to ash at

too high a temperature, (2) use of too dilute testing solution, (3) the solution and char were not heated together for sufficient time, and (4) the chars were tested in some cases on the volume basis and in other cases on the weight basis, using at the same time widely varying ratios of char to total solids.

# The True Dry Substance Content of Beet Molasses[1]

By R. G. Gustavson and J. A. Pierce

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*Sulfur dioxide, carbon dioxide, ammonia, iodoform-producing substances, and an unidentified oil distil from the molasses when dried under conditions approximately similar to those employed in determining dry substance under the method recommended by the Association of Official Agricultural Chemists. The total percentage of these compounds, other than water and oil, passing off is 1.965. At a temperature approximating 104° C. an amido constituent of the molasses decomposes with liberation of ammonia.*

*It is suggested that these results will explain in part the variation existing between dry substance content as found by the refractometer and by oven drying.*

STANDARD methods of determining the true dry substance content of beet sugar juices, and more particularly of molasses, presuppose that, when subjected to a uniform heat of from 100° to 105° C., nothing passes off but water. Since an accurate knowledge of the percentage of dry substance is necessary in formulating the degree of "true purity" in the original substance, any doubt that the standard method is accurate leads to the corollary doubt that the figures obtained by the formula

$$P = \frac{100S}{P}$$

are correct. The method recommended by the Association of Official Agricultural Chemists, usually known as the "Standard Method," is so generally accepted by sugar chemists that it is considered by most of them to be exact. Very little literature on the subject can be found in any published treatises on sugar analysis. Aiken[2] states that "the use of the vacuum oven to determine whether there might be some decomposition of the less stable constituents of beet molasses at 105° C. did not indicate that any such decomposition took place." To the authors this is not a satisfying conclusion.

Lack of data on dry substance determinations, the realization that factory processes of manufacture indicate the possible volatilization of carbon dioxide and sulfur dioxide, and the fact that the analyses of Wiley and Browne[3] show the presence in molasses of comparatively unstable amido compounds were the reasons for the series of experiments described herein.

## Description of Apparatus and Material

Strong efforts were made to parallel as closely as possible the conditions existing when molasses is dried by the standard method. The fact, however, that the volatile fraction and not the residue was the object under investigation made it necessary to employ a still and a series of flasks and bulbs to collect the distillate. This train of apparatus resulted in the formation of atmospheric conditions different from those found in the standard method, and it was necessary to counteract this effect. The authors believe that in all essentials the conditions of drying the substance were exactly as they would have been under the official method.

A small, double-walled drying oven, containing in the jacket a glycerol solution of such a strength that a constant temperature of from 100° to 105° C. might be maintained, was employed. A large Liebig condenser, mounted vertically, preserved a constant boiling point by preventing the evaporation of the water in the solution.

Instead of the aluminium dish used in the standard method, a flask of about 75-ml. capacity was employed. This modification was suggested by Paul M. Grissinger, research chemist with the Great Western Sugar Company, with the statement that experiments have indicated that glass and aluminium vessels give identical results.

Three small holes were bored through the door of the oven to permit the insertion of a plain glass tube, a thermometer, and a soda-lime bulb. All three had entrance to the distilling flask through a tightly fitting rubber stopper. The thermometer bulb was inserted into the mass of sand and molasses, since preliminary experiments showed that the interior of the mixture did not reach the temperature of the empty part of the flask for at least 20 minutes when the latter registered 105° C. A small soda-lime bulb was used to prevent the ingress of carbon dioxide from the air. The other end of the plain tube was attached to a small Liebig condenser.

The receiving vessels consisted, at various times, of a 200-ml. flask containing 50 ml. of distilled water, a similar flask containing 50 ml. of 0.1 N sulfuric acid, a similar flask containing 50 ml. of 0.1 N sodium hydroxide, one containing 50 ml. of saturated bromine water, and a potash bulb of the usual type. Protection by means of calcium chloride tubes was employed at necessary points. A bent tube attached to the discharge end of the Liebig condenser was kept at all times below the surface of the solution in the flasks as in the Kjeldahl method. A suction apparatus of sufficient strength to neutralize the pressure in the train of apparatus was used continuously, and regulated to maintain as closely as possible a pressure of one atmosphere.

The material investigated was a molasses known as "standard molasses," from a factory whose lime rock and water were of sufficient purity to result in a product considered to be typical. It had a Brix of 93.2° and a slight negative alkalinity. Dry substance by the refractometer was 79.2 per cent.

The sand employed was prepared by the standard method of sifting, treating with hydrochloric acid to remove soluble iron, washing, and drying on a hot plate. Sand between 40 and 60 mesh was used exclusively.

## Experimental

Sand and a known quantity of molasses were mixed in proportions of about 25 to 1. Great care was taken to make

[1] Received July 11, 1923.
[2] This Journal, 12, 979 (1920).
[3] Sherman, "Food Products," 1914, pp. 421, 427, 431.

the resulting mass uniform in texture. The conclusions of Aiken were followed as far as possible in this regard. The completely mixed mass was very porous, and had a tendency to "crawl" when held in an inclined position. The amount of molasses used in each trial was approximately 4 grams. The maximum temperature reached in any one run was 105° C.; the average maximum was 104° C. The oven was heated until the thermometer in the glycerol-water solution registered a steady temperature of 105° C., and then the distilling flask was inserted and the apparatus connected. It was found that if the flask was placed in the oven when the latter was cold and the mass allowed to heat gradually, it had a tendency to impact on the surface and form a more or less impermeable layer. It was also found that in a sample of the size used it took 1 hour and 20 minutes for the interior of the mass to register the same degree of heat indicated by the glycerol-water solution.

The distillate, which came over very slowly and at a uniform rate, was colorless, with an acid, empyreumatic taste. The odor was very distinct, somewhat alcoholic, but reminding one of the odor of the original material. Even before the liquid passed through the condenser tube into the receiving flask, the contents of that flask acquired the odor of the distillate. At the end of several hours the liquid, when distilled into water or 0.1 $N$ sulfuric acid, lost its transparency and became turbid. This turbidity could be removed by repeated filtration through kieselguhr, but could not be determined quantitatively. The aqueous solution of distillate precipitated heavily with basic lead acetate and with barium chloride. It tested strongly for ammonia with Nessler's solution. It was distinctly acid even to litmus paper. The dried substance left in the flask was neutral to litmus.

Thus, the total percentage of the original material, exclusive of water and oil, which passed over at 104° C., was 1.965.

Sulfur, estimated as sulfur trioxide, was obtained by three methods:

(1) By distilling into 50 ml. of neutral water in a 200-ml. flask, adding copper sulfate and phosphoric acid solutions to this distillate, redistilling into saturated bromine water in an atmosphere of carbon dioxide, boiling off the excess of bromine, adding 2 ml. of dilute hydrochloric acid, precipitating with barium chloride solution, filtering through asbestos, igniting, and weighing.[4] This method was used in Trial 2.

(2) By distilling into neutral water as above and titrating with 0.1 $N$ sodium hydroxide for total acidity of the solution. (Trials 1 and 3)

(3) By distilling into 0.1 $N$ sodium hydroxide and titrating with 0.1 $N$ sulfuric acid. (Trial 4)

Carbon dioxide was determined (approximately) by the gravimetric (potash bulb) method. No claim is made for exactness.

Iodoform-producing substances were determined quantitatively by a slightly modified form of the Messinger method. The only deviation was the use of 0.05 $N$ iodine and sodium thiosulfate solutions, instead of 0.2 $N$ as recommended.

In addition to the foregoing qualitative and quantitative determinations, it was found that if the temperature is approximately 104° C. at the beginning of the distillation, a mixture of sulfur dioxide, carbon dioxide, ammonia, iodoform-producing compounds, and oil is given off. However, if a temperature of 90° C. is maintained for several hours, an *acid* fraction containing sulfur dioxide, carbon dioxide, iodoform-producing compounds, and oil passes over. Then, if the temperature is raised to 104° or 105° C. a strongly *alkaline* distillate appears which tests for ammonia by Ness-

| | | | | | Per cent | | | | Per cent Iodoform Producers |
|---|---|---|---|---|---|---|---|---|---|
| Trial | Weight of Sample | Per cent Loss | Time Hours | Temperature ° C. | Sulfur as SO₂ | Per cent NH₃ | Per cent CO₂ | Oil | Calculated as Acetone |
| 1 | 2.4839 | 17.71 | 10 | 104 | 0.937 | ... | ... | Trace | ... |
| 2 | 3.4762 | 17.44 | 18 | 104 | 0.918 | ... | 0.06 | Trace | 0.041 |
| 3 | 4.4152 | 17.69 | 17 | 104 | 0.924 | 0.914 | 0.09 | Trace | ... |
| 4 | 4.9000 | 17.56 | 19 | 105 | 0.920 | 0.927 | ... | Trace | 0.050 |
| Av. | 3.8189 | 17.60 | 16 | 104 | 0.925 | 0.920 | 0.075 | Trace | 0.045 |

TABLE I

As a check on the results obtained by distillation of the molasses-sand mixture, a 4-gram sample of molasses was diluted with 100 ml. of neutral water and distilled from an ordinary retort. Conditions of pressure and temperature were maintained as closely as possible to those mentioned above. At 90° C. an *acid* distillate was evolved which gave a positive iodoform test. When this fraction had passed over and the temperature was raised to 105° C., the distillate was found to be *alkaline*, and tested strongly for ammonia by the Nessler reaction. The undistilled residue in the flask, as in the case of the molasses-sand mixture, was *neutral*.

The distillate from the molasses-sand mixture was tested qualitatively for iodoform-producing substances, carbon dioxide, ammonia, and sulfur dioxide, with positive results. Qualitative tests for cyanogen and furfural were made, with negative results. An attempt was made to determine the presence of the fatty acids by means of the Duclaux constants, but the presence of sulfur dioxide, and the small amount of the distillate interfered. The turbidity found after the distillate had stood for several hours was determined by saponification with sodium hydroxide, and by absorption with ether, to be some unidentified oil. The foregoing qualitative determinations were made by standard, recognized tests. When a substance was found by one test, confirming tests were made with other reagents. The results are give in Table I.

ler's reagent. This indicates that at 104° or 105° C. an amido component of the molasses decomposes. It is suggested that this compound might be aminosuccinamic acid. This is indicated chiefly by the well-recognized analyses of Browne and Wiley, mentioned above, of sugar beet juice, discard molasses, and *schlempe*. Thorpe[5] also states that, in the presence of certain mineral acids, asparagine (aminosuccinamic acid) splits into ammonia and aspartic acid.

[4] Great Western Sugar Company, "Methods of Analysis," **1920**, p. 120.
[5] Dictionary of Applied Chemistry, Vol. I, p. 310.

## 25th Anniversary of the Discovery of Radium

The anniversary of the epoch-making discovery of radium by Becquerel and M. and Mme. Curie was celebrated by appropriate exercises in the Grand Ampitheater of the Sorbonne on Wednesday, December 26. President Millerand was in the chair and gave a brief address at the close of the meeting. The most important addresses were by Perrin on "Radioactivity and Its Importance in the Universe," and by Béclere on "Radium in Medicine." One interesting feature of the meeting was the reading of two of the first published communications on the subject of radium. Several experiments were shown to illustrate the fundamental phenomena of radioactivity. Of especial interest were the discharge of an electroscope by the proximity of radium, the effect of single alpha particles emitted from polonium under such conditions that a sound, amplified to be audible to the large audience, was produced, and the fluorescence produced by radium emanation with a tube a meter in length. Madame Curie was present and made a brief address.—W. A. NOYES

# The Rapid Analysis of Sugars[1]

## Purification and Concentration of Enzyme Solutions

### By F. W. Reynolds

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*Yeast extracts may be freed of color and substances causing turbidity by dialyzing, or by washing on an ultra-filter, and subsequently acidifying with acetic acid, whereby the substances causing turbidity are flocculated and can be removed by filtration on paper.*

*Highly active preparations of invertase and melibiase may be obtained by concentrating crude or purified yeast extracts by ultra-filtration. A simple ultra-filter may be constructed of materials readily available.*

*Ultra-filtration should be useful as a means of concentrating other enzymes for use as analytical reagents and also in the study of enzymic action of plant and fruit juices.*

THE value of certain enzymes as hydrolytic reagents in the analysis of polysaccharides has long been recognized. Their use, however, has been limited by the fact that, with the dilute solutions available the time required for hydrolysis was in many cases too long for satisfactory work and the results were somewhat uncertain. This is especially true of some of the so-called weak enzymes, such as melibiase, maltase, and lactase. Enzymes are no more difficult to use than other reagents, provided certain fundamental conditions are sufficiently controlled. By far the greater portion of these difficulties and uncertainties disappear when enzyme solutions of sufficient activity are used. It is quite practicable to prepare invertase solutions which, when used in the proportion of 10 cc. of the enzyme solution to 100 cc. of the clarified sucrose solution, will complete the hydrolysis of the sucrose in less than 15 minutes at room temperature. The advantage of using concentrated enzyme solutions is not limited to a saving of time. The end point of the hydrolysis is sharp and distinct, instead of being somewhat uncertain as is the case when dilute enzyme solutions are used. The enzyme has the advantage over an acid in that no destruction of sugar is possible and the hydrolysis is specific.

When used as an analytical reagent, it is desirable that the enzyme solution be free from inactivating substances, color, turbidity, and optically active substances the optical activity of which may change during the hydrolysis. The present paper describes a method for preparing highly active solutions of the enzymes invertase and melibiase which meet these requirements.

### Purification of Enzyme Solutions

Enzymes have frequently been purified by precipitation of the enzyme from solution by means of alcohol, acetone, and other reagents, the precipitated material being redissolved in water. Some investigators have employed selective adsorption on aluminium hydroxide, fuller's earth, finely divided carbon, etc. The most important work along this line is probably that of Willstätter.[2] Such methods are usually attended by a rather large loss of enzymes unless the work is done with extreme care by an experienced investigator.

Neutral lead acetate has been frequently used as a reagent for precipitating impurities from autolyzed yeast extract. Lead salts have an inactivating effect on enzymes, and excess of such salts must therefore be carefully removed by precipitation, hydrogen sulfide or potassium oxalate being satisfactory deleading agents. The acetic acid or potassium acetate remaining in the solutions may be removed by dialysis. Enzyme solutions prepared in this way are usually too dilute to be used in rapid analytical work, especially in the case of the so-called weaker enzymes, such as melibiase.

The writer has found in the case of invertase and melibiase that efficient clarification of the autolyzed yeast extract[3] can be accomplished in a simple manner —that is, by dialyzing the crude extract in collodion dialyzing sacks for 24 hours or longer against running tap water and then acidifying with glacial acetic acid in the proportion of about four drops per 100 cc. of the dialyzed extract. This treatment causes flocculation of a considerable amount of material, and after standing over night the precipitate may be filtered off on fluted paper. This treatment causes no inactivation or loss of either invertase or melibiase, as was shown by a number of activity tests made before and after clarification. The activity of solutions clarified in this manner is practically the same as that of solutions prepared by the lead acetate and dialysis method. Neutral lead acetate causes no precipitate in yeast extracts clarified as described above.

During the course of dialysis the enzyme solution is considerably diluted owing to the passage of water to the inside of the dialyzing bag. This added water, together with most of the water originally present, may be removed by the process of ultra-filtration described below. Dilution during dialysis may, however, be largely prevented by fitting the collodion dialyzing sack with a cork stopper and cementing it thereto with collodion. An upright glass tube of small diameter should penetrate the stopper and reach to a height of about 4 feet above the stopper. The bag is completely filled with the enzyme solution to be dialyzed and is then immersed in running water. Osmotic pressure forces the liquid inside the bag up into the upright tube to a height of 3 or 4 feet. As the dialysis proceeds the height of the liquid gradually falls, reaching a minimum of 2 or 3 inches. It should be possible actually to concentrate the enzyme during dialysis by admitting fresh enzyme solution through the upright tube as fast as the pressure falls. This has no advantage over ultra-filtration, however, and has therefore not been further investigated.

### Concentration of Enzyme Solutions by Ultra-Filtration

The means available for concentrating enzyme solutions are rather limited. Concentration *in vacuo* at low temperature may be used, but in this case there is also more or less destruction of enzymes, especially in cases where the temperature is not carefully controlled. The fact that collodion membranes of suitable composition are impermeable to enzymes but are permeable to water and to highly dispersed substances present in the enzyme solution, renders ultra-filtration through such a membrane an ideal method for concentrating enzymes. Enzyme solutions purified by any method may be readily concentrated by filtering off the required amount

of water; the enzyme, being retained by the filter, is thereby concentrated. Any suitable type of ultra-filter may be used. The one employed in this laboratory was improvised from materials which are generally available, and on account of its simplicity and adaptability to this purpose will be described in detail.

### Construction of a Collodion Ultra-Filter

For the preparation of a suitable type of collodion membrane 5 grams of Anthony's snowy cotton[4] are dissolved in a mixture of 50 cc. 95 per cent alcohol, 50 cc. U. S. P. ether, and 5 cc. glacial acetic acid. About 100 cc. of this solution are poured into a cylinder of about 2000 cc. capacity and the open end of the cylinder is covered immediately with the hand. The cylinder is then inclined and rotated, keeping the open end covered to prevent evaporation, until the inside surface of the cylinder is uniformly coated with the collodion. The cylinder is then inverted and uncovered and allowed to drain and dry for 10 minutes. At the end of this time it is placed in an upright position and filled with water. In 10 or 15 minutes the collodion membrane will have loosened from the cylinder and can be removed after pouring out the water. The sack should be filled with water and wiped dry on the outside and examined for leaks. It is then emptied and cut open longitudinally and the flat membrane which is obtained is spread out on a wet piece of filter paper. The membrane should never be allowed to dry, as it then becomes impermeable. A circular piece about 7 or 8 inches in diameter is then cut out with a pair of scissors. The bottom is cut from a large wide-mouth bottle or 2-liter Erlenmeyer flask and the edge ground flat and smooth with emery powder on a flat piece of metal or glass. The bottle or flask is placed concentrically on the circular piece of collodion, and the edges of the membrane are folded up to the sides of the
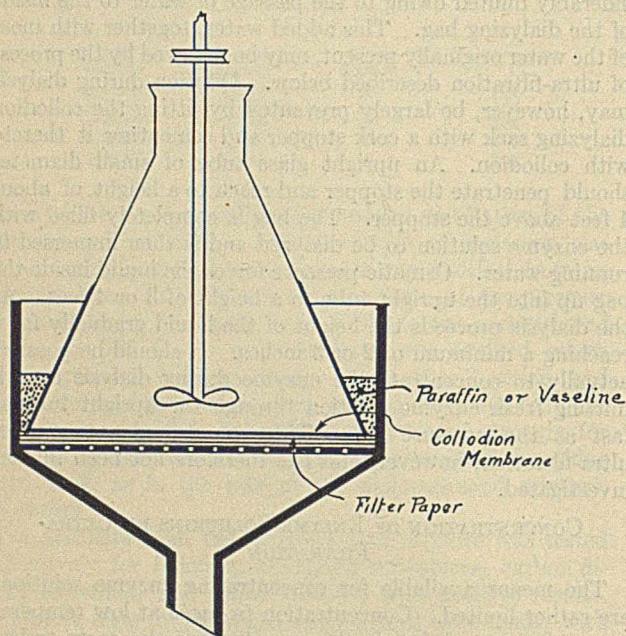


FIG. 1—DIAGRAM OF ULTRA-FILTER

bottle and cemented thereto with collodion. This cementing collodion should contain an increased percentage of ether (about 4 parts of ether to 1 of alcohol), as a collodion of this composition dries quickly to a hard, impermeable film. It is well to coat most of the outside surface of the

[4] All types of nitrocellulose do not give the same results. It is therefore recommended that Anthony's snowy cotton be used as this was found to yield the most satisfactory results of any variety readily obtainable in the United States.

bottle with this cementing collodion, making it continuous with the filtering membrane; a small varnish brush is conveniently used. Three or four thicknesses of wet filter paper are placed in a Büchner funnel having an outside diameter of about 8 inches. The bottle, fitted with the collodion membrane, is then placed in the Büchner funnel with the collodion membrane resting on the filter paper. Melted vaseline is poured between the edge of the bottle or flask and the side of the funnel to a depth of an inch or so in order to make an air-tight seal. The Büchner funnel is then used in the customary manner, with vacuum, and a suction flask as a receiver. Water filters through this membrane at the rate of about 500 cc. per hour, depending on the vacuum. With yeast extracts the rate of filtration is slower, varying from 100 cc. per hour to 25 cc. per hour, depending upon the character of the solution. When not in use the membrane should be kept covered with water to which a little camphor or chloroform has been added as a preservative. Ultra-filtration may be kept going continuously, day and night, with very little attention, by using a constant-level siphon for supplying the enzyme solution, thus compensating for the relatively slow rate of filtration.

Fig. 1 shows the construction of the complete filter. It is necessary to keep the enzyme solution thoroughly agitated during the ultra-filtration, as the enzyme is apparently precipitated—possibly owing to the high concentration at the surface of the membrane—unless this precaution is taken.

### Simultaneous Concentration and Purification by Ultra-Filtration

A crude, autolyzed yeast extract may be concentrated to small volume and then washed with distilled water. This can be very conveniently accomplished by means of a constant level siphon arrangement shown in Fig. 2. This process accomplishes the same results as dialysis so far as purification is concerned, and is much more convenient owing to the fact that smaller volumes are handled. About 5 liters of the crude extract may be concentrated to approximately one-fifth this volume and washed with 1 liter of water. If the extract is then removed from the funnel and diluted to 5 liters and 10 cc. of glacial acetic acid are added, flocculation occurs to the same extent as if the extract had been dialyzed. After standing over night the flocculated material may be filtered off and the enzyme solution returned to the ultra-filter and concentrated to the desired volume. It may then be washed with distilled water to remove any remaining color. It has been found preferable to bring about the flocculation of impurities after a relatively small amount of washing, inasmuch as the filtration after flocculation is much more rapid than before. The rate of filtration of the crude extract through a membrane 6 inches in diameter is usually about 50 to 75 cc. per hour at the start, and gradually decreases to about 20 to 25 cc., owing probably to an increase in the viscosity of the extract. The rate of filtration during washing continues practically unchanged. After flocculation the rate of filtration is about 75 cc. per hour. A given membrane may be used continuously for months and maintains practically the same permeability. When not in use it should be kept covered with water to which some preservative has been added. A 1:2000 solution of chinosol (potassium oxyquinoline sulfonate) is an excellent preservative. If the membrane is to be allowed to stand for some time without use, some of the chinosol solution may be filtered through the membrane to disinfect the apparatus. Even when the apparatus is in continuous use, it is well to wash it out occasionally with pure water to which some of the preservative may be added. Toluene and chloroform are satisfactory preservatives when the filter is not idle for any great length of time.

### Expression of Activity of Enzyme Solutions

The method of expressing the activity of the enzymes invertase and melibiase employed by the writer consists in using as an index the hydrolysis velocity constant $k$ in the unimolecular reaction formula $k = \frac{1}{t} \log \frac{a}{a-x}$, where $t$ is the period of hydrolysis expressed in minutes, $a$ is the total change in degrees polarization during complete hydrolysis, and $x$ is the change in degrees polarization produced in the time $t$. For comparative testing of invertase activity a solution containing 10 grams sucrose per 100 cc. diluted to 110 cc. with the enzyme solution and acidified with glacial acetic acid to a pH value of 4.4 was employed in all cases. Portions of the mixture were removed at appropriate time intervals and made slightly alkaline with sodium carbonate and the optical rotation determined in a saccharimeter. For comparative determination of the activity of melibiase a melibiose solution was used, but since the melibiose available was not always in highly purified form it was found more convenient to prepare a solution to polarize 20.0° V. (2-dm. tube) and use this as a standard. This solution was so prepared by addition of glacial acetic acid or a buffer mixture as to have a pH value of 4.4. To 15 cc. of the melibiose solution were added 1.5 cc. of the enzyme solution. When the hydrolysis was about 50 per cent completed the mixture was made slightly alkaline with sodium carbonate and the polarization obtained. All polariscopic readings were corrected for the optical activity of the enzyme solution. The acidified melibiose solution may be made up in fairly large amounts to polarize 20° V. and kept covered with toluene in a stoppered flask.
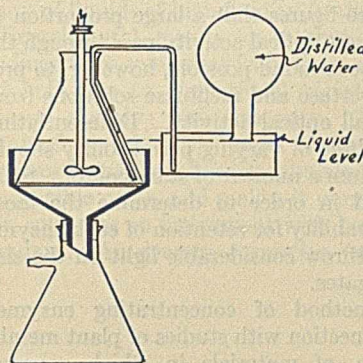


Fig. 2—Apparatus for Concentrating Yeast Extract

### Experimental Results

Ten pounds of bakers' yeast were broken up and mixed with 5 liters of water. Two liters of toluene were added and the mixture was stirred at frequent intervals throughout the first 24 hours. The autolysis was allowed to continue for 7 days. The extract was then filtered by gravity on large fluted filters; 5 liters of filtrate were obtained. The residue was then mixed with 2 liters of water and filtered. The two filtrates were combined. Previous experiments had shown that this second filtrate had approximately half the invertase activity of the first. The activity of the combined filtrate was $k = 0.028$. The 7 liters were transferred to the ultra-filter, concentrated to 1 liter, and washed with 1 liter of distilled water. The concentrated extract was then removed from the ultra-filter, diluted to 7 liters,[5] acidified with 14 cc. of glacial acetic acid, and allowed to stand over night. The next day filtration through paper from the flocculated material was started. Filtration of this material is rather slow, but may proceed continuously by means of an arrangement similar to the continuous washing device shown in Fig. 2. As soon as a sufficient amount of filtrate had been obtained

[5] A certain degree of dilution at this point is required in order to promote rapid flocculation of the separated material. This dilution is in large measure compensated for by the increased rate of ultra-filtration after the flocculated material is removed. Even after diluting 1:7 the volume of liquid is not more than half of that which would be obtained if dialysis were employed.

it was transferred to the ultra-filter and the concentration continued simultaneously with the filtration. The extract was concentrated to a volume of 800 cc. and washed with 2 liters of water. The invertase activity of the final product was $k = 0.22$. This activity is about double that of the standard product in use in this laboratory for the determination of sucrose in low-grade sugarhouse products. Concentration may be continued further, if desired.

Two and one-half gallons of beer yeast were filtered on a large Büchner funnel to remove the wort. Fifty-five hundred grams of compressed yeast were obtained. Upon drying a small portion of this with sand in an oven at 100° to 104° C., it was found to contain 77 per cent moisture. The yeast was placed in a large stoneware jar and 3 liters of toluene were added. After standing a few hours the yeast became liquid. The autolysis was continued for 7 days, the mixture being agitated once or twice each day. The extract was then filtered by gravity on large fluted filters, about 48 hours being required for filtration. Three liters of filtrate were obtained. The residue in the filters was then mixed with 1200 cc. of water, allowed to stand over night, and again filtered. The two extracts were mixed, 4200 cc. of liquid resulting. Two hundred cubic centimeters were kept for reference and the remaining 4 liters purified and concentrated. The 4 liters of crude extract were ultra-filtered until the volume was reduced to 600 to 700 cc. After washing with 1 liter of distilled water the extract was removed from the filter and the volume increased to 4 liters with distilled water; 8 cc. of glacial acetic acid were added. The liquid was allowed to stand over night, filtration through paper being started the next morning. After sufficient filtrate was obtained, ultrafiltration was resumed and proceeded at the rate of 50 to 60 cc. per hour. When the volume of purified extract had been reduced to about 600 cc., washing was started with distilled water and 3 liters of wash water were used. The extract was then removed from the ultra-filter and filtered through paper to remove material which had flocculated during ultra-filtration. Beer yeast extract contains both the enzymes invertase and melibiase. The activity constant for invertase in the crude extract was $k = 0.0818$. In the purified, concentrated preparation the activity was $k = 0.554$. This figure was obtained by diluting the concentrated extract and multiplying the value obtained by the correct factor. The activity constant for the melibiase in the crude extract was $k = 0.00363$, and in the purified, concentrated extract was 0.024. It can be seen by comparing volumes that there was no loss of activity either of invertase or melibiase by the purification or concentration. The activity of invertase and melibiase in the final concentrated bottom yeast extract was sufficient to cause complete hydrolysis of the raffinose in diluted beet molasses in 3 hours at room temperature; this molasses contained 5 per cent raffinose calculated on the basis of total solids. An enzyme preparation of this kind usually contains about 5 per cent solids. The ash contained in 5 cc. when ignited on platinum is not weighable. The total amount of time required for the purification and concentration was 10 days, during which time filtration continued day and night. The amount of time required on the part of the operator, however, was less than 3 hours, as the filtration may proceed without attention after it is started.

### Discussion of Results

It is believed that the methods of purification and concentration here described present a number of advantages for producing enzyme solutions to be used as analytical reagents. This is especially true as regards the stability of the preparation. Complete data as to stability have not yet been obtained, but highly concentrated preparations, clari-

fied by the acetic acid method and concentrated by ultra-filtration, have been preserved for a period of nearly a year at room temperature with only an insignificant loss of activity of either the invertase or melibiase. Ultra-filtration probably results in the concentration in the enzyme solution of a very large proportion, if not practically all, of the emulsoid colloids present in the original yeast extract, and these colloids doubtless have a protective and stabilizing effect on the enzymes (possibly by means of adsorption). It will be noted that only two chemical reagents, toluene and acetic acid, are directly employed during the entire procedure of preparing concentrated enzyme solutions from yeast, and that the process is extremely lenient as regards possible inactivating or destructive action on the enzymes. The degree of concentration of enzymes may doubtless, if desired, be very considerably increased beyond that described above.

When first prepared the solutions are quite clear and colorless in the case of a top yeast extract and of amber color in the case of a bottom yeast extract. Upon standing, a slight opalescence develops. This is not accompanied by loss in activity. In some cases this opalescence may be removed by filtration through paper. In some cases it disappears if the enzyme solution is poured through a funnel with a constricted tip or is allowed to flow out of a pipet. After this treatment the opalescence gradually disappears and is entirely gone in an hour, returning in 2 or 3 days. The explanation of this apparently colloidal phenomenon is not known; it occurs only in solutions which have been subjected to long-continued washing on the ultra-filter. This opalescence, however, is not objectionable when the solution is used in analytical work, as it is too faint to interfere with polarization. The opalescence may be removed from the solution in all cases

by filtering with a small amount of infusorial earth. This treatment results, however, in appreciable loss of activity.

Ultra-filtration is superior to low temperature evaporation as a means of concentrating enzymes because of the fact that a great many of the impurities in the enzyme solution pass through the filter and are not concentrated. Optically active substances present an example. In one experiment the original stock invertase solution gave a polariscopic reading of 1.05° V.; the ultra-filtrate gave a reading of 0.58° V. It will be seen from these figures that a large proportion of the substances which possess optical activity pass through the membrane. It has not been found possible, however, to produce by this method invertase and melibiase solutions from yeast which are free of all optical activity. Differentiating experiments with ultra-filters of varying permeability should yield interesting results from a number of standpoints. Such experiments are required in order to determine the most suitable membrane permeability for retention of each enzyme studied, and would also throw considerable light on the size of various enzyme aggregates.

The ultra-filtration method of concentrating enzymes should be of value in connection with studies of plant metabolism and translocation of materials in which aqueous extracts of plant portions are tested for enzyme action against various substrates. The literature of this subject is frequently contradictory and the enzymic effects often indecisive. Perhaps this may be largely due to the low concentration of enzymes in the extracts studied. The enzymes in such extracts could be readily concentrated by ultra-filtration prior to testing against substrata without the loss of activity which might result from such concentration methods as precipitation by alcohol, low temperature evaporation, etc.

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# A Reliable Plant Viscometer[1]

## By Martin Marasco

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THE principle involved in this viscometer is undoubtedly quite old, but this particular form of instrument has given such satisfactory service in measuring the viscosity of liquids in plant operations that others will doubtless be interested. It consists simply of a rubber bulb, a rubber stopper, and a piece of glass tubing assembled as shown in the accompanying sketch. The material of construction may be varied to suit different cases; probably a metal bulb with metal capillary tube would be more suitable for lubricating oils and other liquids which are harmful to rubber. The apparatus is dropped into the liquid whose viscosity is to be measured and the time required for submersion is a measure of the viscosity.

The following advantages have been observed:

(1) The capillary is down in the liquid whose viscosity is being tested.
(2) Only ordinary skill is required to use it correctly.
(3) It is practically unbreakable.
(4) A high degree of sensitivity can be obtained by selecting glass or metal tubing of suitable bore.
(5) It is applicable to opaque solutions.
(6) It is inexpensive and always replaceable—extra viscometers, including a standard, can be kept just as readily as thermometers.
(7) It is easily cleaned.

The time in seconds required for submersion using this viscometer can be converted to centipoises by a linear equation, $V = at - b$, where $V =$ viscosity in centipoises,

$t =$ time in seconds, and $a$ and $b =$ constants obtained by calibration against liquids of known viscosity. Since the force tending to submerge the viscometer is a function of the weight and specific gravity of the instrument and also of the specific gravity of the liquid being tested, a specific gravity–time correction curve must be made if it is desired to use the viscometer for a variety of liquids differing in specific gravity. This curve can be determined when necessary by calibration of the apparatus with three or four liquids of different specific gravities but the same viscosity. For example, a heavy mineral oil was diluted with benzene until it tested 35 seconds per 100 revolutions (approximately 30 centipoises) by a Stormer viscometer, and its specific gravity at this viscosity was found to be 0.91; a gelatin solution of somewhat higher viscosity was diluted with water and the temperature altered until it gave a reading of 35 seconds per 100 revolutions on the Stormer at 39° C.; the specific gravity was 1.03 (the viscosity of gelatin solutions reaches a point of equilibrium very quickly at temperatures above 38° C., hence it is advisable to work at temperatures above 38° C.); glycerol diluted with water tested 35 seconds per 100 revolutions at 26.5° C.; the specific gravity was 1.19.
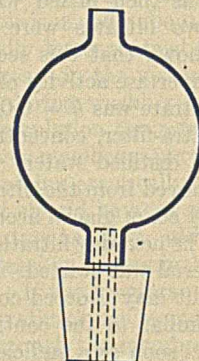
The proper dimensions of the parts in order to obtain an apparatus of the desired degree of sensitiveness are readily determined by trial. The satisfactory viscometer is then designated standard and used in calibrating any number of similar instruments. A viscometer consisting of a 65-cc. bulb, a 3.5-cm. glass tube with a 3 mm. bore, and a No. 5 rubber stopper is sensitive to 0.2 centipoise for liquids of 10 to 30 centipoises viscosity and 0.9 to 1.1 specific gravity. A capillary tube of 0.06-mm. bore is suitable for measuring the viscosity of liquids of high fluidity (water, ether, etc.).

Experimental results show that for extra bulbs whose readings vary somewhat from those obtained with the standard bulb due to dimensional variations, the correction increases slightly with viscosity. An average correction, obtained by taking the mean of the correction over a range of viscosity, as the following tabulated results show, gives only a negligible error, and makes it unnecessary to use a correction curve for an instrument with but slight departures from standard. An average correction (see table) should usually

be sufficient for readings with Viscometers 1 and 2, but 3, 4, and 5 probably require the use of a correction curve in order to obtain a suitable correction. With proper care, dimensional variations can be made very small and this correction eliminated entirely.

CORRECTIONS FOR RUBBER BULB VISCOMETERS DUE TO DIMENSIONAL VARIATIONS

| Viscometer No. | Correction Additive in Seconds | | | | Average Correction |
|---|---|---|---|---|---|
| | 70 | 80 | 100 | 120 | |
| Standard | 0 | 0 | 0 | 0 | 0 |
| 1 | −1.4 | −1.6 | −2.8 | −3.8 | −2.4 |
| 2 | −1.2 | −0.9 | −1.8 | −1.8 | −1.7 |
| 3 | +6.6 | +7.3 | +7.7 | +11.1 | +8.2 |
| 4 | +9.6 | +12.4 | +13.5 | +16.6 | +13.0 |
| 5 | +12.8 | +15.8 | +18.2 | +21.2 | +17.0 |

### ACKNOWLEDGMENT

# Some Factors Affecting the Growth of Crops on Acid Soils[1]

By S. D. Conner

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*The Hopkins potassium nitrate acidity is believed to be largely mineral. The Jones calcium acetate acidity is total acidity.*

*The formula $K = H^2/J\text{-}H$, which is the square of the mineral acidity divided by the organic acidity, gives an index which appears to be a better indication of the lime needs of both organic and inorganic soils than any single method can give.*

*The toxicity of soil acidity may be due to both aluminium ions and hydrogen ions. Some crops, corn and radishes, are more sensitive to aluminium ions than to hydrogen ion; others, red clover and beets, are more sensitive to hydrogen ions than to aluminium ions. Both phosphates and lime are needed to correct the toxicity of aluminium and hydrogen ions in most acid soils.*

PROBABLY more than half of the soils of humid regions are acid. As soil itself is composed of an exceedingly variable mixture of different materials, it is obvious that the condition known as soil acidity should be variable and complex. Soil acidity has been studied by a large number of investigators and the problem attacked from many angles. It has been found that different soils vary, not only in the kind and degree of the acidity due to the different kinds of materials they are composed of, but that individual soils vary in their acidity from time to time. The number of methods for estimating soil acidity is almost as great as the number of investigators. Some investigators, not being satisfied with one method, have proposed several. As none have had time to investigate completely this most complex material called soil, they are somewhat in the position of the "six blind men of Hindustan" who came to see the elephant—they do not always agree.

At the Purdue Experiment Station the study of acid soils has been going on for about twenty years and over ten thousand samples of soils for acidity have been tested. Many field plot, greenhouse pot tests and laboratory investigations have been made. Yet almost every week puzzling cases of soil acidity come to notice.

When it was first discovered that certain soils were acid and that an application of lime sometimes increased crops, the conclusion was drawn that all soil acidity was injurious to all crops and that enough lime should be applied to neutralize all the acidity. This idea was soon found to be erroneous. In fact, large applications of lime often prove

harmful. Experiments indicate that most of our agricultural plants make optimum growth with a slight degree of acidity. It is a well-known fact that plants vary in the degree of acidity at which they grow best, but it is not so well known that some plants are injured more by one kind of acidity, while other plants are affected by a different kind of acidity.

Practically all soils contain an excess of silica. Silica when free and uncombined with water is insoluble and inactive as an acid; but it is potentially acid, and under humid conditions tends to form chemically active, acid-reacting silicates of aluminium, iron, and manganese. Under some conditions of decay the organic matter of plants takes on an acid character. When there is sufficient calcium and magnesium in the soil to take care of the organic acids and the active mineral acids, the soil is neutral. Because calcium and magnesium are quite soluble and soon leach, humid soils tend to become acid.

Among the early methods for estimating soil acidity, the capacity of the soil to neutralize calcium hydroxide or calcium carbonate was determined. This type of method measured the total quantity of acids, both organic and inorganic. Later, methods depending upon the action of a salt of a strong acid and a strong base, such as potassium nitrate, were used. This type of method, according to the writer's experiments, measured the inorganic acid silicates, but did not react to any great extent with organic acids. Many controversies have arisen between the advocates of these two classes of methods. At a rather recent date some soil chemists have claimed that the intensity of the acid as measured by the hydrogen-ion concentration was the only true method of determining the lime needs of an acid soil.

As a matter of fact, there are acid soils which may be accurately tested by each of these classes of methods and not by either of the others. If a long experience in testing soils has been checked by field tests, it is possible for an investigator to interpret quite accurately either kind of method. Without experience many mistakes are sure to be made. At present in the Purdue Station the soil acidity is determined by all three methods, because it is necessary to get an estimate of the three general classes of acidity which may be found in soils.

Kappen[2] has called the three forms of acidity "free or active acidity" (measured by the hydrogen-ion concentration); the "exchange acidity" (measured by the action of a strong acid salt such as potassium nitrate); and the "hydrolytic acidity," which may be estimated by subtracting the exchange acidity from the total acidity (determined by limewater, calcium acetate, and similar methods). Kappen classes the so-called humus acids with the hydrolytic acids. According to him, hydrolytic acidity is not injurious to plants. Exchange acidity is thought to be injurious because it allows both hydrogen ions and aluminium ions to be developed in the soil moisture, each of which may be toxic to plant growth.

Organic acidity is not only of extremely slight toxicity, but the organic matter which accompanies it seems to have some action in reducing the toxicity of the more active acidity. Given two soils of equal exchange acidity, the soil with the greater organic acidity is the least in need of lime.[3]

The Hopkins soil acidity method measures the exchange acidity, which seems to be largely mineral. The Jones calcium acetate method measures the total acidity—exchange plus hydrolytic acidity or mineral plus organic acidity. There is little inorganic hydrolytic acidity in Indiana soils. If the Hopkins acidity is subtracted from the Jones acidity we have a close approximation of the organic acidity. By using the formula $K = H^2/J-H$, an index is obtained which in the experience of the writer is a very good indication of the lime needs of crops in either inorganic or organic acid soils. This is the only method which has worked without exception on both dark and light-colored Indiana soils which have had their lime requirements determined by means of crop tests. This formula, which is regarded as approximately the square of the mineral acidity divided by the organic acidity, is based upon the same principles involved in Ostwald's dilution formula which is used to determine the strength of acids. The value of this formula lies in the fact that it would enable an inexperienced analyst to determine in the laboratory whether a soil needed lime or not; a $K$ value of over 25 would indicate a lack of lime for alfalfa, $K$ 100 or over would indicate that all grain crops needed lime.

## Aluminium Ions and Hydrogen Ions

During the last ten years soluble aluminium compounds have been considered, by many workers, important toxic agents in acid soils. The aluminium salts found in the soil moisture are highly hydrolyzed, giving rise to both hydrogen ions and aluminium ions. Both kinds of ions have been shown by several investigators[4] to reduce plant growth in water cultures. With some plants the injury seems to be due to the aluminium more than to the hydrogen ion.

Gile,[5] in a recent paper in which toxicity is discussed, is of the opinion that the evidence on the toxicity of aluminium is not conclusive. Gile's argument is that the injury caused by aluminium salts might be due to its action in producing a

phosphorus deficiency. If aluminium did act in this way to reduce plant growth, it should be considered toxic just as much as if it killed the plant by coagulating protoplasm in the cells or in any other manner. While it is true that aluminium toxicity may be corrected by the application of phosphates, it makes no particular difference whether an excess of phosphorus corrects the toxicity of the aluminium ions or whether an excess of aluminium ions causes phosphorus starvation.

Hoffer and Carr[6] injected 30 cc. 0.1 $N$ sulfuric acid into cornstalks without injury. An injection of 5 cc. of 0.08 $N$ aluminium nitrate caused very serious injury. If the injury caused by the aluminium salt was due to the hydrogen ions, it would seem that the vastly greater acidity of the sulfuric acid would have caused injury. Two-tenths normal sulfuric acid was sufficient to kill corn. Aluminium chloride caused injury while hydrochloric acid did not.

## Experimental

In some pot experiments with different crops on a dark, acid, loamy, fine sand soil, it was found that large applications of monocalcium phosphate, while increasing the hydrogen-ion concentration of the soil, were beneficial to corn, while applications of lime alone which almost neutralized the acidity were of no value in growing corn. To study the relative value of some acid soil treatments with various crops, other pot tests were started.

TABLE I—Pot Tests on Acid, Dark, Loamy, Fine Sand
(Yields of corn, wheat, and clover in grams per pot)

| TREATMENT PER 2,000,000 POUNDS SOIL | Corn | Wheat | Red Clover | pH of Soil |
|---|---|---|---|---|
| Untreated | 30 | 5 | 0 | 5.0 |
| Monocalcium phosphate, 4 tons | 122 | 48 | 14 | 5.3 |
| Dicalcium silicate, 4 tons | 82 | 64 | 35 | 6.1 |
| Calcium carbonate, 4 tons | 64 | 58 | 38 | 6.2 |
| Calcium carbonate, 4 tons } Monocalcium phosphate, 500 pounds } | 128 | 58 | 45 | 6.2 |

Table I gives the results obtained with corn, wheat, and red clover. The beneficial action of the monocalcium phosphate, which did not reduce the hydrogen-ion concentration more than slightly (in a previous test it slightly increased the H-ion concentration), is attributed to its action in correcting the toxicity of the aluminium ions naturally present in the soil moisture. Its beneficial action could hardly be attributed to a reduction of hydrogen-ion concentration. While the action of the calcium carbonate could be explained by a reduction of H ions, it might be partly due to its action on aluminium. The benefit caused by dicalcium silicate is appreciably greater than that of the calcium carbonate. Dicalcium silicate seems to have an almost equal action in correcting acidity and a somewhat greater action in precipitating aluminium than calcium carbonate.

The results shown in Table I indicate that clover is more affected by hydrogen ions than corn, and that corn is more affected by aluminium ions than clover. The treatment which has proved most profitable on this soil in the field is 4 tons of limestone plus 0.5 ton acid phosphate. Three hundred pounds acid phosphate gave little increase on corn when used in addition to lime. Without the phosphate the lime alone failed in the field.

TABLE II—Pot Tests on Acid, Black, Sandy Soils
(Yields in grams per pot of various crops)

| TREATMENT | Corn 3 Tests | Radishes | Rye | Barley | Oats | Wheat 2 Tests | Red Beets 3 Tests | Buckwheat 2 Tests | Red Clover |
|---|---|---|---|---|---|---|---|---|---|
| Untreated | 14 | 1 | 2 | 1 | 1 | 4 | 0 | 1 | 0 |
| Monocalcium phosphate, 4 tons | 52 | 77 | 18 | 14 | 26 | 34 | 31 | 6 | 14 |
| Calcium carbonate, 4 tons | 24 | 29 | 2 | 6 | 24 | 35 | 82 | 23 | 38 |

[2] Landw. Vers.-Sta., 96, 277 (1920).
[3] Conner, "Inorganic and Organic Compounds in Relation to Soil Acidity," Proc. Agricultural Lime Conference, Knoxville, Tenn., 1922.
[4] Conner and Sears, Soil Science, 13, 23 (1922).
[5] J. Am. Soc. Agron., 15, 305 (1923).
[6] J. Agr. Research, 23, 801 (1923).

Table II gives results comparing the action of monocalcium phosphate with that of calcium carbonate on nine different crops. Corn, radishes, rye, and barley seem to be more affected by aluminium toxicity than by hydrogen-ion toxicity. Wheat and oats are affected by both, while red beets, buckwheat, and red clover seem to be affected by hydrogen ions more than by aluminium ions. These results were obtained in three tests on corn, three on red beets, two on buckwheat, and two on wheat—all in duplicate pots. It is obvious that an investigation of soil acidity should include a study of the response of different crops as well as of different types of soils. The soil used in these pot tests contains a large amount of active (soluble) acidity, much exchange acidity, and much hydrolytic acidity (organic).

Just how phosphorus prevents aluminium toxicity is not definitely known. Analyses of corn plants grown on six acid soils were made by Hoffer and Trost.[7] The average of the analyses showed 0.37 per cent aluminium oxide in the corn on untreated soils, 0.27 per cent on soils treated with 3 tons of lime, and 0.23 per cent on soils treated with 500 pounds of acid phosphate. It would appear that phosphate might act partly in preventing the intake of aluminium and partly in correcting its toxicity within the plant.

It is a well-known fact that acid soils need phosphate as well as lime. Undoubtedly, much of the benefit due to phosphate on such soils is to help correct aluminium toxicity. No doubt there are acid soils which may at times be unproductive on account of iron or manganese compounds, but it is thought that in the majority of soils aluminium is more prevalent as a toxic agent in connection with the hydrogen-ion toxicity.

[7] *J. Am. Soc. Agron.*, **15**, 323 (1923).

# A Special Slide Rule for Apparent Purity Calculations[1]

### By H. J. Bastone

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THE laboratory of the sugarhouse is liable to be overrun by the drudgery of common-place work unless every means is utilized to simplify and systematize the testing of the numerous samples which are received daily. Tests of the apparent purities of the various liquors, sirups, and magmas in process are a heavy burden on the laboratory and at the same time are exceedingly important and necessary to the refiner. Anything, therefore, which speeds up the determination of such tests not only increases the efficiency of the laboratory, but makes the work much more valuable to the refiner.

Among the various improvements used in this laboratory is a special slide rule for purity calculations which eliminates the use of factor tables. The rule is of the 20-inch Mannheim type with two scales placed in proper logarithmic relation to each other. Inasmuch as polarity and purity are percentage figures, it is obvious that one scale should answer for both. A second scale is constructed based on the logs of the Brix factors, and both scales are made to read in direct percentage and Brix numbers, respectively. The polarity and purity scale is mounted on the movable part of the rule and

is the ordinary *A* scale of the Mannheim rule with the main divisions renumbered to read from 0.8° to 100°, with subdivisions ranging from 0.01° at the lower end to 0.5° at the upper end of the scale. The Brix, or fixed scale, reads from 0.2° to 23.7°, with subdivisions of 0.1°. This gives the density range required for any apparent purity determination and covers all grades of materials.

To operate the rule one arranges the movable part so that the division thereon corresponding to a given polarization coincides with its proper Brix division on the fixed scale. Thus the required purity is shown directly on the movable scale by an indicating arrow which is at the right of the fixed scale.

The slide rule is compactly housed in a polished mahogany box and is operated by an extension bar projecting through the right-hand end of the box. The scale is covered with glass, making the whole unit dust and dirt proof. The outfit is arranged to mount on a table and its sturdy construction permits constant use.

The slide rule may be operated by a school boy without difficulty; it takes up little space; it eliminates charts and factor tables; it saves time, and gives accurate results. In short, the apparatus is thought to be the simplest and most complete yet devised for apparent purity calculations.
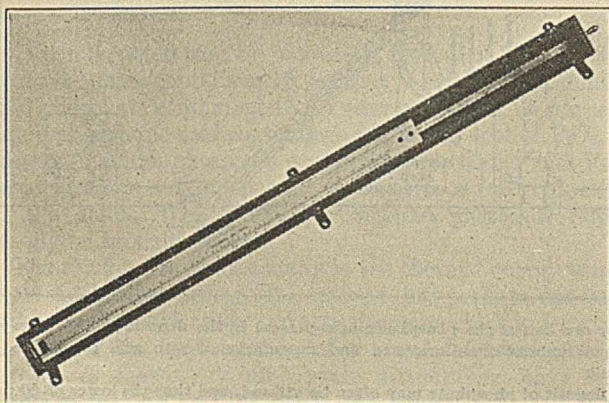


FIG. 1—SPECIAL SLIDE RULE FOR APPARENT PURITY CALCULATIONS AS MOUNTED READY FOR USE
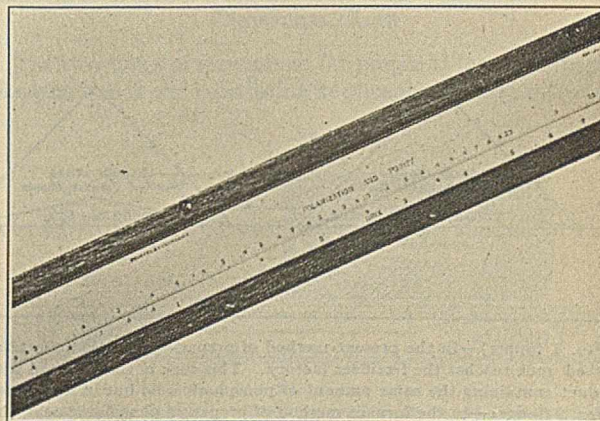


FIG. 2—SCALE OF THE SPECIAL SLIDE RULE FOR APPARENT PURITY CALCULATIONS

# Manufacture of Phosphoric Acid by the Volatilization Process[1]

## Some Technical Problems

### By Wm. H. Waggaman

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*The production of phosphoric acid by the volatilization method has distinct advantages over the sulfuric acid method—(1) low-grade phosphates can be used, (2) costly filtration and evaporation are obviated by using the Cottrell method of precipitation, and (3) the cost of the thermal energy required should be less than the cost of chemical reagents necessary to effect the same results.*

*The fuel furnace has been shown to cause volatilization as efficient as the electric furnace, although radiation and heat losses are considerably less in the electric smelting. Such losses, however, can be considerably reduced.*

*The question of what temperature is best adapted for the volatil-*

*ization, especially in the fuel furnace, is still only partially answered, since it is dependent upon other factors, such as the lime-silica ratio in the charge, the fineness of division and intimate contact of the reacting materials, the amount of reducing agent present, the time factor, and the type of furnace used. The first of these factors is equally important in both electric and fuel smelting.*

*Another important problem of commercial importance studied at this laboratory is the determination of the proper $P_2O_5$ content of the residual slag for the most economic operation. There are a number of others which also offer fields for valuable research.*

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THE volatilization method of producing phosphoric acid is now an assured commercial success where relatively pure acid and high-grade phosphate products are desired. This method, however, has not become a factor in producing phosphates for fertilizer purposes, but with increased efficiency and a better utilization of the heat units generated by the reactions involved there is little question in the mind of the writer that the process will eventually play an important role in the fertilizer industry. At least one commercial concern in this country is producing phosphoric acid by this general method on quite an extensive scale, and while ferrophosphorus was at first the main product of

[1] Presented before the Division of Fertilizer Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

this company the phosphoric acid output has now become a factor of prime consideration.

### THEORETICAL CONSIDERATIONS

From a strictly theoretical standpoint the production of phosphoric acid by the volatilization method, using either fuel or electric power as a source of thermal energy, has three distinct advantages over the sulfuric acid method:

(1) It makes possible the use of low-grade and run-of-mine phosphates generally considered unfit for treatment with sulfuric acid.

(2) By using the Cottrell method of precipitation to collect the volatilized phosphoric acid, a concentrated product is obtained directly without involving costly filtration and evaporation steps.

(3) The quantity of electric energy or fuel theoretically required should be an item of expense appreciably less than the cost



FIG. 1 (upper)—In the present method of preparing phosphatic fertilizers, only one-half of the phosphoric acid present in the deposit in the form of washed rock reaches the fertilizer factory. This rock is then treated with an equal amount of sulfuric acid and manufactured into acid phosphate, a product containing the same amount of phosphoric acid but in fully twice the bulk

FIG. 2 (lower)—In the furnace method of preparing phosphoric acid, the entire deposit of phosphate may often be utilized, and thus the losses of 50 per cent entailed in washing or purifying the rock eliminated. Assuming a 90 per cent efficiency in the furnace plant, the final product is a liquid containing nearly twice as much phosphoric acid ($P_2O_5$) as acid phosphate in a little more than one half the weight. This acid may be manufactured into a number of concentrated products suitable for fertilizer use

TABLE I—THEORETICAL HEAT BALANCE OF ELECTRIC FURNACE OF SIMPLE CRUCIBLE TYPE
(Capacity 10 tons P$_2$O$_5$ per day of 24 hours)

| Item | ACTIONS AFFECTING TEMPERATURE | HEAT GENERATED (Plus) | | HEAT CONSUMED (Minus) | |
|---|---|---|---|---|---|
| | | Thousands of Kg. Calories per Ton[d] of P$_2$O$_5$ | Per cent of Total | Thousands of Kg. Calories per Ton[d] of P$_2$O$_5$ | Per cent of Total |
| 1 | Absorbed by burden before fusion[a] | ... | ... | ... | ... |
| 2 | Absorbed by burden in fusing[a] | ... | ... | ... | ... |
| 3 | Absorbed by endothermic reactions | ... | ... | 4100 | 36.1 |
| 4 | Evolved by exothermic reactions | 420 | 3.7 | .. | .. |
| 5 | Evolved by oxidation of C to CO | 1140 | 10.0 | ... | ... |
| 6 | Evolved by oxidation of this CO to CO$_2$ | 2660 | 23.4 | ... | ... |
| 7 | Evolved by oxidation of P to P$_2$O$_5$ | 2850 | 25.0 | ... | ... |
| 8 | Removal of heat by cooling masonry | ... | ... | 1619 | 14.2 |
| 9 | Removal of heat by slag[b] | ... | ... | 1707 | 15.0 |
| 10 | Removal of heat by evolved gases (at 650° C.) | ... | ... | 2350 | 20.6 |
| 11 | Removal of heat by unburned CO[c] | ... | ... | 1600 | 14.1 |
| 12 | Heat supplied by electric energy | 4306[e] | 37.9 | ... | ... |
| 13 | TOTAL | 11,376 | 100.0 | 11,376 | 100.0 |
| 14 | Economy[f]   Pounds P$_2$O$_5$ per kilowatt hour | 0.44 | | | |
| | 2000 pounds P$_2$O$_5$ per kilowatt year | 1.90 | | | |
| | 2000 pounds P$_2$O$_5$ per horsepower year | 1.43 | | | |
| | Over-all thermal efficiency, per cent | 36.10 | | | |

[a] Included in Item 9.      [d] Metric ton.
[b] Including small amount removed by ferrophosphorus.      [e] 5010 kilowatt-hour.
[c] Assuming one-third of Co unburned in furnace.      [f] Production based on 90 per cent recovery of P$_2$O$_5$ in furnace charge.

of the sulfuric acid necessary to convert an equivalent amount of phosphate rock into an available form.

The first point may be illustrated in the following sketches, which compare the yield of phosphoric acid (in the form of acid phosphate) actually obtained from a given quantity of run-of-mine phosphate with that which may be recovered where this same quantity of run-of-mine material is treated directly in an electric or fuel furnace. Since in many cases the washing of phosphate rock may be dispensed with where the latter process is employed, the losses of valuable phosphate thus entailed are largely eliminated and a much fuller utilization of phosphate deposits is thus effected.

The second point, the saving in handling and transportation charges which may be brought about where a relatively concentrated product is obtained, is illustrated in the following sketches, drawn to scale, which show the amount of car space occupied by equivalent quantities of phosphoric acid in several types of finished products.
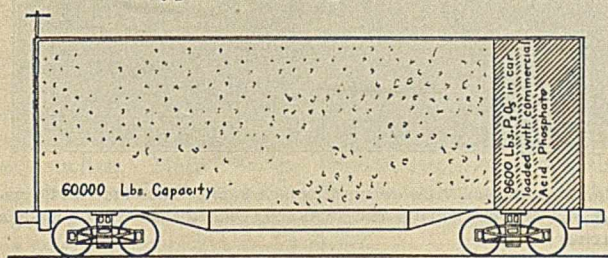


FIG. 3

A car loaded to capacity (60,000 pounds) with 16 per cent acid phosphate (standard phosphate fertilizer of today) contains only 9600 pounds of actual phosphoric acid (P$_2$O$_5$). Yet transportation and handling charges must also be paid on 84 per cent of gypsum and other impurities contained in this product.

It will be noted that by producing, instead of the ordinary acid phosphate containing 16 per cent of soluble P$_2$O$_5$, double acid phosphate containing 45 per cent of P$_2$O$_5$, or 75 per cent liquid phosphoric acid containing over 50 per cent of P$_2$O$_5$, or monoammonium phosphate containing over 60 per cent P$_2$O$_5$ besides an appreciable amount of nitrogen, a great reduction in the annual freight bills for fertilizer materials might readily be brought about.

The third point, the economy in the thermal energy where the volatilization process is employed, has perhaps not been given the thorough study and consideration which it deserves. In Table I the heat balance of a simple electric crucible furnace is shown. While certain assumptions have been made in making up this table, the figures are considered conservative as far as they show the relative quantities of heat generated and heat consumed in a furnace of this type.

The various items are based on the assumption that the furnace has a capacity of 10 tons of P$_2$O$_5$ per day, that sufficient coke is present in the charge to reduce completely the phosphoric acid to elemental phosphorus, and that the ratio of silica to lime is approximately the same as that in calcium metasilicate (CaSiO$_3$). Under these conditions the over-all furnace reactions are exothermic; in other words, if no sensible heat were lost in the evolved gases, in unburned carbon monoxide, by radiation through the walls of the furnace and in the slag which is tapped off, the reaction when started should go to an end without power consumption.

It is impossible, of course, to eliminate entirely any of these losses, and some of them can only be partially reduced. The heat units contained in the slag tapped off are almost entirely wasted and certain loss of heat by radiation through the walls of the furnace is unavoidable, although by the use of the highest grade refractories it might be considerably lowered. Items 10 and 11 in this table, however—namely, the removal of heat by evolved gases and by unburned carbon monoxide—could be cut down very greatly if proper regenerative apparatus were employed, and it will be noted that the sum of these two items is 34.7 per cent of the total heat consumed, and only 3.2 per cent below the quantity of thermal energy supplied to a furnace of this type by electric power. Therefore, with proper equipment designed to conserve a large amount of this avoidable loss of heat, it seems quite possible that the electric energy required for the pyrolytic process might be reduced to a point where its cost would be less than that of the sulfuric acid required for rendering an equivalent quantity of phosphate rock available.

## ELECTRIC vs. FUEL FURNACE FOR THE VOLATILIZATION OF PHOSPHORIC ACID

The two types of furnaces so far proposed for decomposing phosphate rock and volatilizing its phosphoric acid content are
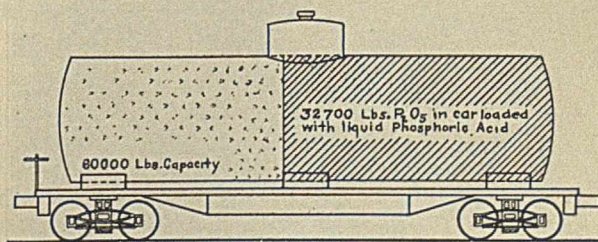


FIG. 4

A car loaded to capacity (60,000 pounds) with liquid phosphoric acid (75 per cent H$_3$PO$_4$) manufactured by the pyrolytic or furnace process contains 32,700 pounds of actual P$_2$O$_5$, or nearly three and one-half times as much as that in a car of acid phosphate.

the electric arc furnace and a modification of the blast or open-hearth furnace. The first type is the only one which has yet been applied in a commercial way, but whichever is used the process is based on the same fundamental principles. The main function which the electric arc furnace performs is to furnish high temperatures in a localized zone, and it permits the maintenance of strictly reducing conditions during the smelting operation. It has been conclusively demonstrated that where similar temperatures and reducing conditions are obtained in a furnace heated by fuel a volatilization of phosphoric acid fully as efficient as that obtained in the arc furnace can be brought about.
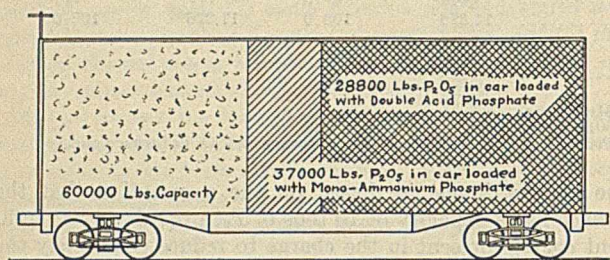


FIG. 5

A car loaded to capacity (60,000 pounds) with either double acid phosphate or monoammonium phosphate contains from 28,800 pounds to 37,000 pounds of actual $P_2O_5$, or from three to four times as much as that in a car of acid phosphate. By shipping phosphoric acid ($P_2O_5$) in these concentrated forms an annual saving of from $8,000,000 to $9,000,000 in freight charges alone might be eventually affected on this fertilizer ingredient.

Each method, however, has its own chemical and mechanical problems. In electrical smelting, where oxidation is not depended upon to generate the necessary heat, the highest temperature is confined to a relatively narrow zone, and since only a minimum amount of air is introduced, few gases are generated except from the constituents in the charge. It is readily seen, therefore, that radiation and heat losses in evolved gases are considerably less than in smelting by means of fuel, where the introduction of air is necessary to burn the fuel and furnish the high temperature required. In the latter case large volumes of nitrogen, water vapor, carbon monoxide, and carbon dioxide are produced, which carry in latent and sensible form an immense amount of thermal energy, which must be extracted in order to obtain an efficiency approximating that obtained in the electric furnace. Fortunately, modern furnace practice has given to us recuperative and regenerative apparatus which has proved highly effective in recovering the heat evolved in
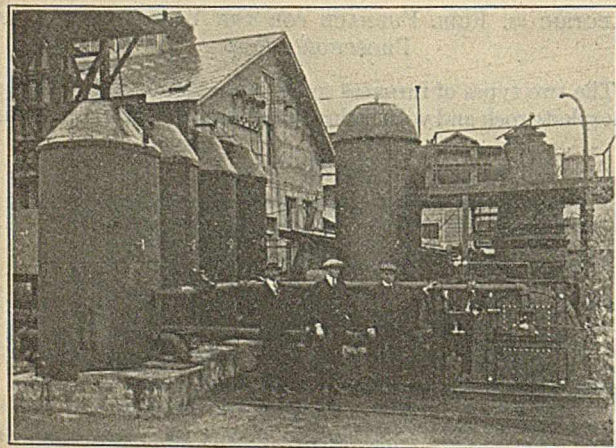
fuel smelting, and therefore it seems that much of this energy may be utilized.

It would appear that one of the first and most important problems to be solved in connection with the pyrolytic process is the determination of the temperature best adapted to bring about the volatilization of phosphoric acid from mixtures of phosphate rock, silica, and carbon, but, while much work has been done along this line, considerable doubt still exists regarding the minimum temperature required. The reason for this is that the temperature necessary for complete volatilization is dependent on a number of other factors, such as the lime-silica ratio in the charge, the fineness of division and intimate contact of the reacting materials, the quantity of carbon or reducing agent present, the time factor, and the type of furnace employed. Probably this problem is more strictly applicable to the fuel furnace than to the electric arc furnace, since in the latter type it is hardly possible to work at anything below a smelting temperature.

Nielsen,[2] Peacock,[3] and Guernsey and Yee[4] all state that phosphorus or phosphoric acid can be evolved either completely or in part from mixtures of phosphate rock, silica, and carbon at temperatures ranging from 1150° to 1350° C. The writer and his co-workers have found in both laboratory and large-scale experiments that a partial evolution of $P_2O_5$ is obtained from briquetted mixtures of phosphate rock, silica,
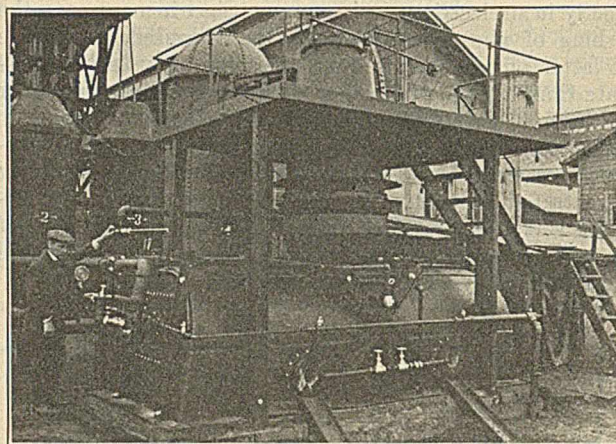


FIG. 7—A CLOSER VIEW OF THE FURNACE PROPER SHOWING THE EQUIPMENT FOR WATER-COOLING THE FURNACE, OIL BURNERS, AND CINDER NOTCHES

and coke at temperatures appreciably lower than the fusing points of such mixtures, and considerably below the temperatures attained in the arc furnace; but in no case where such briquetted charges were exposed directly to the flame did complete evolution of the $P_2O_5$ take place until the temperature was raised sufficiently high (1500° to 1600° C.) to reduce the mass to a fluid slag.

Whether or not it is commercially practicable to drive off the greater part of the $P_2O_5$ from such mixtures at temperatures below their fusing points under the conditions existing in direct fired furnaces or kilns yet remains to be proved, but if this can be accomplished without unduly prolonging the time factor, it may simplify the furnace design and materially reduce the cost of production.

The writer's experience has been that, in order to bring about the nearly complete volatilization of $P_2O_5$ from briquetted charges of phosphate rock, silica, and coke, and at the same time insure the working conditions necessary to make such a process continuous, a very fluid slag must be



FIG. 6—GENERAL VIEW OF SMALL OIL BURNING FURNACE FOR THE VOLATILIZATION OF PHOSPHORIC ACID. ARLINGTON, VA.

[2] *Ferrum*, **10**, 97 (1913).
[3] *Am. Fertilizer*, **39**, 63 (1913).
[4] U. S. Patent 1,422,699 (1922).
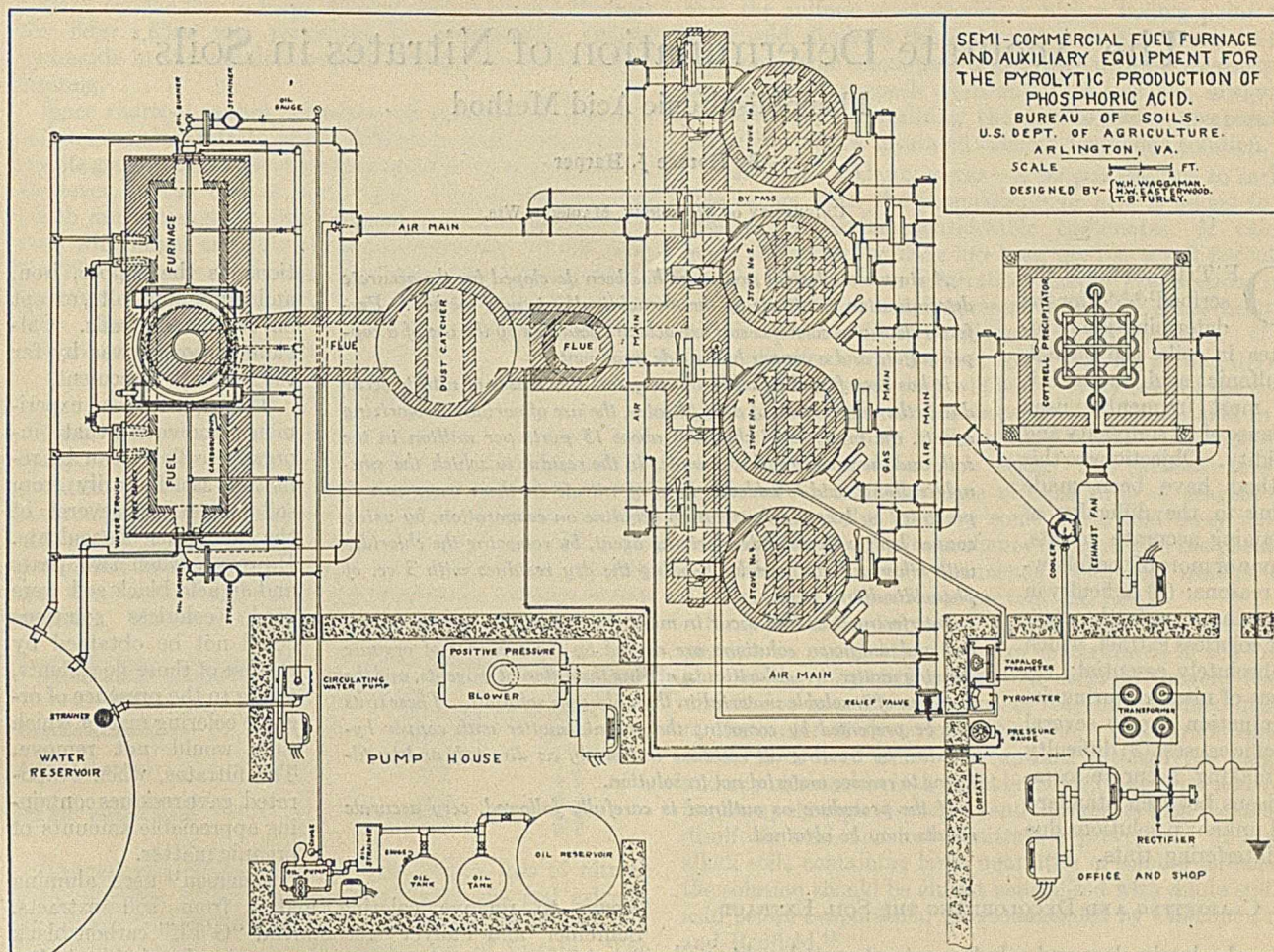
FIG. 8

produced, for even under reducing conditions a viscous acid slag tends to retain or hold the phosphorus either in solution or in chemical combination, whereas this element may be readily boiled out of such a slag when it becomes very molten. Moreover, the successful operation of either the open-hearth or blast furnace depends upon the production of a slag which will flow freely from the tap holes when the smelting operation is completed.

In Figs. 6 and 7 are shown views of the small oil-burning furnace and its auxiliary equipment at Arlington Farm, Va., where experiments on a semicommercial scale are being conducted, and in Fig. 8 a plan view of the entire plant is shown.

The determination of the silica-lime ratio in the phosphate charge best adapted to the rapid volatilization of $P_2O_5$ is a problem equally important in both electric and fuel smelting. The writer and his co-workers have conducted a number of experiments with a view to determining the mixtures which will give a rapid evolution of phosphorus and yet yield a slag sufficiently fluid to admit of its being readily tapped from the furnace.

The details of these experiments will be published shortly in a bulletin of the U. S. Department of Agriculture. In a general way, however, it was found that at a definite temperature (1600° C.) the more acid slags give up their $P_2O_5$ content the quickest, but when the ratio of silica to lime in the mixtures is increased beyond 61 : 39 the melting point of the resultant slags increases to such an extent as to introduce serious difficulties in the tapping operation. Furthermore, these more acid mixtures involve the addition of so much silica that the phosphate content of the mass is considerably

diluted, so that any advantage gained in the more rapid evolution of phosphorus is largely offset by the greater bulk of relatively valueless material which must be raised to a smelting temperature.

This brings up another important point which is of considerable commercial importance—namely, how low the $P_2O_5$ content of the residual slag should be reduced for the most economic furnace operation.

While it has been proved beyond question that the $P_2O_5$ can be eliminated almost entirely from the slag either in the electric or fuel-fired furnace, the recorded data showing what proportion of the total heat energy is required to drive off the last few per cent of this acid are as yet rather incomplete. Obviously, it would be poor economy to consume large amounts of power or fuel for the sake of freeing the slag entirely from $P_2O_5$, when the bulk of it may be driven off with considerable rapidity.

### OTHER PROBLEMS

There are a number of other important problems in connection with this process, such as the possible commercial utilization of the slag or furnace residue and the effect at high temperature of $P_2O_5$ and other volatilized products on refractory linings and metal parts used in construction of a furnace plant. Some of these problems are partially solved and others have been scarcely attacked. It seems probable that most of them will be worked out in large-scale operations and an economic balance eventually established, but there is a field here for valuable laboratory research which may perhaps save considerable time, money, and energy.

# The Accurate Determination of Nitrates in Soils[1,2]

## Phenoldisulfonic Acid Method

### By Horace J. Harper

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O F THE methods described[1,2,3,4,]* for the determination of nitrates in soils, the phenoldisulfonic acid method is the most frequently used because of its simplicity and rapidity. Objections to this method have been made owing to the difficulty of obtaining accurate results, for one or more of the following reasons: (1) difficulty in obtaining a perfectly clear and colorless extract, which is absolutely essential; (2) losses of nitrates during determination due to several specific causes; (3) difficulty in making accurate comparisons between standard and unknown solutions due to interfering tints.

*A simple analytical procedure has been developed for the accurate determination of nitrate by the phenoldisulfonic acid method. Perfectly clear and colorless soil extracts are obtained by the use of a copper sulfate and a copper hydroxide treatment.*

*It has been found by other investigators that losses of nitrate occur due to the evaporation of acid filtrates, the use of various decolorizing agents, the presence of chlorides above 15 parts per million in the soil, and the presence of carbonates in the residue to which the phenoldisulfonic acid is added. Loss of nitrate in these ways can be prevented by keeping the solution alkaline on evaporation, by using copper hydroxide as a decolorizing agent, by removing the chlorides with silver sulfate, and by flooding the dry residues with 3 cc. of phenoldisulfonic acid.*

*Interfering tints that occur in making comparisons between standard and unknown solutions are caused by the presence of organic coloring matter, irregularities in adding the different reagents, and the presence of insoluble material in the unknown solution. These tints can be prevented by removing the organic matter with copper hydroxide, by treating all residues uniformly as directed, and by filtering to remove material not in solution.*

*If the procedure as outlined is carefully followed, very accurate results may be obtained.*

tions as the copper, iron, and aluminium salts, except on two sandy soils. Calcium carbonate was by far the poorest flocculent.

This and further experiments indicated that inorganic colloids can be removed satisfactorily from soil extracts by several of the different flocculents. However, when two peats and an acid black soil were used, colorless solutions could not be obtained by the use of these flocculents, owing to the presence of organic coloring matter which they would not remove. The filtrates, when evaporated, gave residues containing appreciable amounts of organic matter.

Emerson[11] uses alumina

## Clarifying and Decolorizing the Soil Extract

An absolutely clear and colorless extract must be obtained in order to secure accurate results with this method. Pasteur-Chamberland filters are sometimes used to clarify soil extracts, but they do not remove color due to organic matter. Their use requires more apparatus and time than is desirable, and hence numerous flocculating agents have been used, making it possible to use paper filters. The different flocculating agents recommended for clarification are calcium oxide,[5] calcium hydrate,[6] calcium carbonate,[7] copper sulfate,[4] and potash alum.[8] A comparison of these flocculents and also ferric and aluminium sulfate was made, using twelve soils having widely different physical and chemical properties ranging from sand to clay loam, from low organic matter content to raw peat, and from very acid to alkaline in reaction. Each of the flocculents recommended by the previous investigators was added to 50 grams of soil and 250 cc. of distilled water. The iron and aluminium sulfates were added at the rate of 1 gram to 100 grams of soil. The suspensions were shaken for 30 minutes and filtered, using ordinary filter paper (S. & S. 597). Seventy-five cubic centimeters of each of the filtrates were compared in Nessler tubes, and 25 cc. were evaporated to dryness and comparisons made between different residues. There was very little difference in color between the filtrates or dry residues from the copper sulfate, ferric sulfate, aluminium sulfate, and potash alum treatments. In the case of peats, calcium oxide and calcium hydrate increased the color of the extracts over that of pure water extracts, and did not give such clear and colorless solu-

cream to remove coloring matter from soil extracts. Schreiner and Failyer[12] recommend "G Elf" carbon black for this purpose. A comparison was made of the clarifying power of three different charcoals and the hydroxides of copper, iron, aluminium, zinc, and manganese. A 0.2 per cent caramel solution similar to that employed by Emerson[11] was used in this experiment. The charcoal was added at the rate of 1 gram to 100 cc. of the solution. Five cubic centimeters of a normal solution of copper, ferric, aluminium, zinc, and manganese sulfates were added separately to 100-cc. portions of the caramel solution, and 0.25 gram of calcium hydroxide was added to precipitate the hydroxides of the metals. The solutions were shaken for 20 minutes, filtered, and the filtrates compared. The results are given in Table I.

TABLE I—Effect of Different Decolorizing Agents on a 0.2 Per cent Caramel Solution

| Clarifying Agent | Order of Efficiency in Removing Color | Color of Filtrates |
|---|---|---|
| Charcoal (animal) | 1 | No color |
| Carbon black ("G Elf") | 2 | No color |
| Cu(OH)$_2$ | 3 | Slight color |
| Fe(OH)$_3$ | 4 | Slight color |
| Al(OH)$_3$ | 5 | Considerable color |
| Mn(OH)$_2$ | 6 | Considerable color |
| Zn(OH)$_2$ | 7 | Little change |
| Charcoal (blood) | 8 | Little change |

This experiment was repeated using an alkaline peat extract, an acid peat extract, and two alkaline extracts secured from a manure compost heap. All the extracts except the alkaline peat were darker in color than a 1 per cent caramel solution. The same relative results were obtained as given in Table I. The animal charcoal and "G Elf" carbon black were the best decolorizing agents, copper and ferric hydroxide were superior to alumina cream, while the blood charcoal was least effective in removing the color from the different solutions. The "G Elf" carbon black filtrates, although they always appeared very clear, on evaporation contained

a black residue due to finely divided carbon passing through the filter. This was prevented by precipitating copper hydroxide in the solution treated with carbon black before filtering.

Since charcoal cannot flocculate soil suspensions, may adsorb more or less nitrate, and is difficult to wash from apparatus, its general use as a decolorizing agent is not recommended. However, in the case of very highly colored soil extracts, which are occasionally obtained and cannot be decolorized, even with larger amounts of copper hydroxide, "G Elf" carbon black may be used along with the copper sulfate–copper hydroxide treatment recommended under analytical procedure. This combination will decolorize very highly colored solutions with only a slight loss of nitrate.

### Nitrate Losses

Loss Due to Adsorption—Emerson,[11] Lipman and Sharp,[5] and others have shown that some charcoals adsorb nitrates. In this investigation it was found that animal charcoal adsorbs large amounts of nitrate while the "G Elf" carbon black removes very little. In each case 10 parts per million of nitrogen as nitrate were added to the solution and the charcoal suspension was shaken 20 minutes before filtering. The results are given in Table II.

Table II—Loss of Nitrate When Different Charcoals Are Used as Decolorizing Agents on a Solution Containing 10 P. P. M. of Nitrogen as Nitrate

| Decolorizing Agent | Grams in 250 Cc. | Nitrogen as Nitrate | |
| --- | --- | --- | --- |
| | | Recovered P. p. m. | Lost P. p. m. |
| Animal charcoal | 0.5 | 8.6 | 1.4 |
| | 1 | 7.7 | 2.3 |
| | 2 | 6.6 | 3.4 |
| "G Elf" carbon black | 0.5 | 9.7 | 0.3 |
| | 2 | 9.5 | 0.5 |

Lipman and Sharp[5] have also reported a loss of nitrate when alumina cream was used to clarify the soil extract. Tests were made to determine the effect of copper, aluminium, and ferric hydroxides on the adsorption of nitrate. The amount of hydroxide used was equivalent to 5 cc. of a normal solution. It was precipitated from a sulfate solution by adding 0.25 gram of calcium hydroxide. The total volume was 250 cc. No adsorption of nitrate by any of the hydroxides used could be detected in a solution containing 10 parts per million of nitrogen as nitrate.

Another experiment was conducted on a silt loam soil receiving 24 tons of manure annually. The sample was taken in November and the nitrate content was low. Fifty grams of soil were shaken up with 250 cc. of solution containing the flocculating agent.

It was found that large increases in amount of copper hydroxide caused only a slight increase in adsorption of nitrates. From this it may be inferred that adsorption of nitrates by the amount of copper hydroxide required is negligible.

Loss during Evaporation—Several investigators have reported loss of nitrate when potash alum was used as a soil flocculent. Dilute solutions of potash alum, aluminium sulfate, and ferric sulfate have an acidity greater than pH = 4. Unless soils are alkaline in reaction these salts will produce acid filtrates. Davis,[8] using potash alum as a flocculating agent, added 10 to 15 cc. of a saturated solution of calcium hydroxide to the aliquots before evaporation and prevented loss of nitrate. His results have been confirmed in this investigation. Chamot, Pratt, and Redfield[13] recommend that acid waters be neutralized before evaporation to prevent loss of nitrate.

The loss of nitrate which has often been attributed to the presence of sulfates in solution is not due to the sulfate, but is governed by the reaction of the evaporating solution. No loss of nitrate occurs if it is alkaline. If it is acid, the loss of nitrate is proportional to the acidity, owing to the fact

that the sulfuric acid, having a higher boiling point than nitric acid, displaces the nitric acid from its salts at the temperature of the steam bath and causes it to be volatilized as the residues approach dryness. This loss can always be prevented by neutralizing the filtrate before evaporation, preferably with a saturated calcium hydroxide solution.

Loss Due to Carbonates—A serious loss due to carbonates occurs when the phenoldisulfonic acid is added to dry residues containing considerable carbonates. If calcium oxide or calcium hydrate has been used as a soil flocculent, if acid extracts were neutralized before evaporation, or if carbonates were naturally present in the soil, some carbonate will be present in the residue after evaporation. If the phenoldisulfonic acid is added slowly in a ring around the edge of the residue,[6] each drop will move slowly toward the center of the dish. The reaction between the sulfuric acid in the reagent and the salts in the residue results in the liberation of free nitric and carbonic acids. The carbonic acid gas passes off around the edges of each drop of reagent and mechanically helps to carry some nitric acid away with it before the nitric acid has a chance to react with the phenoldisulfonic acid. Davis[8] recommends flooding the residues with 5 cc. of reagent in order to prevent this loss.

Since nitrates are more soluble than the other salts present, on evaporation they are concentrated in the lowest part of the evaporating dish. In order to prevent loss of nitrate due to carbonates, 3 cc. of reagent are added quickly to the center of the evaporating dish. The carbon dioxide which is evolved must pass upward through the reagent, and any nitric acid which might be carried away with it also has to pass up through the reagent and thus reacts with the phenoldisulfonic acid, and loss of nitrate is prevented. In case of alkali soils containing large quantities of soluble carbonates, the solution should be almost neutralized with dilute sulfuric acid before evaporation, as recommended by Chamot, Pratt, and Redfield.[13]

Loss Due to Chlorides—Stewart and Greaves,[14] Davis,[8] and others have shown that chlorides cause a loss of nitrate. Lombard and Lafore[15] have shown that the loss was due to the formation of aqua regia when the phenoldisulfonic acid was added to a dry mixture of chloride and nitrate. Pouget[16] and others recommend the removal of the chlorides by the use of silver sulfate in order to prevent loss of nitrate.

A test was made of the effect of chlorides on the loss of nitrate by adding a solution of potassium nitrate containing 10 parts per million of nitrogen as nitrate and varying amounts of chloride to a nitrate-free black clay loam. The results were similar to those secured by Stewart and Greaves[14] and Lipman and Sharp,[5] which indicate that there is loss of nitrate when the chloride content exceeds 4 parts per million in the solution evaporated, which is equivalent to 20 parts per million of chloride in the dry soil.

In another experiment it was found that complete recovery of nitrates was obtained when a solution of silver sulfate was added as recommended in the analytical procedure.

An excess of 100 parts per million of silver is necessary to insure complete removal of chloride from the soil extracts when the chloride content is very high. The amount of chloride in an unknown sample of soil can be quickly determined[12] by titrating a portion of the filtrate with standard silver nitrate solution using potassium chromate as an indicator. In case of pot tests or in field studies where fertilizers containing chlorides have been added to the soil, the amount of silver necessary to remove the chloride can be quickly calculated and the proper amount of silver sulfate solution can be added with the water and copper sulfate solution.

Davis[8] reports that nitrate can be completely recovered in the presence of chlorides by flooding the dry residues with 12

cc. of phenoldisulfonic acid. It is usually better to remove the chloride with silver sulfate than to use such a large quantity of reagent, which is very apt to cause color tints.[13] Moreover, a very large volume of liquid is obtained on dilution and neutralization, which prevents accurate comparison with the standard when the nitrate content is low.

### Elimination of Color Tints

The presence of color tints in the unknown nitrate solution prevents an accurate comparison with the standard. These tints are due mainly to three factors: (1) organic matter in the residues; (2) salts not in solution; and (3) irregularities in adding phenoldisulfonic acid, subsequent dilution, and neutralization. When copper hydroxide is used as a decolorizing agent, organic matter should not be a factor in causing color tints.

If the phenoldisulfonic acid is neutralized before all the residue is dissolved, it will be necessary to filter the solution and remove the insoluble salts in order to make an accurate comparison of the unknown and standard. If they are not removed these salts will cause a refraction of the light rays, and color tints will be produced. This can easily be demonstrated by adding a little calcium sulfate to a portion of a standard solution and comparing it with some of the regular untreated standard.

The errors resulting from irregularity in adding different reagents can only be eliminated by accurately following the directions given in the analytical procedure.

### Completeness of Extraction of Nitrate from Soils with the Procedure Later Recommended

Allen and Bonazzi[18] report that only 77.4 per cent of the total nitrate (average for ten soils) was secured in the first extraction. Potter and Snyder[7,19] report that 93 to 97 per cent of the nitrate added to a soil was recovered by the phenoldisulfonic acid method and that complete recovery of nitrate was obtained by the reduction method when a known amount of nitrate was added to a soil which had previously been analyzed for nitrates. Kelley and Brown[20] find that approximately as much nitrate is extracted from alkali soils in 5 minutes as in 8 hours, and that further extraction does not yield appreciable amounts of nitrate. Similar results were secured in this investigation. Noyes[6] reports that nitrates added to a soil, in addition to those already present, can be completely recovered in one extraction with water.

In the following experiments seven soils which possessed very different properties were washed free of nitrates and dried in a steam oven at 55° C. None of them gave a test for nitrate when a 25-cc. aliquot from a 1:5 extract was evaporated and treated in the usual manner for nitrates. A known amount of nitrate was added and the amount recovered was determined by the analytical procedure recommended. The results of this experiment are given in Table III.

Table III—Recovery of Nitrate from Soil Containing Known Quantities of Nitrate

| Soil | Reaction | P. p. m. Nitrogen as Nitrate Recovered | | |
| --- | --- | --- | --- | --- |
| | | 10 P. p. m. Added | 25 P. p. m. Added | 100 P. p. m. Added |
| Black clay loam (Texas) | Neutral | 10.00 | 24.70 | ... |
| Carrington loam | Acid | 9.85 | 24.20 | ... |
| Kewaunee loam | Very acid | 9.85 | 25.15 | 101.4 |
| Miami silt loam | Neutral | 9.30 | 23.70 | 97.2 |
| Plainfield sand | Acid | 10.00 | 24.82 | ... |
| Raw peat | Very acid | 9.85 | 24.30 | 97.2 |
| Peat | Alkaline | 9.85 | 25.15 | 100.0 |

The recovery of nitrate in the foregoing experiment is undoubtedly as accurate as could be obtained by any other method. Complete recovery of nitrate was not always obtained, but the amounts not recovered were very small and negligible for most purposes. The largest loss was with the Miami silt loam, and shaking for an hour did not give any

better results than shaking 15 minutes. This soil contains a very high percentage of colloidal material and it is possible that the nitrate which was not recovered was held by adsorption. Gustafson[21] and also King[22] report that some nitrate is firmly held by the force of adhesion in the surface film of water surrounding the soil particles, and that one extraction will not remove this nitrate. This same slight error due to adsorption of nitrates occurs also with any other method.

When calcium carbonate was used as a flocculent as recommended by Potter and Snyder,[7] or calcium hydroxide as recommended by Noyes,[6] it was impossible to determine the nitrate content of the two peat soils owing to the large amount of organic matter in the extract.

### Recommended Analytical Procedure

Pulverize and mix the soil thoroughly by passing it through an 8-mesh sieve. In the case of heavy soils which contain considerable amounts of small, hard granules, due to intense drying, it is advisable to grind the soil so that it will pass a 60-mesh sieve in order to facilitate complete wetting in the time allowed. Weigh out 50 grams of soil (25 grams in case of peat) and place it in a 500-cc., wide-mouth bottle. Add 250 cc. of distilled water containing 5 cc. of a normal copper sulfate solution and shake 10 minutes. If the soil is not very acid and does not give a colored extract, add 0.4 gram of calcium hydroxide and 1 gram of magnesium carbonate to the soil suspension and shake 5 minutes more to precipitate the copper. Filter on a dry filter and discard the first 20 cc. of filtrate. If the soil is very acid or gives a colored extract, allow to settle after the first shaking of 10 minutes, and decant about 125 cc. of the supernatant liquid into a flask. Add to this flask 0.2 gram of calcium hydroxide and 0.5 gram of magnesium carbonate, shake 5 minutes, and filter as before. In either case transfer 10-cc. portions (use 25 cc. or more if the nitrate content is less than 10 parts per million) with a pipet to 7.6 cm. (3-inch) evaporating dishes. Evaporate aliquots to dryness on a steam bath. Cool the dishes, add rapidly 2 cc. of phenoldisulfonic acid from a pipet or buret having the tip cut off directly to the center of each evaporating dish, and then rotate the dish in such a way that the reagent comes in contact with all the residue. Let the reagent act 10 minutes, then add 15 cc. of cold water and stir with a short glass rod until residue is in solution. When cool, slowly add dilute ammonium hydroxide (1 volume $NH_4OH$, specific gravity 0.90, to 2 volumes of water) till slightly alkaline. Transfer solution to a cylinder or Nessler tube, dilute, and compare with standard solution containing 1 part per million of nitrogen as nitrate.

If the soil contains more than 15 parts per million of chloride, which is seldom the case in soils of the humid region, the chloride is removed by including a solution of silver sulfate (4 grams in 1000 cc.) in the 250 cc. of solution with which the soil is treated. Ten cubic centimeters of this solution are sufficient to remove completely 80 parts per million of chloride calculated on the basis of dry soil. After shaking 10 minutes, decant off 125 cc. as in case of colored extracts or very acid soils, add 0.2 gram of calcium hydroxide and 0.5 gram magnesium carbonate to precipitate the silver and copper, shake 5 minutes, filter, and proceed as described above. In case the chloride content is very high, add solid silver sulfate to the soil suspension before shaking.

In case of highly colored soil extracts that rarely cannot be decolorized by the copper sulfate–copper hydroxide treatment, add 1 gram of "G Elf" carbon black to 100 cc. of the supernatant liquid secured as recommended for colored extracts, and shake 15 or 20 minutes before adding the calcium hydroxide and magnesium carbonate to the solution. If the soil is calcareous, an additional 5 cc. of 1 N copper sulfate should be added to the soil extract with the carbon black to

insure enough copper hydroxide to completely remove the colloidal carbon on filtration.

### Discussion of the Analytical Procedure

This procedure is similar to that of Bear[4] in that copper sulfate and hydroxide are used for clarifying and decolorizing the soil extract. The writer found that the copper, as copper hydroxide, could be more advantageously precipitated with calcium hydroxide in the cold than with magnesium oxide and heating, and that this precipitation in most cases could be accomplished in the soil suspension. Magnesium carbonate is added to remove the excess of calcium hydroxide. This procedure is simple and rapid and an alkaline extract is also obtained which prevents loss of nitrate, as shown by Davis,[8] who used potash alum as a flocculent.

It was found that flooding the residue with an excess of phenoldisulfonic acid as recommended by Davis[8] is necessary to prevent loss of nitrate when considerable carbonates are present. The reason for this has been explained. The use of copper sulfate and its removal as outlined in place of potash alum gives a solution which is seldom acid to phenolphthalein and contains much smaller amounts of soluble salts. The residue is thus smaller, contains less carbonates, and hence a less amount of phenoldisulfonic acid is necessary for flooding than that recommended by Davis.[8]

The writer has found ammonium hydroxide preferable to potassium hydroxide for the neutralization of the phenoldisulfonic acid. The use of potassium hydroxide gives rise to insoluble precipitates much more often than the use of ammonium hydroxide. The ammonium hydroxide is also a much more convenient laboratory reagent.

The use of properly prepared phenoldisulfonic acid is important. This reagent is prepared according to Chamot, Pratt, and Redfield,[17] as follows: Dissolve 25 grams of pure phenol in 150 cc. of concentrated sulfuric acid. Add 75 cc. of fuming sulfuric acid, mix, and heat in a flask by placing the flask in boiling water for 2 hours. Store in a brown bottle.

The standard nitrate solution was made according to directions given by Bear and Salter.[4]

The analytical procedure given embodies the best points of several methods with certain modifications of the writer.

### Acknowledgment

The writer wishes to express his appreciation of the suggestions and criticisms offered by Professor E. Truog in connection with this study.

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# Erskine Douglas Williamson

THE death of Erskine Douglas Williamson on December 25, 1923, several days after an operation from which he seemed to be recovering, was a sudden blow to his friends and colleagues at the Geophysical Laboratory. Born in Edinburgh, Scotland, on April 10, 1886, he was only thirty-seven at the time of his death.

Mr. Williamson obtained his early education at George Watson's College in Edinburgh, where he showed marked ability in science and mathematics. He graduated with high honors from the University of Edinburgh, receiving the degrees of B.Sc. in 1908 and M.A. in 1909. During the two years 1910 to 1912 he was science master in Galashiels Academy, which he left to take up research work in physical chemistry at the University of Edinburgh. While here he was granted a Carnegie scholarship, and in 1914 he went to America to take a position on the scientific staff of the Geophysical Laboratory of the Carnegie Institution of Washington.

By training a mathematician as well as a physical chemist, Mr. Williamson was able to bring this happy combination of faculties to bear upon problems in many fields of scientific endeavor. Although well versed in chemistry and in physics, he had that mathematical temperament which allowed him to deal with the purely abstract side of a problem, and to reach its solution with an apparent ease and with an elegance which was always a source of wonder to his colleagues. His first published researches dealt with the solubility relations of the various forms of calcium and magnesium carbonates. Later he became interested in the thermodynamics of solutions as applied to equilibria in solutions, particularly at high pressures, and was one of that unfortunately rather small circle which understands and appreciates the work of Willard Gibbs. During the war he was a member of a

E. D. WILLIAMSON

group which went out into the factories and supervised the manufacture of optical glass for military needs. His particular field was the annealing of glass, and investigations begun while he was at the glass plant were completed later at the Geophysical Laboratory. For his share in this investigation the Franklin Institute awarded him in 1921 the Edward Longstreth Medal of Merit. Another wartime activity in which he took part was the determination of the compressibility of mustard gas. Since the close of the war he has been engaged in the investigation of several phases of the behavior of materials under very high pressures, particularly the compressibility of solutions and of minerals and rocks, the transmission of earthquake waves, and the bearing of these on the constitution of the interior of the earth. His latest activity was the construction of an apparatus for the determination of gravity. This work was unfinished at the time of his death.

Mr. Williamson joined the American Chemical Society soon after coming to this country and continued to be an active member during the ensuing nine years. He was also a member of the Edinburgh Mathematical Society, a fellow of the American Physical Society, a member of the Geological Society of Washington, and of the Washington Academy of Sciences, and one of the editors of the Academy's journal.

With the passing of Mr. Williamson a very real loss is suffered by his colleagues. A brilliant scholar and a quick thinker, he possessed the unusual faculty of applying his attainments to the solution of problems which required the coöperative effort of several investigators. His thorough knowledge of a wide range of subjects made collaboration with him both pleasant and profitable, and his generous nature endeared him to all his associates.

L. H. Adams

# New Catalytic Effects of Zinc Chloride and Aluminium Chloride[1]

## By J. F. Norris

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ONE of the major problems being studied at the institute is the change in reactivity of atoms and groups in organic compounds as affected by changes within the molecule and in its environment. Relative reactivities are measured by comparing the rates at which the several members of a series of compounds of the same type react with a second compound which is the same in all cases. In this way the effect of changes within the molecule can be measured. The influence of the presence of substances outside the molecule, such as solvents or catalytic agents, can be measured in the same way. The solvent or catalytic agent affects the bonds in the activated compound in the same way that changes within the molecule bring about this effect. In many cases compounds made up of the catalyst and the activated molecule have been isolated. It is highly probable that in cases where such addition compounds are not formed, a molecular attraction exists, which results from residual affinities. Two molecules, when brought together, must exert an influence, one on the other, and this must result in a change in the attractions between the atoms within each molecule. Solvents have a marked effect on the rate at which a given reaction proceeds. From the foregoing point of view, they act as true catalysts by altering the strength of the affinities between the atoms in the dissolved molecule. When the changes set up in the affinities lead to increased reactivity, the added substance is a positive catalyst. If, on the other hand, the reactivity is reduced, the substance functions as a negative catalyst. The normal rate of reaction between two molecules occurs when these two kinds alone are present.

The work referred to above led to a knowledge of the effect of changes within the molecule on the reactivity of the following bonds: C—OH, CO—H, C—Cl. In this paper will be described briefly some of the results of the study of the activation of the C—Cl and the C—OH bonds by aluminium chloride and zinc chloride, substances known to form molecular compounds with one of the reacting compounds. When benzoyl chloride reacts with aluminium chloride, the resulting compound contains a very active chlorine atom. Advantage is taken of this in preparing benzophenone by the Friedel-Crafts reaction. The molecular compound has been found to react with a wide variety of substances, and condensations have been effected with ethers, esters, ketones, unsaturated hydrocarbons, and saturated hydrocarbons. At this time, however, a second type of reaction, which has a bearing on some of the views put forward by Professor Bancroft, will be considered.

When the molecular compound of triphenylchloromethane and aluminium chloride is treated with ether, triphenylmethane is formed. A study of the mechanism of the reaction led to the view that it took place in steps, the first being represented by the following equation:

$$(C_6H_5)_3CCl + C_2H_5OC_2H_5 = (C_6H_5)_3COC_2H_5 + C_2H_5Cl$$

An analogous reaction occurs in the cold when benzoyl chloride dissolved in ether is treated with aluminium chloride. Ethyl chloride and ethyl benzoate are formed. Further action of aluminium chloride on $(C_6H_5)_3COC_2H_5$ proceeds as follows:

$$(C_6H_5)_3COC_2H_5 = (C_6H_5)_3CH + CH_3CHO$$

In the presence of aluminium chloride the carbon-oxygen bond, the weakest in the compound, is first broken. The oxygen saturates itself by drawing upon the carbon, which consequently loses a hydrogen atom:

$$(C_6H_5)_3C— + —O—\overset{H}{\underset{H}{C}}—CH_3 = (C_6H_5)_3CH + O = \overset{H}{C}—CH_3$$
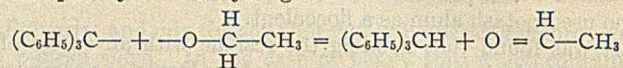
It seemed of interest to determine if such a decomposition could be produced by heat. The pure ether broke down on heating, as indicated above. By an analogous reaction butyric aldehyde was prepared from the normal butyl ether of triphenylcarbinol. In these cases heat alone brought about a decomposition which aluminium chloride effected at room temperature. The work suggests the possibility of finding other reactions in which the catalyst will produce the same results as exposure of the compound to high temperatures.

The work leads to a very simple way of preparing triphenylmethane in quantity. A mixture of carbon tetrachloride, benzene, and aluminium chloride is allowed to react over night. Ether is then added, and after standing some hours the mixture is decomposed by water and triphenylmethane is obtained from the reaction product. Excellent yields and very pure materials have been obtained.

The second case of activation of a chemical bond which will be considered briefly is that of the carbon-oxygen bond in primary alcohols. These alcohols will not react with aqueous hydrochloric acid in an open vessel, and as a consequence alkyl chlorides are prepared from anhydrous alcohols, zinc chloride, and hydrogen chloride. The zinc chloride has been supposed to act as a dehydrating agent. Zinc chloride forms compounds with alcohols, and it is possible that in this synthesis it acts catalytically by activating the hydroxyl group. Zinc chloride forms a compound with water. The question naturally arose whether the molecular compound of the chloride with alcohol would be stable in the presence of water. Experiments showed that primary alcohols react readily with concentrated hydrochloric acid if zinc chloride is present, indicating that even in the presence of water enough of the molecular compound of the chloride with alcohol is present to make the reaction possible. The results serve to emphasize the facts established by Whitaker in his study of the preparation of organic esters in the presence of water, and also the observations of Kendall that the compounds of organic acid and hydrochloric acid exist in water solution. It is probable that other catalytic reactions involving the formation of water, which are ordinarily carried out in anhydrous solvents, can be brought about in the presence of water. Whitaker's work led to the preparation on an industrial scale of ethyl acetate from dilute acetic acid, and as a result a great organic chemical industry was built up.

Summing up, the facts presented show, first, that a catalyst can cause, at ordinary temperatures, the severing of the same bond that breaks when decomposition takes place as a result of high temperatures; and, second, that a substance that has been thought to act as a dehydrating agent in bringing about a reaction involving the elimination of water, effects the condensation as a result of its catalytic influence, even though water is present.

# Petroleum as a Chemical Raw Material[1]

## By Benjamin T. Brooks

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IN THEIR efforts to impress upon the layman the importance of chemistry to industry, popular writers have sometimes referred to the petroleum industry as a chemical industry, and have also stated, always in a very vague way, that petroleum is similar to coal tar, and that by chemical research it is capable of yielding a wealth and variety of substances comparable to the number and commercial importance of the coal-tar derivatives. There are several reasons for objecting to this kind of careless writing, first of all because it savors so much of blue sky promoting that the interest which the business principals in this industry are taking in petroleum research is liable to be dispelled, and also because it contributes nothing and arouses no interest among scientific men who can also see through such transparent stuff. The explanation of such fanciful writing is either that these propagandists, like religious reformers, must go too far in their zeal in order that others should go far enough, or that they shirk the task of carefully examining into the facts. As organic chemists we should be gifted with a fair amount of imagination, but we should also have a wholesome regard for the truth.

In the light of our present chemical knowledge of petroleums and the types of hydrocarbons which are probably contained in such oils, it ought to be possible for organic chemists to indicate what can, within reason, be done chemically with this raw material and along what lines research should be undertaken to achieve these ends. Even this is a task of no small magnitude, at least for an individual, and it is to be hoped that in view of the enormous spread and number of subjects for research others will contribute freely to this theme. It is only by laying out a program of work which competent organic chemists can agree upon as being attractive and rational that we can ever convince anybody that *petroleum chemistry*, using the term in a very broad sense, is worth while.

### Reasons for Slow Development of Petroleum Chemistry

It is a fair question to ask *why*, since we have had this great quantity of raw material confronting us for about sixty years, such chemical research and industrial development along chemical lines has never been carried out. It has been suggested that we need a second Adolph Baeyer, or, in other words, that it has been for lack of brains that this development has not taken place— a rather grave charge against American organic chemists. Such statements were frequently heard during the early days of the revival of the American dye industry, and in 1914 certain importers told us that we could not produce pharmaceutical white paraffin oil like the Russian product because we did not have the technical skill, and also did not have the proper raw material. The results indicate that we have an abundance of both. In many other situations, as in this case, the only question is one of interest and effort in the right direction.

However, one might gain such an impression by considering only the results achieved thus far, as regards both academic research relating to nonbenzenoid hydrocarbons and chemical work within the industry itself. It ought to act as a challenge and spur to our efforts to take a brief glance at the position from which we start. Billions of dollars have been invested in the petroleum industry and it is highly organized. It owes its present strength and magnitude to skilful business management plus good engineering, and probably no great industry is less indebted

to chemistry. In its whole history chemical contributions have been rare, and the report submitted by Professor Silliman in 1856 stands out as a monument. Of course, there have been other contributions of a chemical character, but the "refining" department of the industry has been built upon the art of fractional distillation. Other major operations of the refineries are also essentially physical in nature, such as the freezing and pressing of paraffin wax, the recovery of condensable vapors from gas, and the brightening of oils by fuller's earth or similar materials. Also, without taking into account exceptional cases, it is clearly a matter of record that the *testing of petroleum products* has often been regarded as *petroleum chemistry*. Many people have apparently confused determinations of flash point, Baumé gravity, degrees Engler, degrees Saybolt, etc., with chemical research, and as long as chemists permit such an idea to persist we cannot hope that chemists will influence the industry more than in the past. In the marketing of present-day refinery products these tests are naturally of value, and no useful purpose would be served by repeating here what some petroleum men say about them. The point is that petroleum testing should be called just that and nothing more, and the much wider horizon of scientific research be emphasized. Undoubtedly, *one* of the reasons why the chemistry of petroleum has remained relatively undeveloped has been the stress laid upon testing and its misconception as petroleum chemistry.

To those not familiar with the industry a word of explanation is due the petroleum technologist. The industry has been built up on the business of supplying the public with a limited number of products, most of which exist as such in the crudes, and which in the early days when oil of the Pennsylvania type was produced in relatively much greater amounts were not refined chemically at all. Even today some lubricating oils from this crude are not chemically refined. The task of the refiner has been to furnish products of a quality acceptable to the public, and there has been no reason, or any prospects sufficiently tangible and offering hope of more lucrative returns, presented to induce him to do more than this. The various petroleum companies have done a big and fairly profitable business in producing their familiar products, and this is probably another reason why practically no attempts in other directions have been made.

The most potent reason, however, for lack of chemical development and research within the industry itself is the lack of theoretical, or rather systematic, organic chemistry relating to the nonbenzenoid hydrocarbons. The extent of such work which is needed is so enormous that its cost would be prohibitive to individual concerns. University workers have seldom become interested in such research, probably for a variety of reasons—on account of the impetus given to the chemistry of the benzene series and which still greatly influences all organic chemical research, on account of the reluctance of refiners to discuss even theoretical questions relating to their work with outsiders, the tendency of organic chemists to become interested in something having a puzzling constitutional formula, the difficulty of isolating pure substances from petroleum for investigation, and also, perhaps, the curious drift of chance by which interest seems to be capriciously directed into certain channels and not in others.

There would appear to be many reasons why independent investigators, such as university men, would select such a field for their research, since with a raw material of such great commercial importance and which is available in such enormous quantities

there would be inherent in almost any theoretical research the possibility of discovering something of industrial value.

There are doubtless other reasons which have obstructed work of this kind, particularly within the industry. Of course, an unknown amount of work of industrial importance has been done and the results have been withheld from publication; it is perhaps too Utopian to hope that results of this particular character should be made public and it is not really necessary that this be done. But there has been a fear that investigation of certain subjects, lubrication for example, might impose new burdens or new requirements on the refiner, and with respect to some such problems some refiners would rather leave things as they are. The following discussion, however, should bring out the fact that there is a vast amount of work of a pioneer character to be done which would benefit the entire industry, or rather those units of it which have the proper personnel to take industrial advantage of such investigations.

### Isolation of Hydrocarbons from Petroleum

Without going too much into detail it can readily be shown that the number of hydrocarbons that have been isolated from petroleum is much smaller than is commonly supposed. The most careful work on the isolation of hydrocarbons from petroleum is evidently that of Young and his assistants, and his work is especially illuminating as regards the difficulty of separating such hydrocarbons in a reasonably pure condition. Thus, thirteen fractional distillations in a special apparatus were required to separate pentane and isopentane, whose boiling points are 8.4 degrees apart, and no other substances are present. Very probably the regulated temperature still-head method of Rosanoff could advantageously be applied to this general problem. Young was able to prove the presence of hexane and isohexane, heptane and isoheptane, and considered that other isomeric hexanes and heptanes were present in small proportions in the particular light naphtha studied by him, but these minor constituents were not isolated. Investigations of this kind have often been carried out on commercial samples not referable to any particular crude petroleum. In the light naphtha from Baku the presence of cyclopentane, methyl cyclopentane, cyclohexane, and methyl cyclohexane has been proved, but beyond this the data are uncertain. Some of our American petroleums also contain these cyclic hydrocarbons, and Midgley has recently isolated what is evidently a new hydrocarbon, a dimethyl cyclobutane, from a gasoline from a California petroleum. Mabery has isolated naphthalene from one of the California oils, and benzene and toluene have been shown to be present in most gasolines that have been carefully examined, and the gasoline from Borneo petroleum is particularly rich in these aromatic hydrocarbons—a fact of considerable interest since the work of Midgley in this country and of Ricardo in England on the relation of the composition of motor fuel to detonation or engine knock. The dicyclic hydrocarbons tetrahydronaphthalene and decahydronaphthalene have also been identified in the Borneo oil. Coates has shown the presence of a series of dicyclic hydrocarbons, $C_{10}H_{18}$ to $C_{13}H_{24}$, in one of the Louisiana oils, and Wagner has shown that liquid sulfur dioxide extracts a series of hydrocarbons from the kerosene from Oklahoma (Cushing?) oil which are even poorer in hydrogen but whose chemical character is not known. Such hydrocarbons are naturally available in large quantities, and since Wagner found that the boiling points of these hydrocarbons were separated by considerable intervals, their separation was not difficult —a fact which suggests that the use of liquid sulfur dioxide as an aid in separating such hydrocarbons could be greatly extended. Space forbids discussion of the hydrocarbons that are *probably* present in petroleums; one of the largest published volumes on the subject of petroleum chemistry is virtually a catalog of all known hydrocarbons. However, there is ample evidence that petroleums are far from being a simple mixture of normal paraffins, as is suggested by the older literature, and bear no simple genetic relation to the fatty acids such as one might expect from the theory that petroleums have been formed by the decomposition of fish oils or other fatty oils.

Industrial distillation apparatus, when specially designed for the purpose, is much more efficient than laboratory apparatus, but the separation of individual hydrocarbons above heptane in the paraffin series, or above cyclohexane in the naphthene series, in a reasonable degree of purity comparable with the purity of toluene for chemical purposes, is exceedingly improbable, at least by distillation alone. This admittedly increases the difficulty of such work and detracts from its scientific value and interest. In the case of the simpler hydrocarbons it has been shown, in connection with the separation of helium from natural gas, that pure methane and ethane can be cheaply isolated by fractional distillation at low temperatures, and it may be inferred from this and the analytical work of Burrell and his assistants that propane and butane can also be isolated in substantially the same manner.

### Study of Typical Pure Hydrocarbons

Much would be gained by the synthesis and study of pure hydrocarbons of different types. Of the saturated paraffins very few are definitely known beyond the isomeric octanes prepared by Clarke. Most of the normal paraffins which can be prepared from normal fatty acids are known and ordinary paraffin wax is evidently a mixture of such hydrocarbons, but there is good evidence that waxes of the ceresin type are branched chain hydrocarbons. The chemical behavior of these higher paraffins is only very meagerly known. Only recently, work done on the oxidation of paraffin wax by air at about 120° C. to fatty acids has caused us to greatly modify our ideas regarding their stability to oxygen. Apparently, certain saturated hydrocarbons, of unknown type, can be readily sulfonated to true sulfonic acids. The higher substituted ethylenes are of particular interest. Their chemical behavior is entirely unknown, with the exception of those which nature has placed in our hands—namely, the terpenes and similar substances studied in connection with these hydrocarbons.

### Problems with Regard to Unsaturated Hydrocarbons in Lubricating Oil Distillates

This at once raises a series of questions of industrial interest with regard to the supposed unsaturated hydrocarbons in lubricating oil distillates. Whether or not these oils contain substantial proportions of unsaturated hydrocarbons of the substituted ethylene type is not positively known. Tars are formed when such oils are treated with sulfuric acid; they oxidize and darken in color when exposed to air, and they show more or less indefinite iodine or bromine absorption numbers. But the higher simple olefins, as far as they are known in a pure state, are relatively inert to sulfuric acid and do not form tars. Thus, a substituted ethylene, $C_{12}H_{24}$, gave the polymers $C_{24}H_{48}$ and $C_{36}H_{72}$ almost quantitatively, and stability toward sulfuric acid appears to increase with increasing molecular weight. The committee on tests of the Institute of Petroleum Technologists now recognizes that there is no analytical method for determining the per cent by volume of unsaturated hydrocarbons in petroleum distillates.

The study of the properties of pure unsaturated hydrocarbons may settle a number of questions. They may prove to be more resistant to air oxidation and resinification than is commonly supposed, and a study of unrefined lubricating distillates themselves may show that the darkening in color and oxidation of such oils is due to, or promoted by, very small proportions of substances not now known. Methods of retarding or preventing such oxidation can very probably be found, since Midgley has discovered the remarkable effect of traces of lead tetraethyl in retarding the gas phase oxidation of motor fuels and thus preventing their reaching detonation velocities, and it has recently been

found that as little as 1 part of resorcinol or hydroquinone in 100,000 parts of benzaldehyde prevents the characteristic and ordinarily rapid oxidation of benzaldehyde by air. Such a discovery would be of great value in conserving the lubricating oil used in gasoline motors, and also in transformer and switch oils, or other oils subjected to air oxidation in service.

Another unsettled question is the lubricating value of the unsaturated hydrocarbons. It is generally known that oils which have been highly refined by acid—for example, the colorless pharmaceutical oils—are poorer lubricants than the same oils unrefined or very lightly refined. The theory has been proposed that unsaturated hydrocarbons are more firmly adsorbed or held by the metal surfaces, and Dunstan and Thole believe that a lubricating oil should contain a certain proportion of unsaturated hydrocarbons, as large a proportion as is compatible with not too much susceptibility to oxidation, polymerization, and gumming. Most of our ideas as to the behavior of the higher unsaturated hydrocarbons have been inferred from the behavior of unsaturated fatty oils, many of which contain two or more unsaturated groups, tung oil probably having such groups in a conjugated position. All we do know positively is that certain unrefined oils form a film between metal surfaces which no mechanical test pressures have broken down, that sulfuric acid adversely affects this property, but also that acid corrects the other defects of such oils. Hence, the refiner compromises and accepts the relatively large losses incident to the refining of such oils to meet the standards to which the public is accustomed. In America these refining losses vary from practically nothing up to about 25 per cent, and in the Scotch shale oil industry amount to 25 to 35 per cent.

Nevertheless, as indicated above, there is great doubt as to whether the losses experienced in refining such oils with sulfuric acid are really due to the unsaturated hydrocarbons of the ethylene type present in such oils. These unsaturated hydrocarbons in lubricating distillates are peculiarly resistant to catalytic hydrogenation under conditions in which fatty oils, even when present in the same mixture, are readily hydrogenated. If unsaturated hydrocarbons themselves can be successfully employed as lubricants in the absence of other substances which promote their oxidation (like paint driers), then a more rational method of refining such oils should be found. If it should prove necessary to remove them, liquid sulfur dioxide should remove them and conserve them for other uses, as at least one large refining company is doing. It is possible that the substances which are responsible for the tars actually found in refining practice are labile bridged ring hydrocarbons easily reacted upon by the acid. It is even possible that the best lubricants may be made from cracked oils. Aluminium chloride has, in fact, already been employed to make a superior cold-test lubricating oil by polymerizing lighter cracked hydrocarbons. In Germany superior lubricating properties are claimed for certain viscous benzene substitution products.

This question of the chemical properties of the higher unsaturated hydrocarbons is bound to become more and more important. The low temperature distillation of coal is an accomplished industrial fact and will probably grow to much greater importance, and the crude tar from such processes, though containing about 50 per cent pitch, also contains large proportions of highly unsaturated hydrocarbons now evidently useful only as fuel oil or as raw stock for the manufacture of gasoline by pressure distillation. It is worth noting that much the greater proportion of the chemical investigations of low temperature tars has been done in Germany, since 1918. Shale oil distillates also are highly unsaturated and, although the development of this industry may have to wait upon the depletion of our petroleum reserves before it grows to any magnitude, will certainly yield enormous quantities of such highly unsaturated oils. At present the best proposal for their use seems to be to burn them

as fuel or polymerize them, as by Brownlee's aluminium chloride method, or by heat and pressure, or other methods. But even at the present time the quantity of such unsaturated or ethylenic hydrocarbons available is much greater than would be required by any conceivable chemical method of utilization.

To be somewhat more specific with respect to these higher olefins, it may be pointed out that the "acid oil," obtained by diluting the acid layer after treating cracked oils, contains secondary alcohols, and one company is now manufacturing a series of secondary alcohols, isopropyl alcohol from the propylene of oil gas evidently being the most important commercially. It has also prepared in this manner secondary butyl, amyl, hexyl, and heptyl alcohols, and has prepared them in a higher state of purity than is described in previous work. With the higher olefins, however, polymerization is the chief result and new conditions or an entirely new method must be found to prepare the higher alcohols. Some of these should be solid waxes, and all the known solid waxes have considerable commercial value.

The behavior of the higher olefins with sulfur or sulfur chloride is not known, but to a certain extent may be inferred from the reaction of sulfur and rubber in vulcanization. At moderate temperatures sulfur adds directly to the double bond; by heating to higher temperatures decomposition with the formation of hydrogen sulfide and doubly unsaturated oils would probably result. Chlorine should react in a similar manner, and a method for so treating semidrying fatty oils in this manner, converting each double bond into a pair of double bonds, or a good drying oil, has recently been patented. It has long been known that hydrogen sulfide is readily evolved on heating sulfur and paraffin, but unsaturated hydrocarbons cannot be prepared in this manner, probably because the unsaturated hydrocarbon first formed reacts more energetically with free sulfur than the excess saturated hydrocarbon present.

Although certain of the most useful reactions employed in the study of the terpenes—for example, the reaction with nitrosyl chloride and with nitrogen tetroxide—were discovered in connection with work on amylene, these old reactions as applied to the higher olefins have been but little studied. Another series of reactions which seems particularly deserving of study is the reaction with hypochlorous acid to form the chlorohydrins, and these in turn with their very reactive chlorine can readily be converted into the corresponding glycols or oxides, or be coupled with a variety of other substances. At least the simpler chlorohydrins react readily enough, but among the higher boiling olefins these reactions have been studied only in the case of pinene, by Slavinski, and more recently with camphene and bornylene by Henderson. Hypochlorous acid is one of the most remarkable substances in chemistry. The term acid is really a misnomer, since, as W. A. Noyes has shown, it is really amphoteric and much weaker as an acid than carbonic acid; yet in cold, dilute aqueous solutions it reacts rapidly with the ethylene group. Since this reaction takes place in neutral solutions and gives nearly quantitative yields of the chlorohydrins, it would seem to be a better reagent for the study of the constitution of organic compounds than the permanganate oxidation method made popular by Baeyer.

It is a curious fact that the chlorohydrins, oxides, and glycols of the higher boiling olefins and also most of the unsaturated fatty acids are not known. Nicolet has recently brought out a curious fact that, though oleic acid reacts smoothly with hypochlorous acid, the oxide obtained by the action of strong alkalies is remarkably stable and is not readily hydrolyzed by acids to the glycol, a property not heretofore observed with organic oxides of the triatomic ring type. Many of these higher glycols should be commercially valuable substances. Thus, cetyl alcohol melts at 49.5° C., but the cetyl-1,2-glycol melts considerably higher—namely, at 75° to 76° C. Very few of these glycols are known in nature. One, $C_{25}H_{52}O_2$, isolated from carnauba wax,

is known and melts at 103.5° C. Another glycol, of unknown constitution, cocceryl alcohol ($C_{29}H_{62}O_2$) melts at 101° to 104° C. A simpler one, undecane diol (2,3), melts at 51° to 53° C. If one were successful in forming such alcohols or glycols, they could probably be separated from oil mixtures by freezing and filter pressing.

The preparation of the higher ethylene homologs in a pure condition is a matter of considerable difficulty, but, as indicated by their chemical behavior with sulfuric acid, their chemical behavior cannot safely be inferred from the known simpler ones. There are indications that, on eliminating halogens as hydrogen halide from the more complex alkyl halides, ring formation takes place with extraordinary ease. Many reactions employed for the synthesis of simpler compounds—for example, the Grignard reaction, which was so successfully employed by Clarke in synthesizing the octanes—are of practically no value in building up hydrocarbons of twenty or more carbon atoms. The Grignard reaction or the Wurtz-Fittig reaction can be very satisfactorily employed to condense two molecules of the higher alkyl halides to give new hydrocarbons, but, to get substances of definite constitution, we are practically limited to alkyl halides prepared from the few known higher alcohols occurring in natural waxes or prepared by rather difficult methods. With the higher alkyl halides this condensation reaction is the only successful application of the Grignard reaction.

### Research on Individual Hydrocarbons

The study of the constitution of individual hydrocarbons actually occurring in petroleum is hardly to be urged, primarily on account of the difficulty of isolating pure substances for study. One may get some idea of the difficulty which would be involved, first assuming that pure individuals could be isolated, by studying the research, still far from complete, which has been done on cholesterol. One can explain the large amount of research on some materials—for example, camphor and the camphoric acids—only by the great amount of fascination attaching to such work as a series of purely scientific problems. The number of such equally difficult problems contained in a barrel of petroleum is enormous. It is an almost totally unexplored field and therefore contains no chemical guide posts or contact with the known.

One can obtain a fair idea of what has been done in the way of chemical research and development by first considering the simpler hydrocarbons, including those occurring in natural gas. In the case of these simpler hydrocarbons it should be remembered that we have a fairly complete knowledge of their chemistry, including that of their various derivatives. In the case of methane itself, it was shown only recently by the analytical work of Burrell and his assistants that the hundreds of published analyses of natural gas reporting the hydrocarbon constituents in calculated percentages of methane and ethane were very faulty, and, as noted above, much of the work done in attempting to find a satisfactory method for the chlorination of methane was mostly wasted effort until it was realized that a substantially pure methane is necessary for the satisfactory production of the chlorinated products. Evidently, no satisfactory method of chlorinating methane to methyl chloride has yet been developed, although the conversion of methyl chloride to methanol is not a difficult matter. The manufacture of ethyl alcohol from ethane through ethyl chloride should also be fairly easy, but it is very doubtful if such a process could compete with fermentation alcohol.

Many natural products can be made synthetically from these simpler petroleum hydrocarbons, but the restrictions imposed upon such processes by the low cost of many of these natural products make many of the synthetic processes out of the question commercially. Glycerol has been synthesized from propane or propylene, but at present the process evidently cannot meet the competition of natural glycerol. The conversion of normal pentane and isopentane to isoprene has been accomplished, but cannot be done within the exacting limitations of the comparatively low value of natural rubber. The conversion of monochloropentanes to amyl acetate of satisfactory purity has been carried out on a large scale, but the commercial success of the process has been interfered with by great changes in the use of solvents during the war brought about by the introduction of butyl alcohol made by fermentation and discovery that other solvents could often be substituted for the relatively high priced amyl acetate. The acetates of the secondary butyl and amyl alcohols made by the action of sulfuric acid on butylene and amylene should find certain commercial uses. Oil gas offers several possibilities, relying upon the known chemistry of the simpler olefins. Ethylene in coal gas has been converted to ethyl alcohol on an industrial scale in England, using the sulfuric acid method, but oil gas has not been so employed in this country, although isopropyl alcohol, a new commercial product, is now being regularly manufactured from the propylene of oil gas, or rather, waste still gas from cracking stills. Ethylene glycol was manufactured in Germany during the war and used to some extent as the dinitrate in explosives. Oil gas, if used as such, yields a mixture of ethylene and propylene glycols, with probably minor proportions of butylene and amylene glycols. The easiest method of effecting the conversion appears to be through the chlorohydrins, a class of substances not heretofore industrially known. Ethylene chlorohydrin and the glycol are now being manufactured industrially, but at present the raw material is alcohol. In connection with oil gas it is of considerable interest that Curme has recently developed a process of decomposing fuel oil in a regulated alternating current arc, thus producing a gas containing about 50 per cent hydrogen, 25 per cent ethylene, 12.5 per cent acetylene, 7 per cent methane, and 5 per cent of other hydrocarbons including diacetylene. Von Baeyer vainly attempted to prepare this hydrocarbon in his classic work on the acetylene carboxylic acids, but Curme separated it in fairly large quantities in a pure condition and accurately determined its properties. From a purely technical standpoint the process is quite satisfactory as a manufacturing process for acetylene and ethylene.

### Drying Oils and Resins from Petroleum

It has frequently been suggested that drying oils similar to linseed oil could be made from petroleum oils. When the heavier kerosene or lighter gas oil fractions are chlorinated and the chlorine is removed by the usual methods of heating with alkalies, aniline, etc., the resulting oil does not show the expected unsaturation, probably due to ring closing. By heating *in vacuo*, particularly in the presence of a catalyst such as barium chloride on pumice, highly unsaturated oils which dry to a hard film are obtained, but such a process cannot compete economically with the natural drying oils. It is of interest, however, in view of the fact that linoxyn is apparently formed with anhydride formation of the partially hydrolyzed glyceride.

Closely allied to the question of drying oils is the formation of resins or "gum." Cracked gasolines have sometimes given trouble due to the oxidation of such oils by air with the formation of resinous substances. Such resins can be obtained in the form of honey-yellow, alcohol-soluble material, and it is possible that a nuisance can be turned to profitable account by study of the problem. Should there be any demand for such highly unsaturated oils, a method for the separation of the saturated and unsaturated hydrocarbons would be needed. It is well known that by cracking at atmospheric pressure the gasoline so produced is very rich in unsaturated hydrocarbons. Catalysts such as nickel also promote this by dehydrogenation, but as far as this has been studied the catalyst is soon rendered inactive by the deposition of carbon.

When one considers the probable constitution of abietic acid, it is somewhat to be wondered at that it is a crystalline solid

of such a high melting point. This fact, however, and the nature of other resin or copal acids, as far as is known, hold out the promise that the polycyclic hydrocarbons of lubricating oil distillates or the heavier fractions of gas oil can be oxidized to such resinous and commercially valuable compounds. No method of effecting such oxidations has yet been discovered which will not give black asphaltic products. However, a cheap process of oxidation which would give resins as the principal product, and from which the black asphaltic matter could be separated if formed, would be valuable. It may be mentioned that the air oxidation of paraffin, referred to above, has been shown to proceed through the formation of alcohols, and at one stage substantial percentages of saponifiable esters can be isolated. Such esters might prove to be more valuable than the fatty acids thus made, since the latter have the defect, from the soap-makers' standpoint, of turning yellow or brown with alkali.

### Removal and Utilization of Impurities

It has been suggested above that the obvious defects of unrefined lubricating distillates may be found to be due to very small percentages of impurities, perhaps diolefins of the conjugated type, aldehydes, and possibly traces of metallic soaps acting as catalysts to their oxidation by air. The suggestion may be made clearer by mentioning that some of the most conspicuous properties of cracked gasolines, particularly odor, are due to the merest traces of impurities, as indicated by the fact that the bad odor and other properties associated with such unrefined gasoline can be entirely removed in some instances by treating with a hypochlorite solution in the proportions of about 1 pound of chlorine to 15 barrels, or about 4500 pounds of gasoline. In terms of oxygen, as hypochlorite, this means that the vile odor of such cracked gasolines may be removed by 1 pound of such oxygen to about 10,000 pounds of the gasoline. The largest proportion of chlorine so far industrially employed in this method of refining is 1 pound per barrel.

In the foregoing discussion no attempt has been made to catalog problems of actual refinery practice but rather to indicate in a general way our lack of systematic knowledge of the organic chemistry in this general field of the nonbenzenoid hydrocarbons. It is naturally capable of considerable amplification. Some of the constituents of crude petroleum, such as nitrogen and sulfur derivatives, are present in some oils in substantial proportions— for example, the sulfur derivatives in Mexican petroleum and the nitrogen bases in certain of the California oils. These impurities are at present a nuisance to the refiners, but would seem to be deserving of scientific study. Even when these so-called impurities are present only in very minor proportions, the quantities which could be made available for scientific study, and possibly even industrial utilization, would be very large indeed. The only sulfur compounds from such general sources which have found commercial application have been the shale oils rich in sulfur, which on sulfonation yield the well-known pharmaceutical product, ichthyol, a product which has been closely duplicated in this country since the supply of the Austrian product was shut off in 1914. It should be mentioned, perhaps, that many of these sulfur compounds do not have bad odors. Even new or improved methods of decomposing these sulfur compounds, many of which are quite stable in petroleums, should be of interest industrially. The reactions of sulfur and sulfur chloride on hydrocarbons would appear to be worthy of study also from the industrial standpoint, with the possibility of making new plastic compositions and possibly fungicides and insecticides.

### Other Possibilities

It is quite reasonable to expect that new chemical reactions may be discovered which will yield results of the greatest interest. The recent discovery by Lynd of the reaction of nitrosyl chloride on the paraffins under the influence of sunlight opens up the possibility, as pointed out by Kremers, of preparing a host of new ketones, and since certain petroleums evidently contain a large number of cyclic hydrocarbons, it is quite conceivable that, even though we do not know the constitution of these cyclic hydrocarbons, some of the ketones made from them would prove to be crystalline substances resembling camphor. However, our knowledge of the hydrocarbons of the terpene group is quite sufficient, if applied to the chemistry of petroleum hydrocarbons, to yield an enormous mass of new knowledge.

If the course of research in this general field follows the history of other researches in other fields, things of the greatest scientific and industrial interest will be discovered which cannot now be foreseen, but if the foregoing discussion has indicated, not only that we lack scientific knowledge of an enormous number of hydrocarbons, but that also there is a sufficient number of definitely discernible objectives of research, then the purpose of this discussion will have been fulfilled.

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## National Committee on Prize Essay Contest

Headed by Herbert Hoover, Secretary of Commerce, and made up of the following men and women leaders in practically every field of endeavor, a national committee has been formed to act as judges in the American Chemical Society's Prize Essay Contest:

Jane Addams, 800 S. Halsted St., Chicago, Ill. Author, lecturer, and settlement worker.

James Rowland Angell, president of Yale University, New Haven, Conn.

Arthur Capper, Topeka, Kansas. U. S. Senator, editor, ex-governor of Kansas.

John J. Carty, vice president, American Telephone & Telegraph Co., 195 Broadway, New York, N. Y. A pioneer in the development of the telephone.

Robert J. Cuddihy, *The Literary Digest*, 354 Fourth Ave., New York., N. Y.

George Eastman, 900 East Ave., Rochester, N. Y. President, Eastman Kodak Company, and leader in business and philanthropic movements.

Henry Noble MacCracken, president of Vassar College, Poughkeepsie, N. Y.

Charles H. Mayo, Rochester, Minn. Prominent physician and surgeon.

J. C. Merriam, Carnegie Institution, Washington, D. C. Paleontologist, educator, president of the Carnegie Institution.

R. A. Millikan, California Institute of Technology, Pasadena, Calif. Director of Norman Bridge Laboratory of Physics and chairman of administrative board of institute. Distinguished physicist.

Julius Rosenwald, Sears, Roebuck & Co., Chicago, Ill. Merchant and philanthropist.

Edgar F. Smith, University of Pennsylvania, Philadelphia, Pa. Ex-president American Chemical Society, provost emeritus of University of Pennsylvania.

Ida M. Tarbell, 120 East 19th St., New York, N. Y. Author.

James W. Wadsworth, Jr., Mt. Morris, Livingston Co., N. Y. U. S. Senator.

F. E. Weyerhaeuser, Cloquet, Minn. Lumberman.

Mrs. Thomas G. Winter, 2617 Dean Blvd., Minneapolis, Minn. President of the General Federation of Women's Clubs.

The Prize Essay Contest is made possible by a gift of Mr. and Mrs. Francis P. Garvan, of New York, in memory of their daughter Patricia. Every high school and secondary school student in the country is eligible to participate. Six cash prizes are being offered to the winners in each State and six four-year scholarships to Yale or Vassar, each carrying with them $500 a year in cash in addition to tuition fees, will be the awards in the national competition between the State winners.

Each contestant may submit one essay of not to exceed twenty-five hundred words, which must be confined to one of the following subjects: The Relation of Chemistry to Health and Disease; to the Enrichment of Life; to Agriculture and Forestry; to National Defense; to the Home; and to the Development of the Industries and Resources of Your State. The best essay on each of these six subjects in each State will be awarded $20.00 in gold. The six best essays will be selected by the National Committee from among the State winners. National and State educational officials have endorsed the project and over twenty thousand sets of reference books have been donated to schools and libraries all over the country.

Committees similar in form to the National Committee are being formed in each State, and these State committees will select the six best essays written by the boys and girls of their respective States. The competition will close April 1, 1924, on which date all competing essays must be in the hands of the designated State authorities.
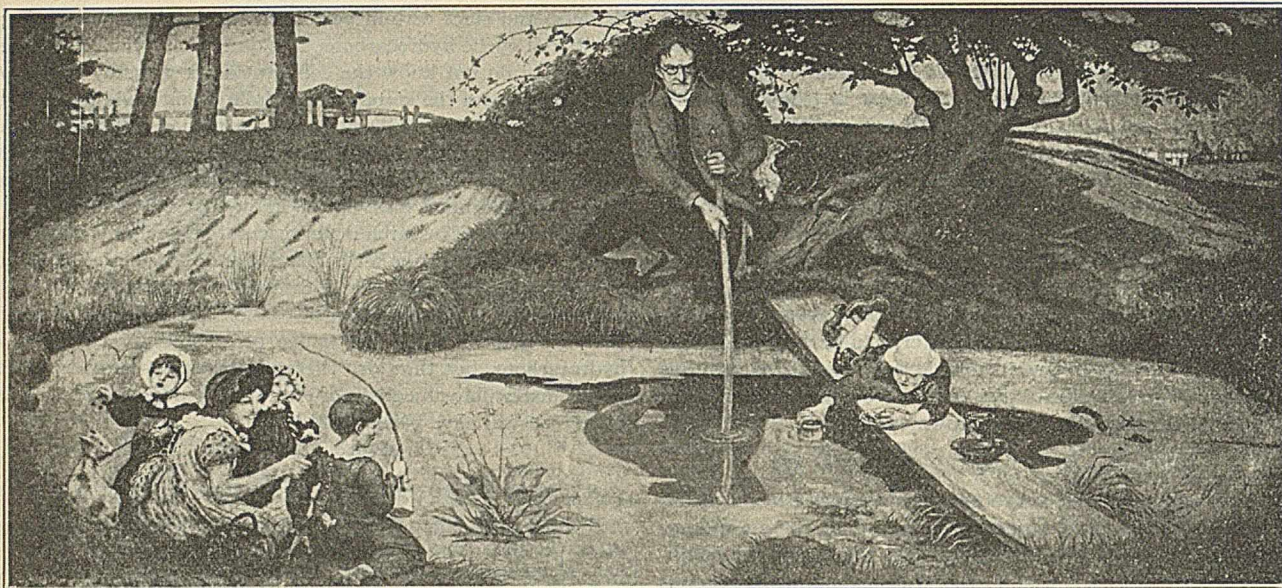
PANEL NO. 12

FIG. 1—DALTON COLLECTING MARSH-FIRE GAS. PAINTING BY FORD MADOX BROWN IN COUNCIL CHAMBER, TOWN HALL, MANCHESTER.
BY PERMISSION OF TOWN HALL COMMITTEE OF THE MANCHESTER CORPORATION

# Dalton Memorials in Manchester, England[1]

## By A. D. Thorburn

INDIANAPOLIS, IND.

THE Town Hall of Manchester, England, built about forty-five years ago at an expense of several million dollars, has in its Council Chamber twelve mural paintings, four of which commemorate events of interest in science. Perhaps these illustrations of the search for ultimate truths and their application have had an influence on the political and economic discussions which have taken place in this room. Panel No. 6 commemorates an edict of 1556 requiring all dealers and merchants to submit all measures and weights to be tested for accuracy. Panel No. 7 shows Wm. Crabtree, a cloth merchant of Manchester, observing the transit of Venus, concerning which Jeremiah Horrox, assisted by Crabtree, had made some historic astronomical calculations. Panel No. 10 acknowledges the indebtedness of the textile industry to the invention of the flyshuttle, which was the basis of fundamental improvements in cloth weaving. Panel No. 12, of especial interest to chemists, is entitled "Dalton Collecting

FIG. 2—STATUE OF DALTON IN THE ENTRANCE OF THE TOWN HALL, MANCHESTER, ENGLAND

Marsh-Fire Gas." It is a good representation of some circumstances under which Dalton and other chemists of the long ago must have worked. Dalton's name for marsh gas was "carburetted hydrogen from stagnant water." The artist's representation conforms to this name.

Dalton's conception of the marsh-gas molecule, or, as he called it, "ultimate atom," is shown in the chart reproduced from the Memoirs of the Manchester Literary and Philosophical Society, Vol. LIX (No. 12). Just what use Dalton made of this chart is not clear from his notes.

The schoolroom where Dalton taught and where he made his experiments leading to the formulation of the theory of atomic weights and the law of multiple proportions is now used as the office of the secretary of the Literary and Philosophical Society. Pelletier, of Paris, who was the first to isolate some important alkaloids, traveled to Manchester to visit Dalton in 1826. After some difficulty he found No. 36 George St., and being admitted, he went into the

*Manchester Memoirs, Vol. LIX.*   (*No. 12.*)    Plate VI.
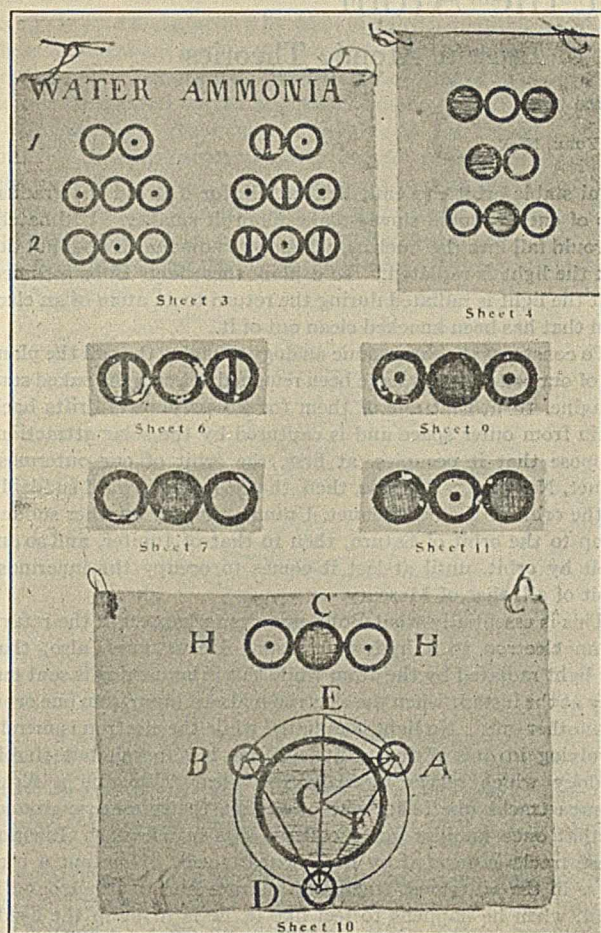


FIG. 3—DALTON'S CONCEPTION OF THE ULTIMATE ATOM OF MARSH-FIRE GAS (SHEET 10)

room at the left of the hall and saw a tall man standing at the side of a boy, who was figuring on a slate. Unwilling to believe that a chemist whose fame extended over all Europe would be teaching a boy his first four rules, Pelletier questioned, "Do I have the honor of addressing Monsieur Dalton?" Dalton answered "Yes, wilt thou sit down while I set this lad right about his arithmetic."
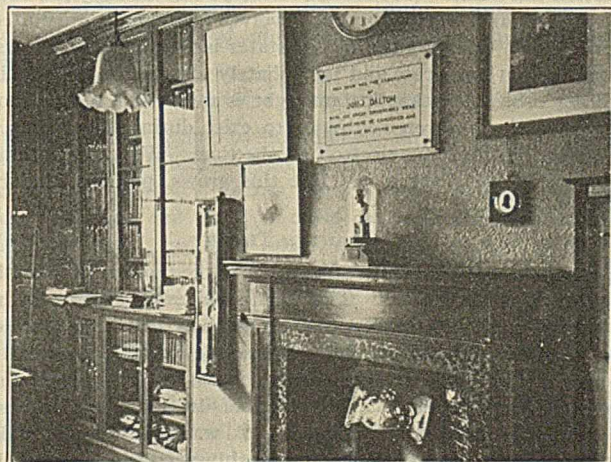


FIG. 4—DALTON'S SCHOOLROOM AND LABORATORY, NOW OFFICE OF MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY, No. 36 GEORGE ST.

Notwithstanding this simplicity of life and thought, the people of Manchester held Dalton in high regard, as is shown by the fresco and statue in the Town Hall, his statue in Piccadilly, the leading retail business district, the street named John Dalton Street, and the Dalton Fellowships in Manchester University. His position in this respect is unusual among men of science.



FIG. 5—THE "LOUNGE," LITERARY AND PHILOSOPHICAL SOCIETY ROOMS, SHOWING THE CLOCK MADE AT DALTON'S REQUEST AND WHICH STRUCK AT NINE O'CLOCK, THE HOUR SET FOR CLOSING THE MEETINGS. WHEN THE CLOCK STRUCK DALTON ADJOURNED THE MEETING AND WENT HOME FOR SUPPER

## Reprints from Annual Tables

The Secretary-General of Annual Tables announces that the following list of reprints from Volume IV is available for sale at the prices indicated:

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| "Electricity, Magnetism, Conductivity of Electrolytes, Electromotive Forces," by Malapert, Weisse, Slade, and Higgen. Preface by F. B. Jewett | 144 | 30 | 40 |
| "Radioactivity, Electronics, Ionization of Gases, etc.," by Saphores and Bourion. Preface by Sir E. Rutherford | 19 | 10 | 18 |
| "Crystallography and Mineralogy," by Spencer. Preface by Sir Henry A. Miers | 65 | 15 | 25 |
| "Biology," by Terroine and Colin. Preface by Jacques Loeb | 37 | 12 | 20 |
| "Engineering and Metallurgy," by Descroix. Preface by G. K. Burgess | 154 | 30 | 40 |
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# Bohr's Model of the Atom[1,2]

## A Review of Some Salient Features of Present Atomic Theories

By E. E. Free

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ACCORDING to the model of Professor Bohr, each atom consists of one central nucleus around which revolve one or more electrons much as the planets revolve around the sun. This model is often called the planetary or solar system model of the atom, or, commemorating the physicist who first investigated it, the Rutherford-Bohr model.

A different model of the atom was suggested by Abegg and more definitely by G. N. Lewis. It is usually called the Lewis-Langmuir model, or the static model. It considers the electrons not to be in orbital motion, but to occupy relatively fixed positions surrounding the nucleus, as, for example, one at each of the six corners of a cube having the nucleus at its center.

There seems little doubt that these two theories are reconcilable and that the Bohr or planetary model is essentially correct. The detailed theory of it is necessarily mathematical and the elimination of all mathematics from the present review results, inevitably, in a certain degree of inexactness. A compensation is hoped for in a greater clarity for the nonspecialist reader, to whom alone this review is addressed.

### The Simplest Atom

The simplest atom known is that of hydrogen. It consists, we believe, of one electron revolving around another single particle which acts as nucleus. Concerning the deeper nature of the electron and of the central particle we know practically nothing. We must merely accept them, for the present, as the ultimate building stones of matter. They are equally and oppositely charged—the electron with negative electricity, the central particle, often called the *proton*, with positive electricity. The numerical value of this charge is $4.774 \times 10^{-10}$ electrostatic unit or $1.60 \times 10^{-19}$ coulomb, a quantity of electricity almost inconceivably minute. Through the filament of a 40-watt, 110-volt incandescent lamp there pass *every second* about 2,300,000,000,000,000,000 electrons.

The central nucleus (or proton) of the hydrogen atom and the planetary electron that revolves around it have for each other the usual electrostatic attraction. It is this which maintains, we believe, the stability of the atomic system, corresponding roughly to the force of gravity in the planetary system of the sun and the earth.

The electron of the hydrogen atom, however, is not a fixture in its orbit. When an assemblage of hydrogen atoms is heated very hot, or is placed in a strong electric field, or is bombarded with fast-moving free electrons or with the alpha particles from radium, the planetary electrons of some of the hydrogen atoms may be driven entirely out of their orbits. The astronomic analogy is the arrival from outer space of some powerful heat ray or some fast-moving heavenly body that hits the earth and knocks it completely out of the solar system.

Under these conditions the hydrogen atoms emit light, the familiar bright lines of the hydrogen spectrum. If was from a study of these phenomena of spectra that Bohr deduced his theory and his atomic models.

### The Origin of Spectra

The ordinary ideas of mechanics will not explain such emission spectra. We cannot believe that an electron revolving in its

[1] Received December 11, 1923.

[2] This is not intended to be a rigorous discussion, but a presentation prepared especially for those who have not followed in detail the development of the present theory of atomic structure.—*Editor's Note.*

usual stable orbit can emit light at all, for if it did the gradual loss of energy would slowly make its orbit smaller. Ultimately it would fall into the nucleus, which we know that it does not do. Yet the light *is* radiated. To explain these facts Bohr assumed that the light is radiated during the return to an atom of an electron that has been knocked clean out of it.

To construct the astronomic analogy, imagine that all the planets of our solar system have been removed, leaving the naked sun. Imagine, then, that one of them (or a new planet) drifts back again from outer space and is captured by the solar attraction. Suppose that it occupies, at first, the orbit of our outermost planet, Neptune. Suppose, then, that it moves inward suddenly to the orbit of the next planet, Uranus, then by another sudden jump to the orbit of Saturn, then to that of Jupiter, and so on, orbit by orbit, until at last it comes to occupy the innermost orbit of all, that of Mercury.

This is essentially what Bohr assumes to happen in the return of an electron to a hydrogen atom. He assumes, also, that the light radiated by the atom while this is happening is sent out only at the instant when the electron makes a jump from one orbit to another one. No light is radiated while the electron is merely revolving in one of the orbits. There is a rough but simple analogy which serves to make this clear. Imagine a series of race tracks one inside the other like the concentric grooves of that once familiar game called "Pigs in Clover." Imagine these tracks separated by high board fences. Now put a race horse in the outermost track and instruct him to run around it until, when he happens to feel like it, he is to jump the inside fence into the next track, run around it for a while, and then jump the next fence, and so on until he reaches the innermost track of all. If, then, you watch this procedure from the field outside the outermost fence, you will not see the horse at all as long as he is running in a single track. The fences hide him. But whenever he jumps a fence from one track into the next you will see him for an instant as he goes over.

So with the hydrogen atom. You see the electron only as it jumps from one orbit to another one, for it is only then that the electron radiates light. This light makes the spectral lines, a different line for each possible kind of orbit-to-orbit jump that the electron can make. (It should be noted, as Lewis suggests, that to speak of an "electron jump" involves really an unwarranted assumption. All that the theory states is that an electron disappears from one orbit and immediately an electron appears in another orbit. At that instant light is radiated. We are not sure that the electron continues to exist during the "jump," or that it is the same electron all the time. We know nothing about what an electron is. But this grows, perhaps, unduly metaphysical.)

### The Quantum Theory

It is an essential of Bohr's theory that the number of possible electron orbits is limited. This idea is entirely contrary to the ordinary laws of mechanics. In our solar system, for example, there are an infinite number of possible orbits. The earth could contract its orbit by a few miles or a few millimeters and move on just the same. If a cloud of dust was encountered in space so that the earth lost energy and was slowed up, it would gradually approach the sun in a smoothly narrowing spiral. It would never make a jump from one orbit to another.

But the atom does not behave this way. An electron can approach the nucleus, the Bohr theory says, only through a fixed

series of orbit-to-orbit jumps. This is an expression of the quantum theory. Each of the possible orbits which the electron can occupy is fixed and specified by what is called a quantum number. These numbers are merely the complete series of whole numbers from one up. For example, the innermost orbit of the hydrogen atom is designated by the quantum number 1, the second orbit is designated by the quantum number 2, and so on. Some power of these quantum numbers actually determines the characteristics of the orbits. For example, the relative diameters of the orbits are fixed by the *square* of the quantum numbers. The innermost orbit has (in appropriate units) a diameter of one, the next orbit has a diameter of four, the third orbit has a diameter of nine, and so on.
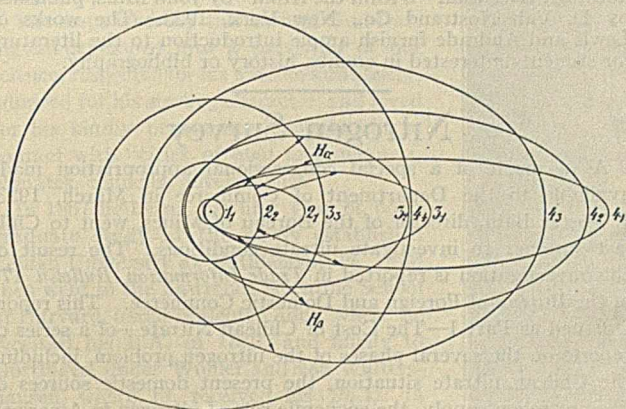


SOME OF THE ELECTRON ORBITS OF THE HYDROGEN ATOM

The quantum numbers of the orbits are designated by the figures, the principal quantum number by the larger figure, the subordinate quantum number by the subscript one. The lines ending in arrows indicate the transitions of the electron from orbit to orbit, which transitions correspond to certain of the spectral lines of hydrogen. [This drawing is from Bohr's Nobel Prize address, *Nature* (London), **112**, supplement, 38 (1923).]

The actual orbits of the hydrogen atom require, however, *two* quantum numbers instead of one. The first or "principal" quantum number is the one just discussed. If the electron orbits were exactly circular this would be the only quantum number necessary. But the orbits are not exactly circular. In reality, they are ellipses. So the principal quantum number fixes the *major axis* of the ellipse while another quantum number is required to fix the *eccentricity* of the ellipse—that is, the degree by which the ellipse departs from exact circularity. In the more complex atoms or in atoms under unusual conditions, such as exposure to intense electric fields, *three* independent quantum numbers may be necessary to specify all the possible variations of the orbits. These second and third quantum numbers are of great importance in many problems of the origin of spectra, but for the interpretation of the chemical evidence, at least to a first approximation, they may be disregarded, only the principal quantum number being considered.

### THE ELECTRON ORBITS AND THE PERIODIC LAW

As we advance beyond hydrogen in the atomic table the other elements contain a larger number of electrons and of the positive particles or protons. Helium, for example, contains four of each. But only *two* of the electrons move in planetary orbits, the other two being held firmly inside the nucleus together with all four of the protons. The third element, lithium, has six electrons and six protons, three of the electrons being planetary ones. The fourth element, beryllium, has eight each of protons and electrons, four of the latter being planetary, and so on.

It is the number and arrangement of the planetary electrons that determine, we believe, the chemical properties of the elements as well as most of the features of their spectra. The essential idea underlying Bohr's interpretation of the periodic law is that when the elements are arranged in the order corresponding to that law each element in the list *possesses one planetary electron more than does the preceding element*. In other words,

the atomic number of an element equals the number of its planetary electrons. This conclusion was reached first from Moseley's work on X-ray spectra, and it is sometimes called Moseley's law.

For Bohr's application of it, we must consider the quantum numbers of the electron orbits as one electron after another is added to the atomic system. Helium, with two planetary electrons, has both of them, Bohr believes, in orbits of the same quantum number as the single innermost orbit of the hydrogen atom—that is, of quantum number 1. The next element, lithium, has three planetary electrons, but, for some reason that we do not understand, it cannot add this third electron in a third orbit of quantum number 1. Only *two* such one-quantum orbits can exist. So the third electron of lithium goes outside into a larger orbit, an orbit of quantum number 2.

The fourth, fifth, and sixth electrons, and so on until the tenth electron, are added in additional orbits having the same principal quantum number as the third electron of lithium. The eleventh electron, however, brings another change. Just as more than two orbits of quantum number 1 seem unable to exist together, so more than *eight* orbits of quantum number 2 cannot exist together; and so the eleventh electron, like the third, must go outside the rest of the atom into a larger orbit, this time an orbit of quantum number 3. This gives us the atom of sodium.

The continuation of these ideas to the other elements will be apparent from the table printed herewith. It will be noted that all the alkali elements, like lithium and sodium, are ones that

<div align="center">BOHR'S TABLE OF THE ELEMENTS</div>

| | $1_1$ | $2_1 2_2$ | $3_1 3_2 3_3$ | $4_1 4_2 4_3 4_4$ | $5_1 5_2 5_3 5_4 5_5$ | $6_1 6_2 6_3 6_4 6_5 6_6$ | $7_1 7_2$ |
|---|---|---|---|---|---|---|---|
| 1 H | 1 | | | | | | |
| 2 He | 2 | | | | | | |
| 3 Li | 2 | 1 | | | | | |
| 4 Be | 2 | 2 | | | | | |
| 5 B | 2 | 2 (1) | | | | | |
| — — | — | — — | | | | | |
| 10 Ne | 2 | 4 4 | | | | | |
| 11 Na | 2 | 4 4 | 1 | | | | |
| 12 Mg | 2 | 4 4 | 2 | | | | |
| 13 Al | 2 | 4 4 | 2 1 | | | | |
| — — | — | — — | — — | | | | |
| 18 A | 2 | 4 4 | 4 4 | | | | |
| 19 K | 2 | 4 4 | 4 4 | 1 | | | |
| 20 Ca | 2 | 4 4 | 4 4 | 2 | | | |
| 21 Sc | 2 | 4 4 | 4 4 1 | (2) | | | |
| 22 Ti | 2 | 4 4 | 4 4 2 | (2) | | | |
| — — | — | — — | — — — | — — | | | |
| 29 Cu | 2 | 4 4 | 6 6 6 | 1 | | | |
| 30 Zn | 2 | 4 4 | 6 6 6 | 2 | | | |
| 31 Ga | 2 | 4 4 | 6 6 6 | 2 1 | | | |
| — — | — | — — | — — — | — — | | | |
| 36 Kr | 2 | 4 4 | 6 6 6 | 4 4 | | | |
| 37 Rb | 2 | 4 4 | 6 6 6 | 4 4 | 1 | | |
| 38 Sr | 2 | 4 4 | 6 6 6 | 4 4 | 2 | | |
| 39 Y | 2 | 4 4 | 6 6 6 | 4 4 1 | (2) | | |
| 40 Zr | 2 | 4 4 | 6 6 6 | 4 4 2 | (2) | | |
| — — | — | — — | — — — | — — — | — — | | |
| 47 Ag | 2 | 4 4 | 6 6 6 | 6 6 6 | 1 | | |
| 48 Cd | 2 | 4 4 | 6 6 6 | 6 6 6 | 2 | | |
| 49 In | 2 | 4 4 | 6 6 6 | 6 6 6 | 2 1 | | |
| — — | — | — — | — — — | — — — | — — | | |
| 54 Xe | 2 | 4 4 | 6 6 6 | 6 6 6 | 4 4 | | |
| 55 Cs | 2 | 4 4 | 6 6 6 | 6 6 6 | 4 4 | 1 | |
| 56 Ba | 2 | 4 4 | 6 6 6 | 6 6 6 | 4 4 | 2 | |
| 57 La | 2 | 4 4 | 6 6 6 | 6 6 6 | 4 4 1 | (2) | |
| 58 Ce | 2 | 4 4 | 6 6 6 | 6 6 6 1 | 4 4 1 | (2) | |
| 59 Pr | 2 | 4 4 | 6 6 6 | 6 6 6 2 | 4 4 1 | (2) | |
| — — | — | — — | — — — | — — — — | — — — | — — | |
| 71 Cp | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 4 4 1 | (2) | |
| 72 — | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 4 4 2 | (2) | |
| — — | — | — — | — — — | — — — — | — — — | — — | |
| 79 Au | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 1 | |
| 80 Hg | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 2 | |
| 81 Tl | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 2 1 | |
| — — | — | — — | — — — | — — — — | — — — | — — | |
| 86 Em | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 4 4 | |
| 87 — | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 4 4 | 1 |
| 88 Ra | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 4 4 | 2 |
| 89 Ac | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 4 4 1 | (2) |
| 90 Th | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 6 6 6 | 4 4 2 | (2) |
| — — | | | | | | | |
| 118 (?) | 2 | 4 4 | 6 6 6 | 8 8 8 8 | 8 8 8 8 | 6 6 6 | 4 4 |

The elements are arranged in the order of their atomic numbers, given at the left. The figures at the top indicate the quantum numbers, the principal quantum number being the larger figure and the subordinate quantum number the subscript figure. The figures in the body of the table indicate the number of electrons in orbits of specified quantum numbers in that particular atom. For example, the atom of sodium has two electrons in orbits having quantum numbers (principal and subordinate) of $1_1$; four electrons in orbits of $2_1$; four in orbits of $2_2$; and one in an orbit of $3_1$. The seven periods of Bohr's periodic arrangement are marked off from each other by the horizontal lines.

(This table is the one used by Bohr in his lectures and published in connection with his Nobel Prize address.)

begin new series of larger orbits. One of their electrons occupies an orbit of higher quantum number than the other electrons. This is typical of the way in which the idea of successive groups of orbits of increasing quantum number fits into and explains the chemical similarities and dissimilarities of the elements.

### Some Atomic Sizes

From the mathematical basis of the Bohr theory and from accepted values for the electronic charge, for Avogadro's number and for other constants, it is possible to calculate the numerical characteristics of the orbits in the Bohr atom. The diameter of the innermost hydrogen orbit comes out as $1.06 \times 10^{-8}$ cm. For the other elements the diameter of the innermost orbit is smaller because of the greater attraction of the increasing nuclear charge. In the carbon atom, for example, the innermost orbit has a diameter of approximately $0.18 \times 10^{-8}$ cm., while the next orbit has a diameter of $0.70 \times 10^{-8}$ cm. The innermost orbit of the uranium atom, which is the smallest electron orbit known, has a diameter of about $0.012 \times 10^{-8}$ cm., still quite large in comparison with Rutherford's maximum value of $6.8 \times 10^{-12}$ cm. for the order of diameter of the nucleus.

These figures for the *orbital* diameters cannot be applied directly to the calculation of *atomic* diameters, inasmuch as the orbits are elliptical and the mutual arrangement of these ellipses in space will have much to do with the effective diameter of the atom.

The following illustration may help to visualize atomic sizes: Suppose that an inch-square piece of graphite is enlarged until it covers the entire orbit of the earth, 190,000,000 miles from side to side. The nuclei of the carbon atoms would be, then, about $1^{1}/_{8}$ miles apart. Each nucleus would be perhaps a foot in diameter (the exact size of the nucleus is in doubt) and each planetary electron would be about $1^{3}/_{4}$ inches in diameter. If you stood on one of the 12-inch globes corresponding to a nucleus, the two nearest electrons would be revolving around you at an average distance of about 350 feet, while the four outermost electrons would be at an average distance of about $1/_4$ mile.

This picture of matter is astonishingly open. The particles of it turn out to be even farther apart, relatively, than the planets of our solar system.

### Some Remaining Mysteries

The Bohr theories have little to say about the problem of atomic energy. It is possible with their aid to calculate the ionization potential of an atom—that is, the voltage necessary to drive an electron entirely out of a given orbit in a given atom. This voltage, however, is presumably much smaller than would correspond to the total energy of the atom. The only kind of atomic energy that we really know much about directly, the energy of radioactivity, is probably related to the still unknown structure of the nucleus.

So, also, are the phenomena of transmutation, recently investigated so brilliantly by Rutherford. It is permissible, the writer believes, to hope for the ultimate attainment both of useful transmutation of the elements and of useful atomic power; but the path to neither of these ends is as yet apparent, nor is there any inkling of the nature of that greatest mystery of all, the mystery of electromagnetic radiation. What *is* light? What really happens when, as we say, an electron "jumps" from one of its orbits to another? About this there is not even a plausible guess. Matter and radiation are the two halves of a puzzle which we do not yet see how to join.

### Bibliography

The best summary of the Bohr theories with which the writer is acquainted is a special issue of *Die Naturwissenschaften* (Berlin), entitled "Die ersten zehn Jahre der Theorie von Niels Bohr über den Bau der Atome," and published as Vol. 11, Heft 27, pages 533–624 (July 6, 1923). This contains numerous articles on the present status of the theory and also the text of

an excellent summary address by Bohr himself, delivered on the occasion of his receipt of the Nobel Prize in physics in 1922. This same address was published in English as a special supplement to *Nature* (London), Vol. 112, supplement pages 29–44 (July 7, 1923). It is available in pamphlet form from the publishers of *Nature*.

The summary of general atomic theory which, in the writer's opinion, is the most satisfactory one for chemists is the brilliant and suggestive monograph of G. N. Lewis, entitled "Valence and the Structure of Atoms and Molecules," published by The Chemical Catalog Co., New York, 1923, as one of the Monograph Series of the American Chemical Society.

For the physicist the best summary seems to be "The Structure of the Atom," by E. N. da C. Andrade, published by G. Bell & Sons, Ltd., London, 1923. As an introduction to atomic theory for students or for workers in remoter sciences, there is nothing better than "Within the Atom" by John Mills, published by D. Van Nostrand Co., New York, 1923. The works of Lewis and Andrade furnish ample introduction to the literature for students interested in credits, history or bibliography.

# Nitrogen Survey

As a result of a special congressional appropriation made available to the Department of Commerce in March, 1923, J. Foster Bain, director of the Bureau of Mines, went to Chile last summer to investigate nitrate conditions. The result of this investigation is reported in *Trade Information Bulletin* **170** of the Bureau of Foreign and Domestic Commerce. This report is issued as Part I—The Cost of Chilean Nitrate—of a series of reports on the several phases of the nitrogen problem, including the Chilean nitrate situation, the present domestic sources of fixed nitrogen supply, the economic role of nitrogen in American agriculture, the status of the air-nitrogen industry, and the nitrogen supply in various countries. All these reports are being prepared under the general supervision of Harry A. Curtis, special agent of the Bureau of Foreign and Domestic Commerce. Julius Klein in the foreword says:

The situation with reference to Chilean nitrate is therefore but one phase of the larger problem of securing a supply of fixed nitrogen adequate to the Nation's requirements and at a price which will permit its use wherever desirable. Considerations of national defense impose the further condition that in event of war the Nation must be able to meet its total military requirement of fixed nitrogen by drawing on domestic sources of supply. There is but one evident solution of the problem under these conditions, and that is through the development of a domestic air-nitrogen industry to supplement the present by-product supply from coal processing.

Apparently there is no reason to anticipate any shortage of Chilean raw material. In fact, the supply is probably sufficient to meet the demand for one or more centuries. The importance of materially reducing the price of nitrate is recognized, but at the same time it is realized that this reduction will be brought about, if at all, in the ordinary way by competition from other forms of fixed nitrogen and will be realized step by step.

Finally, the authors conclude:

Every argument points to favor American participation in production of nitrate and the fixing of its price. There seems no sound reason to anticipate the finding of important supplies of natural nitrate outside of Chile. A natural monopoly exists in that country, a fact not changeable and which is fully appreciated by Chileans. Whether or not artificial nitrates can be produced at a price lower than Chilean nitrate can be imported is a question not within the scope of this particular report. If one may judge from what has happened in the case of other nitrate products in the United States, they are not likely to be sold at a lower than the competing price for a considerable period regardless of their cost of production. Until their volume becomes large in proportion to the consumption, and until the higher costs incident to establishment of a new industry be overcome, it seems likely that in any event the price of Chilean nitrate will continue to fix the price of fixed nitrogen in general in the United States. If this be so, there is added reason for encouraging rather than discouraging American participation in the Nitrate Producers' Association as a national policy, so as to bring the largest possible measure of influence to bear directly in favor of lower prices.

# Samuel Philip Sadtler—Ulysses in Chemistry[1]

WHEN General Robert E. Lee thundered at the gates of the North at Gettysburg in July, 1863, he temporarily interrupted the education of Samuel Philip Sadtler, a student at Pennsylvania College there. Sadtler was then about sixteen years old, having first seen the light of his native State, Pennsylvania, at Spring Grove, July 18, 1847, where his father, Rev. Benjamin S. Sadtler, Lutheran minister and for ten years president of Muhlenberg College, had a charge.

The steps whereby this earnest God-fearing lad developed into a patriarch of our science, respected for his wisdom and ability, admired for his sterling character, and loved for his kindly personality, brought him in contact with "cities of men and manners, climates, councils, governments."

In 1867 he began his first year of postgraduate study at the newly established Lehigh University at Bethlehem, Pa., and then went to the Lawrence Scientific School at Harvard, under Walcott Gibbs, where he received his B.A. in 1870, and finally to Göttingen under Wöhler and von Waltershausen, where he received his Ph.D. in 1871. Henry Carmichael, of Boston, Nathaniel Terry, subsequently professor of physics at Annapolis, and Ira Remsen were at Göttingen in those days.

SAMUEL P. SADTLER

Returning to America, he was successively professor of chemistry at Pennsylvania College, professor of general and organic chemistry and later of organic and industrial chemistry at the University of Pennsylvania, and professor of chemistry at the Philadelphia College of Pharmacy. Upon his retirement a complimentary dinner was given him by the American Pharmaceutical Association, and he was made professor emeritus.

As a lecturer his clear, direct, concise style popularized him and his subject even with obtuse or indolent students, and it was fortified by his custom of giving from memory a resumé of the preceding work as well as writing on the blackboard a synopsis of the current lecture.

He was not merely an efficient teacher. Concurrently, from 1880 to 1918, he was chemical editor of the U. S. Dispensatory, and from 1900 to 1920 he was an active member of the Revision Committee of the U. S. Pharmacopeia, helping to fix the meaning of "U. S. P." Apart from journal articles, his most important publication is his "Handbook of Industrial Organic Chemistry," first published in 1891 and now in its fifth edition (with J. Matos). Authorized German and Russian editions indicate its value. In 1894 appeared his "Textbook of Pharmaceutical Chemistry," and the work known as "Sadtler and Coblentz Pharmaceutical Chemistry" is now in its fifth edition.

Nor did his activities stop there. The Second Geological Survey of Pennsylvania contains analyses of the natural gas and crude petroleums which he gathered and examined, and his practice before the courts as chemical expert extended over forty years. Beginning with the Demarara colored sugar case in 1878, he appeared in many famous litigations, among which were those involving chloroform, chrome tanning, linoleum, calcium carbide, adrenalin, ore flotation, blown asphalt, cement-asbestos slate, hydrogenation, and petroleum cracking.

On the 22nd of June, 1908, a blazing hot day with a temperature

quite in harmony with the enthusiasm of the body of earnest men gathered in Philadelphia to found the American Institute of Chemical Engineers, Professor Sadtler was elected its first president. In 1902 Pennsylvania College conferred upon him the degree of LL.D. He was secretary of the American Philosophical Society from 1898 to 1902, and was long president of the publication board of the Lutheran Church. His society memberships included the American Chemical Society, American Electrochemical Society, Society of Chemical Industry, Société de Chemie Industrielle, Chemical Societies of London and of Berlin, Chemists' Club, Engineers Club, University Club (of Philadelphia), American Pharmaceutical Association, Franklin Institute (emeritus professor of chemistry).

"No man can be a hero to his valet," said Napoleon; but from the intimates and associates of Professor Sadtler one continually learns more to admire in this indefatigable and modest worker. "If any new work appeared," says Virgil Coblenz, "Sadtler was one of the first to have it on his shelves. Personally, he is a most kind, considerate, and tactful man. Never, in all my personal experience have I met a man who possessed such an ideal character."

Professor Sadtler's deliberateness usually meant that the "anecdote" was about the other fellow; but he had nevertheless the saving grace of humor. R. C. Canby, his former student and associate in many patent cases, tells of their agreement to breakfast together. Canby used to read until 7:30 A. M., and as it took him two minutes to reach the breakfast room, remarked that they "breakfasted at seven thirty-two." Sadtler repeated this to his daughter, and chuckled over her disgust with a person who would "breakfast at seven thirty-two, like a railroad train." Canby speaks of his "peculiar quietness of manners and speech, an indescribable charm, yet none the less distinct and powerful. You at all times feel perfect confidence and respect for him, professionally and personally. As for myself it is a real affection."

> I am a part of all that I have met;
> Yet all experience is an arch wherethro'
> Gleams that untravel'd world, whose margin fades
> Forever and forever when I move.

JEROME ALEXANDER

## Passing of Dr. Stillman

It is with regret that we announce the death, on December 13, 1923, of John Maxson Stillman, professor emeritus of chemistry at Leland Stanford University. A sketch of Dr. Stillman's life appeared as one of our series of American Contemporaries in the December, 1923, number of THIS JOURNAL.

India Promotes Technical Education—Notwithstanding the financial stringency which has prevented the initiation of many new schemes in the Punjab Province, India, definite progress has been made in meeting the demand for practical educational facilities. In the interests of industrial activities, therefore, the provincial Government has recently taken over the entire management of eight industrial schools hitherto supported by Government grants but controlled by local organizations.

[1] This material was about to appear as one of our series of American Contemporaries when we were advised by telegraph of the sudden death of Dr. Sadtler on December 20, 1923, following an operation.—Editor's Note.

# PERKIN MEDAL AWARD

THE seventeenth impression of the Perkin Medal was presented to Frederick M. Becket in recognition of valuable original work in applied chemistry, on Friday evening, January 11, at the Chemists' Club, before a large gathering of chemists, at a regular meeting of the American Section of the Society of Chemical Industry. The meeting was presided over by Ralph H. McKee, chairman of the section, and Charles F. Chandler, senior past president of the Society of Chemical Industry residing in the United States, made the presentation.

The meeting was opened with brief introductory remarks by Chairman McKee, who called attention to the fact that the date of the award coincided with the birthday anniversary of the recipient, and related the history of the medal as follows:

On July 26, 1906, there gathered in London in the hall of the Royal Institution, in which Michael Faraday eighty-one years earlier had discovered benzene, a notable group to honor Sir William Henry Perkin for his discovery of mauve fifty years previously. At that meeting Dr. Baekeland presented a congratulatory address in behalf of American chemists.

A little later Perkin came to America, and there gathered at Delmonico's, for a dinner in his honor, four hundred of those interested in chemistry to celebrate in similar manner the discovery of the first aniline dye. Dr. Chandler, whom it is our pleasure to have with us tonight, presided as chairman of that notable dinner gathering. The previous month a sum of money was raised by subscription and presented to the American Section of the Society of Chemical Industry to found a medal for work in applied chemistry. At this dinner W. H. Nichols presented the first Perkin Medal to Sir William Perkin with words of love and appreciation from American chemists. He further called attention to the fact that this medal was "to be given hereafter annually to the American chemist who has most distinguished himself by his services to Applied Chemistry." In the years that have since elapsed this has been done, and the list of Perkin medalists (given below) is now the honor roll of American chemistry.



FREDERICK M. BECKET

J. H. Critchett, one of Mr. Becket's close associates, related some personal impressions of the medalist, calling attention particularly to the thoroughness with which he conducted all investigations. Mr. Becket's boundless energy, constructive imagination, wonderful grasp of detail, and remarkable memory were referred to and illustrated. His ability to read character, his capacity for organization, his fairness to those who worked with him, and his high scientific ability were also emphasized and lauded by Mr. Critchett.

Clinton P. Townsend, patent attorney, who had been associated with much of Mr. Becket's progress, spoke on "Becket and His Work." He mentioned that a total of sixty-four patents had been granted the medalist, the first one in 1906 and the last one in 1923. Each of these patents represents in its specifications a complete technical paper, said Mr. Townsend, and Mr. Becket would never consent to having specifications for any of his patents written until his work had been carried absolutely to completion. The speaker emphasized the points that Mr. Becket always moved toward the larger objective, that he had a keen "economic sense of direction," and that he had designed, built, and operated the largest electric furnaces in the world.
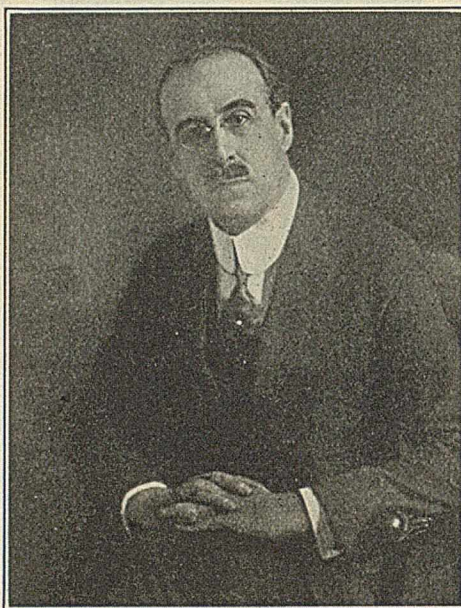
Charles H. Herty brought a "message from Canada," which consisted of a resolution expressing the satisfaction and pride of the Montreal Section of the Society of Chemical Industry in the award of the Perkin Medal to Mr. Becket, who is a native of Montreal. Dr. Herty had been requested to deliver this resolution to the medalist on the former's recent visit to that section.

Leo H. Baekeland, president-elect of the AMERICAN CHEMICAL SOCIETY, congratulated the recipient on behalf of the SOCIETY and expressed pride in the fact that Mr. Becket has been a member of the SOCIETY for many years.

Charles F. Chandler, in presenting the medal to Mr. Becket, gave a brief biographical sketch of the recipient and said that he has been chiefly interested in processes for the extraction of the rarer metals from their ores and in the manufacture of calcium carbide; that he has invented processes for the reduction of the rarer metals, such as molybdenum, vanadium, titanium, tungsten, zirconium, and chromium, and alloys with each other and with the common metals, for which he has received sixty-four patents from the United States Government. In conferring the medal Dr. Chandler then spoke as follows:

Frederick M. Becket, Bachelor of Applied Science and Master of Arts: It gives me great pleasure as 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.

Mr. Becket received the medal amid the prolonged applause of the audience, which had risen during the presentation, and then read the following address:

| DATE OF AWARD | AWARDED TO | PRINCIPAL FIELDS OR INVENTIONS |
|---|---|---|
| 1907 | Sir W. H. Perkin | Discoverer of first aniline color |
| 1908 | J. B. F. Herreshoff | Metallurgy; contact sulfuric acid |
| 1909 | Arno Behr | Corn products industry |
| 1910 | E. G. Acheson | Carborundum; artificial graphite |
| 1911 | Charles M. Hall | Metallic aluminium |
| 1912 | Herman Frasch | Desulfuring oil and subterranean sulfur industry |
| 1913 | James Gayley | Dry air blast |
| 1914 | John W. Hyatt | Colloids and flexible roller bearings |
| 1915 | Edward Weston | Electrical measurements; electrodeposition of metals; flaming arc |
| 1916 | L. H. Baekeland | Velox photoprint paper; bakelite and synthetic resins; caustic soda industry |
| 1917 | Ernst Twitchell | Saponification of fats |
| 1918 | Auguste J. Rossi | Development of manufacture and use of ferrotitanium |
| 1919 | Frederick G. Cottrell | Electrical precipitation |
| 1920 | Charles F. Chandler | Noteworthy achievements in almost every line of chemical endeavor |
| 1921 | Willis R. Whitney | Development of research and application of science to industry |
| 1922 | William M. Burton | Achievements in oil industry; efficient conversion of high-boiling fractions into low-boiling fractions |
| 1923 | Milton C. Whitaker | Great constructive work in field of applied chemistry |

# Perkin Medal Address

By Frederick M. Becket

ELECTRO METALLURGICAL CO., NEW YORK, N. Y.

NEVER having cherished the hope nor even having dreamed of the possibility of receiving the honor represented by the Perkin Medal, I now in truth feel humble—humble because of the achievements of former Perkin Medalists, the most beloved of our chemists, Dr. Chandler, being a present and outstanding example; and, further, because I am only one of several contributors to the development of certain successful electric furnace industries in this country.

When I received notification from Dr. Rogers of this award, my first and immediate emotion was an enhanced determination to perform more and better work, and thus assist in maintaining Perkin Medal standards. Shortly thereafter, the significance of this honor dawning upon me and a wonderment crossing my mind as to how it could have possibly come to me, I took from my pocket a tattered paper bearing a quotation from Cushman K. Davis which has been an inspiration to me, and showed it to an associate, who insisted that it be inserted in an issue of our employees' magazine, with the hope that some of our young men might gain the same inspiration. I quote:

The men who have achieved are the men who have worked, read, thought more than was absolutely necessary, who have not been content with knowledge sufficient for the present need, but who have sought additional knowledge and stored it away for the emergency reserve. It is the superfluous labor that equips a man for everything that counts in life.

Superfluous labor is, I believe, the only reason for my presence before you this evening.

To the Committee of Award and the chemical societies thereon represented I express my deep gratitude for the honor you have conferred upon me, fully appreciating my increased responsibilities.

Rather than ask you to follow a detailed description of a single process or product, I have deemed it more interesting to discuss broadly the field of ferroalloys and certain alloying metals. None of the metals in this category appear as finished industrial materials, and probably for this reason their importance to industry is not generally appreciated, even among chemists. Nevertheless, the members of this group of metals contribute to and in several cases wholly impart the valuable properties to numerous products employed in the arts. I therefore feel justified in attempting to set forth here a fair appraisal of the essentiality of this relatively young industry, in addition to describing briefly some of the historical and technical features of a number of these metals.

Commercial ferroalloys now utilize the specific effects to be obtained from about a dozen metallic elements, although various combinations of these elements lengthen the list to a score or more. Several of these alloys are interesting and important. However, in an address of this character I trust that I may be pardoned for very brief mention of some important alloys and for dwelling at greater length upon others in whose industrial development I have been most actively engaged, especially products in the manufacture of which the electric furnace plays an important part.

You are all aware of the necessity of deoxidizing or scavenging molten steel, whether made by the open-hearth, bessemer, electric furnace, or crucible process. This is the most important role of some of these ferroalloys. Other alloys are designed to remain in the steel in appreciable percentages and result in the remarkable alloy steels of high strength, toughness, hardness, or resistance to corrosion, as well as in other products not classed as steels which will appear as we proceed.

## FERROSILICON

Let us first turn our attention to that alloy most often used for deoxidizing steel—ferrosilicon. Credit is due, I believe, to Guillaume de Chalmot for the experimental work and inventions which eventuated in the commercialization of electric furnace ferrosilicons containing 25 per cent and higher contents of silicon. This work was conducted between the years 1893 and 1895 at Spray, N. C., in the plant where commercial production of calcium carbide was started. Europe (chiefly France and Switzerland) soon thereafter commercialized electric furnace ferrosilicons abroad and exported to the United States in gradually increasing quantities for several years prior to actual manufacture in this country.

In 1907 the commercial production of ferrosilicon was started at Niagara Falls, N. Y., in electric furnaces of considerably larger capacity than had ever before been constructed. The year 1907 is an important one in the history of the American ferroalloy industry, because, in addition to ferrosilicon, this year saw the commercial application of processes for the manufacture of some other alloys the production of which has been also continuously maintained.

Many were the difficulties and disappointments that resulted from this very attempt to utilize relatively large units. Electrical rather than metallurgical problems predominated, and these were chiefly due directly or indirectly to the unexpectedly high electrical inductance and therefore low power factor of these furnaces. Think of designing a furnace for a given load and carefully applying past electric furnace experience in the copper work, electrode, and other details, only to find that because of a very low power factor sufficient electrical energy could not be developed in the furnace to attain the temperature required for efficient metallurgical operation, not to mention specifically the numerous troubles that resulted from the very heavy currents drawn in these low power factor circuits. Bearing in mind that all this was not the work of novices, but of several engineers of considerable commercial electric furnace experience, including my own experience, which had involved a careful study of power factor in more than one particular case, you can readily understand, not only the keen disappointments, but the ultimate great value derived from these failures. The fragility of the large electrodes of those days was a source of much trouble through interrupted operation. Moreover, much was then learned concerning the effect of the physical nature of the raw materials, and particularly the effect of all classes of carbonaceous reducing agents, on the electrical characteristics of the furnace. However, although these sad experiences were dearly bought because of the relatively large scale of the operations, they were later capitalized to great advantage, not only in the manufacture of ferrosilicon, but also in the large furnace production of calcium carbide. The work progressed, and it was not long before still larger and quite efficient furnaces were in operation. In view of your natural pride in the success of domestic industries, it should interest you to know that not only have we regularly operated at Niagara Falls, N. Y., for at least the past fourteen years, appreciably larger furnaces than have been employed in Europe, which I realize is not in itself a criterion of success, but both the energy and metallurgical efficiencies have exceeded the results obtained in the European countries manufacturing ferrosilicon. Indeed, these higher efficiencies have assisted greatly in meeting the competition of Europe, where hydroelectric power, labor, and often the raw materials have been more cheaply obtained than in this country.

Metallurgical difficulties were not great, relatively speaking, during our early history in the ferrosilicon business. However, let me draw your attention to the peculiar phenomenon generally known as the disintegration of ferrosilicon. Numerous explosions and several deaths in Europe led to investigations which resulted in the conclusion that phosphine liberated from disintegrating ferrosilicon was the cause of these disasters. Regulations governing the transport of ferrosilicon were formulated and many of the prominent steamship companies would not accept this alloy for delivery across the Atlantic. Most of the exporters of ferrosilicon to the United States adopted the preventive measure of dipping the alloy in paraffin, but as the paraffin coating was disliked in this country we desired to eliminate the necessity of the treatment by producing a stable 50 per cent ferrosilicon.

Our first commercial supply of siliceous material was red sandstone from the Medina district about thirty-five miles from Niagara Falls. I say "red sandstone" because a fairly exhaustive investigation made in the fall of 1906 led us to the conclusion that the red variety from certain districts was satisfactory, whereas an abundant supply of white sandstone in even closer proximity to the plant was quite worthless, due to the relatively high content of calcium phosphate. Unfortunately, as quarrying progressed the red stone became more and more mottled with the white variety, and serious disintegration difficulties were encountered until supplies of high-grade silica rock could be obtained from Pennsylvania, which were depended upon for some years thereafter and were later largely replaced by even higher grades of quartzite.

On May 22, 1914, Dr. Charles E. Pellew read a paper entitled "Ferrosilicon and Its Dangers" before the Society of Chemical Industry in this room, describing the results of an investigation he had conducted at the request of the American Association for Labor Legislation. I quote Dr. Pellew's conclusion:

As a result, therefore, of all the information that I have been able to gather, it seems to me that it would be a decided mistake for the United States to follow the foreign regulations with regard to the manufacture and shipment of ferrosilicon, based upon the supposition that the grades commonly used (containing between 30 and 70 per cent of silicon) are necessarily dangerous. It seems to me that this supposition is distinctly erroneous, and that the danger attaching to much of the foreign ferrosilicon has been due, not to the percentage of silicon, but to the presence of avoidable impurities—phosphorus, arsenic, and especially calcium.

In the United States and Canada the natural laws of trade have in this particular instance brought about, as satisfactorily as Government regulations could do, the use of pure materials and the production of a safe and stable article. And, in my opinion, it is greatly to be regretted that the export of this pure ferrosilicon is hampered by foreign regulations based, I must conclude, upon insufficient investigations.

To reiterate, disintegration of ferrosilicon is a decidedly peculiar phenomenon. The grades between 50 and 60 per cent silicon are markedly more susceptible to this action than the alloys of higher or lower silicon content. I have prepared ferrosilicons within this range that have completely disintegrated to powder in an ordinary atmosphere after a few hours' cooling, the total impurities having been comparatively low. On the other hand, we have produced in large quantities stable ferrosilicon of all the percentages within this same range, and some samples of these alloys taken fourteen years ago are still in stable condition. Several papers by foreign investigators have been presented in explanation of this singular behavior of ferrosilicon, but from my own study of the subject, which has been chiefly practical in nature, I am convinced that not all the influential factors have been discovered. One thing we do know positively, and that is the practical means of avoiding disintegration. By keeping the phosphorus content of all raw materials extremely low, the trouble vanishes; if this precaution is not observed on economic grounds, then the producer of 50 per cent ferrosilicon

must face the even more troublesome task of maintaining below certain low maxima the percentages of other elements—for example, calcium and aluminium. In certain minor uses powdered ferrosilicon is the preferred form, but these uses generally call for alloys of 75 per cent and higher silicon content in which disintegration is not a difficulty. The manufacturer of open-hearth steel—and this product consumes a large proportion of the total output of ferrosilicon—does not wish to use the grades of lower silicon content, say even the 40 to 45 per cent alloy; he demands, for good reasons, a ferrosilicon in lump form containing approximately 50 per cent silicon. Thus the ferrosilicon operator, like the blast furnace and steel men, must persistently watch the quality of his raw materials, not only because of their influence on the quality of the finished product, but also on account of their effect on furnace efficiencies and general furnace behavior.

What are the principal uses of ferrosilicon, and what of its importance? Over 75 per cent of the total steel produced in the United States is made by the basic open-hearth process. Ferrosilicon of the 50 per cent grade and in lesser extent ferros of higher silicon content are employed as the principal deoxidizers of substantially all basic open-hearth steel. Considering that these grades of ferrosilicon are used to some extent in all other steel-making processes, the figure 90 per cent can be given as an approximation of the proportion of steel in this country into which these alloys enter. The advantages in the use of ferros of 50 per cent and higher silicon content are such that, were we compelled to fall back on the blast furnace product, containing even up to 15 per cent silicon, our steel-making practices would have to be greatly modified, the production costs would increase, and huge investments would be necessary in the way of melting cupolas and other auxiliary equipment.

The steel-casting industry is well-nigh dependent on electric furnace ferrosilicon for the production of sound castings, adding enough of this material to yield about 0.3 per cent in the finished steel. In the manufacture of spring steels sufficient silicon (1.5 to 2 per cent) is added to impart special physical properties, and almost all your precious automobiles are equipped with so-called silico-manganese steels. Passing to steels of still higher silicon content, I must mention the "non-aging" steels so largely used in electrical apparatus. With a silicon content of 3.5 to 4.5 per cent and after proper heat treatment, the hysteresis curves of these steels represent less energy expenditure and remain much more permanent than the previously used best soft irons. These steels have effected a tremendous saving, not only in power, but in the cost of periodic renewals of inefficient transformer cores. In the manufacture of transformer sheet the alloys of 75 to 90 per cent silicon content are preferred.

The inflation of dirigible and other balloons requires the generation of hydrogen in considerable quantities, and in military operations the gas is often needed in large and promptly available quantities at frequently shifting points. During the war large quantities of 80 to 85 per cent ferrosilicon were consumed for this purpose. The simplicity of the well-known reaction between silicon and caustic soda, the large volume of hydrogen liberated per pound of transported raw material, and the portability of the generating plant admirably suited this process to war service. In general, however, this process is not an economical one for large permanent installations.

I believe an erroneous impression existed for a good many years concerning the status of the electric furnace alloy industry of the United States, largely because prior to the war there appeared in the technical and popular press numerous references to the much greater progress that had been made in Europe in the ferroalloy and other electric furnace industries, and also because of similar statements in more recent years to the effect that the war "made" the ferroalloy industry of the United States. May I do a little here toward modifying this adverse view, and

by occasional remarks under the various headings in what follows, have you look more appreciatively upon the enterprise and accomplishments of our own country. So far as ferro-silicon is concerned, there was sufficient producing capacity in this country by the year 1910 to meet the entire consumption, and imports had dropped to a small proportion—in fact, most of the imports came from a plant located at Welland, Ontario, which commenced manufacture not long after the Electro Metallurgical Company started at Niagara Falls. When in 1915 an unprecedented demand for ferrosilicon arose in the United States, as well as in Canada and the European countries, the Electro Metallurgical Company met the domestic emergency by practically doubling the production within a period of a few weeks. Of course, such an accomplishment was not made without sacrifice, which in this case affected the output of an allied industry, calcium carbide. I believe it no exaggeration to state that without this greatly augmented supply of ferrosilicon the United States producers would have been compelled to curtail greatly the orders for steel for European account, especially shell steel, which averaged an unusually high content of silicon. Continuance of the war resulted in still greater demands, and additional equipment was installed to such an extent that at all times during this strenuous period the limitation was that of available power and not producing capacity. As in many other industries, the peculiar conditions of war time invited the formation of new companies and the construction of some new plants; but, again drawing an analogy to other industries, not all of these have survived.

Briefly, then, notwithstanding the relatively small tonnage of imports during that period, the United States has been potentially and, as a matter of fact, actually independent of Europe for all grades of ferrosilicon for at least the past fourteen years. The importance of this military independence from the standpoint of maintaining in the United States an industry upon which the economical production of steel depends can be scarcely overestimated.

## SILICON METAL

Some day the commercial world may decide where ferro-silicons end and silicon metal begins. I have in mind a product containing at least 95 per cent silicon in which iron is generally considered an impurity.

The excellent pioneer experimental work and later commercialization of "metallic silicon" by F. J. Tone, of the Carborundum Company, deserves much praise. I obtained some of the products of Tone's early runs; and how well I remember on one occasion about twenty years ago having induced him to let me have a few hundred pounds of his only supply on hand, which consisted of a fused mixture of silicon and fire brick. Quantitative experimentation with this mixture compelled me to face the then difficult problem of determining the proportion of silicon as metal and that existing as $SiO_2$. To my friend Tone I felt indebted for a good many years for the continued availability of his product.

The most recent important application of silicon is the use of appreciable percentages (up to 17 per cent) in aluminium castings, which actually arose from the brilliant work of Aladar Pacz on aluminium-silicon alloys. The physical properties of these alloys are remarkably enhanced when modified by the Pacz treatment, and probably of even more importance is the fact that their lower shrinkage in castings has done much to remove what was formerly the bane of aluminium foundrymen. If you possess a recently made motor car, it may have a crank case and other parts of aluminium-silicon alloys; if it has not, you will almost surely own one in the future, because these alloys are of high merit and represent a marked improvement.

At Dr. Pacz's request I had prepared for some of his experimental work several different lots of silicon metal, including a lot of very exceptional purity, and I also sent to him a series of silicon-aluminium alloys, the 60-40 grade of which was used to a considerable extent in the early commercial development of aluminium-silicon castings. Dr. Pacz determined early in his work that iron was markedly detrimental, a point since amply confirmed in the industry. The entire demand has been met by our commercial production of a silicon metal containing at least 97 per cent silicon and less than 1 per cent iron.

Finally for this product, it may be of interest to remark that we are regularly producing a silicon metal of less than 0.2 per cent iron and over 98 per cent silicon.

### FERROMANGANESE

Although essential in the making of all steel and used in larger quantities than all other ferroalloys combined, I shall not discuss this series of alloys, because they are generally the products of blast furnaces and the industry has been much longer established than any of the industries employing the electric furnace for the smelting of more difficultly reducible metals. Electrothermic smelting of manganese ores is entirely practicable, but the method is economical only under very exceptional conditions.

The domestic demand for 80 per cent ferromanganese increased so rapidly in 1915, as was the case with ferrosilicon, that some of our steel friends asked us to come to their immediate assistance. This was promptly undertaken, and after a week's contribution to the skies of huge volumes of brown manganese smoke, which caused much comment, the large electric furnace employed for this purpose was brought into first-class metallurgical operation, a satisfactory product and higher recoveries of manganese than represent blast furnace practice having been obtained. Of course, such flexibility as has been indicated would hardly be practicable apart from a very large and diversified electric furnace plant.

Alloys of manganese, silicon, and iron in different proportions are commercial products of the electric furnace. They are somewhat more preferred in the steel-making practice of Europe than in this country, but there is a steady domestic demand which is readily met by home production.

A few words about manganese metal itself, a much more costly product in which iron is considered an impurity. It has been on the market for a good many years, chiefly produced by the alumino-thermic reaction. In recent years we have succeeded in making high-quality manganese metal by electric furnace methods, and a grade is now commercially available containing over 97 per cent manganese, less than 1 per cent each of iron and silicon, substantially no aluminium, and a carbon content of not over 0.05 per cent if desired. Manganese metal finds its chief applications in the electrical alloys of nickel-chromium, in the bronzes, and in alloys of the nickel-silver family. Some manganese is used in practically all forgeable alloys containing appreciable proportions of nickel—a point of considerable metallurgical interest, though far afield in this discussion.

### FERROCHROMIUM

So interesting and extremely important is the element chromium in modern metallurgy that I first thought of taking it as the subject of my entire address, my own interest in the development of chromium alloys and the applications of chromium having been continuous during the past twenty years. Chrome steels were among the very earliest alloy steels developed. During the period between 1880 and 1895 the properties of chrome steel were commercialized for a few specific purposes; for example, chromium-containing projectiles were manufactured which would penetrate any armor then in existence, so nickel and later nickel-chromium armor plate were developed in an attempt to make the armor withstand the improved pro-

jectile. To meet the demand of those days, ferrochrome was produced in furnaces of the crucible type and in small blast furnaces. Both processes were inefficient and costly, and the products were inferior in quality.

Moissan's laboratory work (1892–1895) with electric furnaces in the reduction of refractory oxides has of course become classic, and the Goldschmidt alumino-thermic process was utilized at an early date in the commercial production of chromium. De Chalmot experimented in 1896 at Spray, N. C., on the reduction of chrome ores in the electric furnace. Then in 1897, Major J. T. Morehead, to whom the calcium carbide and ferroalloy industries are so greatly indebted for his perseverance and far-sightedness, converted a section of an old state canal at Holcomb Rock, Va., into a hydroelectric station and started the commercial production of ferrochromium. The demand for this alloy so increased, especially during the Spanish-American War, that Major Morehead deemed it wise to construct a larger plant at Kanawha Falls, W. Va., which commenced operation in 1901. This plant has been operating continuously on ferrochromium ever since that time, and it was purchased by the Electro Metallurgical Company in 1907. The Holcomb Rock plant, also subsequently purchased by the same company, has been producing ferrochromium continuously for many years.

While independent of Europe during this long period in the manufacture of high-carbon ferrochromium—and indeed the two plants mentioned contributed to Europe in the early days of their history—this country had imported all its supplies of the more expensive, low-carbon grades of ferrochromium, these being used to a lesser extent but nevertheless essential in many applications. Through purchase of the Niagara Research Laboratories the Electro Metallurgical Company acquired the rights to several of my early processes for the production of low-carbon ferroalloys, and in 1907 the commercial manufacture of low-carbon ferrochromium was started in earnest. Since that time a very large proportion of the domestic consumption of this alloy has been produced at the Niagara Falls plant.

Metallurgically speaking, the manufacture of high-carbon ferrochromium (5 to 6 per cent carbon) has been a highly efficient operation for many years, gradual improvements having been made in the chromium recoveries and energy yields. Again speaking metallurgically, and also from the point of view of furnace design, the problems involved in the commercial production of low-carbon ferrochromium (under 0.50 per cent carbon) were vastly different and much more difficult. At the Niagara Research Laboratories, where experimentation and occasional manufacture were generally conducted on a 500-horsepower scale, these problems had been substantially solved. Great was the grief in the early days, however. The difficulty with furnace linings was in itself a nightmare, literally; and the electrode problem, together with the necessity of inhibiting contamination of the product by electrode carbon, required many innovations, as did numerous other factors.

Fifteen years ago the lowest carbon content demanded by the steel makers in this series of alloys was 0.50 per cent, but with modified steel practice and the introduction of new steels, carbon contents of 0.30 per cent and later 0.20 per cent were soon requested, and quite recently a demand has arisen for ferrochromium of a maximum 0.10 per cent content of carbon to meet the requirement of a very low-carbon rustless iron containing 12 to 14 per cent chromium. Electric furnace practice has followed the need, and today an alloy of maximum 0.10 per cent carbon is being produced containing 68 to 70 per cent chromium, in which the sum of the chromium and iron contents is not less than 99 per cent.

The various grades of low-carbon and low-silicon ferrochromium have been manufactured during this entire period through the agency of silicon reduction. This method has also been utilized for our production of low-carbon and low-silicon alloys of tungsten, molybdenum, and vanadium, as well as the relatively pure metals manganese and chromium.

Historically, chromium alloys are very important. Probably the first well-established use of chrome steel was in the stamp shoes of milling machinery in the gold mining districts. This use still exists, but it has been greatly expanded to include numerous parts of milling and other machinery, because of the excellent combination of the properties hardness, toughness, and resistance to abrasion that are possible with chrome steels after heat treatment. Great quantities of chromium have been used in warship armor and armor-piercing projectiles, and the efforts of rival armaments greatly hastened development of the art of heat-treating alloy steels. Merely mention the disarmament program and you will appreciate its effect on the manufacture of armor plate, but other important uses of chromium steels and new applications of chromium have been growing at an increasing rate. Either alone or in conjunction with one or more of the elements nickel, molybdenum, vanadium, or tungsten, chromium finds its way into the great majority of alloy steels now produced. Such steels have been described so often in literature and their uses have become so widespread that it will be sufficient to say that the control of both chemical composition and heat treatment permits development of a wide range of the most excellent physical properties. Disregarding the effect of chromium on the hardening transformations, as well as other more or less theoretical points, the value of chromium may be briefly though crudely expressed by stating that it increases the strength and hardness of an engineering steel without destroying the toughness and ductility.

The chromium content of a large proportion of the alloy steels appears within the range up to 2 per cent. Steels for automobiles and other much heavier, high-duty machinery; armor, projectiles, and some ordnance steels; metal-working steels in many applications; and indeed a variety of steels for structural purposes contain less than 2 per cent chromium, many of them approximating only 1 per cent of this element.

Modern high-speed steels take us to a class in which chromium is generally used within the limits 3.5 and 5 per cent, and 4 per cent chromium represents an average. These will be referred to again when discussing ferrotungsten, but in passing it may be well to emphasize the point that the remarkable property of retaining hardness and a cutting edge when operating so fast that the tool becomes red hot is due to a combination of chromium and tungsten, and not to tungsten alone.

Now let us take a higher jump in chromium content and land on the level of "stainless steel," which contains between 12 and 14 per cent chromium and enough carbon to impart the resiliency and hardness required for satisfactory cutlery. The noncorrodibility of chromium metal and ferrochromium has been long known. Aitchison, of England, has shown that chromium is more effective than any other alloying element in retarding the corrosion reactions, because it divides itself between the carbides and solid solution with greater concentration in the latter, and we therefore have one explanation of the nonrusting quality of stainless steel. It is a highly meritorious product deserving of greatly increased popularity, and many uses await it other than in cutlery.

More recently, at least commercially speaking, "rustless iron" made its appearance, first in England and later in this country. It also contains between 12 and 14 per cent chromium; but it differs considerably from stainless steel in its carbon content, the latter usually running between 0.30 and 0.40 per cent carbon, whereas the percentage of carbon in rustless iron is preferably maintained below 0.10 per cent. This difference in carbon appreciably influences the properties. Stainless steel requires a hardening treatment to induce the condition of maximum noncorrodibility. Rustless iron does not require such heat treatment; it is, furthermore, much softer than stainless steel

and more readily rolled, forged, and cold worked. You will understand from a previous statement that in rustless iron containing less than 0.10 per cent carbon almost all the chromium exists in the solid solution phase, and in this state imparts its maximum effect on insolubility; but in stainless steel a much larger proportion of the chromium appears as chromium-containing carbides, which represents a less concentrated and more corrodible chromium-iron solution, as well as a condition affording much greater opportunity for electrolytic action between the carbides and solid solutions. I have used the terms "stainless steel" and "rustless iron" because these terms are being commonly employed in this country.

The cost of producing rustless iron need not preclude diversified application. The material possesses great merit and enormous possibilities. It seems unnecessary to mention specifically present and contemplated uses, since you can easily realize how vast are the quantities of metal annually going to the scrap heap through corrosion, and how great are the expenditures for labor and materials in the use of protective coatings.

By increasing the chromium content to 20 and higher percentages we arrive at a group of products having rather unique and valuable properties. About ten years ago, in order to find a reasonably cheap alloy which would withstand oxidation at over 1000° C. in a tunnel oven, I made a series of experiments with chromium-iron alloys to determine the lowest chromium content at which oxidation would not be progressive, knowing that commercial low-carbon ferrochromium possessed the nonscaling property to a remarkable degree. The results brought to light a rather sharp effect at approximately 20 per cent chromium, above which oxidation was practically negligible after weeks of exposure at 1100° C. The broader field of application possible with forged and rolled alloys of this class was of course obvious, and with additional experimentation this problem was solved.

While contrary to the literature on the subject, I have found that low-carbon chromium-iron alloys containing up to a little over 60 per cent chromium are forgeable, or may be made so by special heat treatments. The 20 to 30 per cent alloys have been readily hot and cold worked, not only into rods, wire, plate, and other shapes, but seamless tubing has been produced. However, in marked contrast to these properties is the extreme hardness of the high-carbon chromium-iron alloys of over 20 per cent chromium, which results in a degree of abrasion resistance equaled by few metallic substances.

In the field of castings, some of these chromium-iron alloys have been commercialized by two or three companies in recent years, and a new industry has been established. In the forged or rolled condition, the combination of high tensile strength and resistance to oxidation at high temperature suggests to the chemical engineer a wider use of the chromium alloys in the manufacture of retorts, stills, and other apparatus in which reactions may be carried on under pressure at temperatures rapidly destructive to ordinary steels.

The remarkable properties of the nickel-chromium series of alloys are well known. Characterized by their high electrical resistivity and their resistance to oxidation at high temperatures, they find use in a great variety of electrical heating devices and in the furnace equipment of many industries.

We have heard of key metals. Tungsten has been so called. But without its companion, chromium, the value of the key would be greatly diminished. Indeed, chromium is essential to an even greater variety of industries, and I believe its potentialities are as far-reaching as any of the less common metals with which it is usually classed.

## Chromium Metal

The iron content of commercial ferrochromium alloys precludes their use in a few important applications, so I shall say a few words about the more costly material, chromium metal, meaning by this term a product containing over 95 per cent chromium.

So called "carbonless chromium" manufactured by the Goldschmidt alumino-thermic process was marketed for many years before production by electric furnace methods was undertaken in the United States about ten years ago. A gradual improvement has been shown in the quality of metal made in the electric furnace, so that we are now regularly producing a metal containing over 98 per cent chromium and less than 1 per cent iron.

Chromium metal is chiefly demanded for use in some of the grades of nickel-chromium electrical resistance elements and in the manufacture of Stellite, an alloy principally employed for tools of exceptionally rapid cutting qualities. In the nonferrous alloys chromium finds use only to a small extent, but some of our own recent work indicates that this offers a fertile field.

## Ferrotungsten

Since cutting tools containing tungsten were commonly used long before tungsten itself was made in the United States, it may be as well to recall very briefly the development of high-speed steel.

The first marked improvement over plain carbon tool steels was made in 1868 by Robert Mushet, who discovered self-hardening steel. Typical Mushet steels contained approximately 5 per cent tungsten, 1.5 per cent manganese, and 2 per cent carbon, and it soon became thoroughly understood that without appreciable manganese—later this also applied to chromium—tungsten would not impart the self-hardening or, as sometimes called, the air-hardening property. No great advance was made for nearly thirty years after the introduction of Mushet steels until Taylor pointed out the great economy to be gained by running them at cutting speeds not previously thought possible. Then Taylor and White, continuing the investigations of the former and working with tungsten-chromium steels, in 1899 made the incalculably valuable discovery that tungsten steels of this class had their cutting qualities enhanced to an extraordinary degree by heat treatment at temperatures supposedly ruinous prior to that time. Developments were rapid, and during the first years of this century Taylor and White's preferred composition showed tungsten and chromium contents of 18 and 5 per cent, respectively—figures which closely approximate those in the best high-speed steels of today.

Taylor-White high-speed steel marked so radical a departure as to revolutionize machine-shop practice and necessitate redesign of machine tools in plants where full advantage was to be taken of the greatly increased machining rates possible; and it was not long before all plants were impelled to modernize in this respect.

There are many other tools not classed as high-speed and other important articles to which tungsten imparts special properties. As a single example may be cited the permanent magnet steels, in which tungsten is always employed to increase their magnetic retentivity.

The greater part of the tungsten employed in early American metallurgical practice was produced by a two-stage process involving chemical preparation of tungsten trioxide and subsequent reduction in crucible furnaces with carbonaceous agents of various kinds. The result was a fairly pure tungsten metal in powdered form.

Europe preceded America in the production of tungsten powder and also in the manufacture of ferrotungsten. About the year 1900 and shortly thereafter, the production of tungsten powder and ferrotungsten was started in the United States by four different companies, including certain steel manufacturers who produced entirely for their own account. The Niagara Research Laboratories developed an electric furnace process for the production of a very low-carbon ferrotungsten from low or high-grade ores, but this was not commercialized by the Electro Metallurgical Company until 1910. The enormously increased demand for high-speed steel which prevailed during the entire period of the war resulted in at least a doubling of the number of plants producing ferrotungsten in the United States and a

large increase in capacity of the older plants. Carbon reduction in electric furnaces was employed at the newer plants, and the installations in most cases were not designed with a view to permanency.

The tungsten-mining industry of this country suffered an almost complete collapse shortly after the war, and only within the past few months has it been restored to a very slight extent as compared with its position during several years preceding the war. Not only were Chinese and other foreign tungsten ores imported into this country at prices far below those necessary to give our tungsten miners a livelihood, but foreign ferrotungsten and tungsten powder were sold here at demoralizing prices. This is one of the cases in which the latest tariff has not yet been effective in reëstablishing a home industry.

Many problems are presented the electric smelter who attempts to prepare himself for the economical production of high-grade ferrotungsten from scheelite, wolframite, and ferberite, in their many commercial grades. As impurities, all the elements—copper, arsenic, tin, lead, antimony, bismuth, manganese, sulfur and phosphorus—must at times be fought, and furthermore, specifications for carbon and silicon in the ferrotungsten must be observed. The preparation of reasonably pure tungsten oxide by wet methods and the electric furnace reduction of this oxide are steps through which a very high-grade product may be obtained, but this procedure can hardly be classed as economical at the present time, at least in this country. All these impurities can be successfully controlled by no other than strictly high-temperature metallurgical methods, with exception of the case of unduly high copper, so far as I am aware. Whether or not exceptionally high phosphorus tungsten ores can be treated most economically in this way is dependent on the character of the particular ore in question.

Phosphorus was so long an elusive element in tungsten materials that you may not think it amiss if I divulge a little history. I had occasion in 1910 to investigate the tungsten ore situation in Colorado. A large number of diverse samples resulted. Portions of many of these samples were given to Mr. Watt, of Boulder, Colo., for determination of tungstic acid, as he had for years most deservedly held the reputation of an accurate and trustworthy umpire. On a number of these samples we were simply unable to check Watt, and he graciously told me his method for tungsten. As application of the Watt method resulted in complete checks for tungsten, an investigation was started to explain the peculiarity that the different analytical methods gave different results for tungsten only on certain ore samples. We soon established the fact that surprisingly high contents of phosphorus existed in the samples which had first shown low tungsten when compared with the reports of Watt. I say "surprisingly high" because the supposition was general that Colorado ferberites were extremely low in phosphorus and because many published statements to that effect were on record. Furthermore, we found that the published methods for the determination of phosphorus in tungsten ores and ferrotungsten were inadequate. Some of the samples to which I have referred ran well over 1 per cent phosphorus.

These high-phosphorus ferberites presented a serious commercial problem in the direct electric smelting of low tungsten ores, the silicon reduction of which possesses unique advantages, and in the two years' experimentation which followed I developed several methods for the extraction of phosphorus from tungsten ores and the elimination of this element from ferrotungsten, the preferable method depending on the class of ore and percentage of phosphorus present. Both methods of attack brought out some very interesting chemistry and just as interesting metallurgy. I have hope that some of these methods will be of greater service in the future, or at such time as all of our tungsten resources must be developed.

In order to round out the accumulated information concerning phosphorus in ferrotungsten, I sent to some of the umpire laboratories and to several of the principal consumers samples of this alloy containing different percentages of phosphorus, all well over the usual limits. Without exception the reports showed low phosphorus, varying from one-half to one-fifth of our determinations according to whether phosphorus was low or high in the samples. Then, to make the crucial test and yet be prepared to suffer the consequences, a very small shipment of high-phosphorus ferrotungsten was allowed to go out to a steel company whose chief chemist was not only an authority on analytical methods but a broadminded man. Friendly notice was received a few months later—some high-phosphorus steel had been produced which was accounted for by the high-phosphorus ferrotungsten, which actually contained four times the specified amount. My friend disclosed that all the materials in this steel had been checked and rechecked and that it was not until he had personally applied himself to a study of the methods that he found it necessary to devise a new one for phosphorus in ferrotungsten. I explained that we had not found anyone else in the country to agree with us. This man is C. M. Johnson, of the Crucible Steel Company of America, who later published his method for the determination of phosphorus in ferrotungsten and tungsten ores.

I think fortuitous circumstances came into play in this phosphorus-tungsten relationship. In the making of tungsten powder from various ores of tungsten, concentrates of high tungsten trioxide content had been always sought, and the chemical method employed to produce tungsten trioxide therefrom incidentally removed phosphorus with the silica and other impurities; furthermore, the ores, selected for their amenability to mechanical concentration, are usually low in phosphorus, particularly so in the case of ferberites, although there are some outstanding exceptions. It must be remembered, also, that the use of tungsten powder predominated over ferrotungsten in the early years of this industry. Sheelite and wolframite concentrates of high percentage tungsten trioxide rarely require special treatment because of their phosphorus contents.

## Ferromolybdenum

In reviewing briefly the metallurgical history of ferromolybdenum, one thinks first of its early use in high-speed steels, then of the commercial development of large American ore deposits, and lastly of the recent accomplishments with molybdenum engineering steels.

Molybdenum in high-speed steels was a foreign development, and for a short period following the discovery of true high-speed steels it was employed and preferred by some large steel makers. The cutting qualities of these steels were satisfactory. However, many troubles existed, not only in manufacture, particularly in the rolling of ingots into bars, but in the use of the tools, which frequently showed a gradual deterioration with subsequent heat treatments. Metallurgically, this deterioration due to "sweating out" of molybdenum on the surface is interesting, and it has generally been ascribed to the relatively low volatilization temperature of molybdenum oxide.

Tungsten regained its supremacy partly for these reasons, especially in the United States, and for many years it has been used almost exclusively in high-speed steels. But there was another factor in the situation. Twenty years ago molybdenite concentrates were so scarce that no producer of molybdenum powder or ferromolybdenum could afford to guarantee a steady supply in considerable quantities. The wide distribution of low-grade molybdenite ores was then well known, but the methods of concentration were very wasteful and in other ways unsatisfactory. Metallurgical practice was also wasteful, as it involved oxidation of molybdenite and subsequent reduction of the readily volatilized oxide. So one can easily understand the reluctance which enterprising steel makers showed in developing and vigorously exploiting any new brands of molybdenum steels.

The Niagara Research Laboratories developed the lime-carbon and the silicon direct-reduction processes for molybdenite. A little incident about the latter may be interesting.

After the thought had occurred to me that silicon might be effective in reducing molybdenum sulfide at high temperature, I succeeded in finding only very meager literature on the sulfides of silicon, so I had little confidence as to whether SiS or SiS₂ would result, if indeed the reaction would take place. The result of the first run was a high silicon–molybdenum alloy, the charge having been based on the formation of SiS. I had used poor judgment, but the quantitative nature of the work pointed clearly to an explanation of the excess silicon. So the second heat was made with a charge calculated on the basis of SiS₂. This resulted in a high quality molybdenum, low in sulfur, silicon, and carbon, and a molybdenum recovery of 95 per cent was obtained.

Whether Dr. Chandler doubted this peculiar reaction, which must have come to his attention through the patent literature, or whether his thought was upon that wonderful chemical museum at Columbia, I have never known. At any rate, on a visit to Niagara Falls in 1907, he asked me to show him some silicon disulfide, and I jokingly told him I should have to cough it up because the only place it had been collected was in the lungs.

The reduction of sulfides by silicon was successfully applied to several other sulfides of the metals, including the sulfide of vanadium, to which I shall soon refer.

However, the commercial development of ferromolybdenum was halted, for reasons I have already stated. Years later came the war, and during its early stages urgent requests for molybdenum were received from European Governments. As a result, the problem was undertaken of working the wulfenite ores from Arizona which were familiarly known as "metallurgical sewers," containing lead, copper, arsenic, phosphorus, vanadium, and gold, in addition to molybdenum. We electrically smelted these ores for lead, afterwards reducing the slags by silicon to ferromolybdenum, which was manufactured on a substantial scale to meet rather severe specifications. Since that time considerable quantities of molybdenite concentrates have been made available and electric furnace processes of direct reduction have been put into practice.

A new era in molybdenum steels appears to have begun shortly after our entry into the war. Two circumstances of great significance seem to make this possible. One is the extensive, masterful work conducted by C. H. Wills and H. T. Chandler on the effects of fractional percentages of molybdenum in the familiar chromium, nickel, and vanadium steels; the other is the development by the Climax Molybdenum Company of a very large deposit of disseminated molybdenite in Colorado and an effective method of concentration. We convert these concentrates into ferromolybdenum by the methods to which I have already referred.

The outstanding examples of the use of molybdenum steels during the war were in "Liberty" motors and baby tanks. Additional progress has been made, however, and within the past year or two these steels have been accepted as standards by a number of manufacturers. The chrome-molybdenum, nickel-molybdenum, chrome-nickel-molybdenum, and chrome-vanadium-molybdenum steels are remarkable for their ready machinability and wide range of heat treatment, in addition to possessing most excellent physical properties.

## FERROVANADIUM

Some rather remarkable vanadium steels were produced experimentally during the late nineties, first in France and then in England. A systematic investigation of the effect of vanadium in steel was conducted by Sankey and Smith in England, and the published (1904) results of this work brought out in particular the exceptional dynamic properties of chrome-vanadium steels, which naturally awakened the interest of steel manufacturers in all countries.

In 1903, A. B. Frenzel, of Denver, who had learned at first hand of the early foreign experiments and who had become in-terested in the vanadium deposits of Colorado, requested the Niagara Research Laboratories to undertake the production of ferrovanadium from vanadiferous sandstone. After experimentation with small lots received early in 1904, both in the wet way and by direct smelting, it was decided to apply the latter method on a larger scale. Toward the end of 1904, shipment was made of a one hundred-ton lot of vanadiferous sandstone (Roscoelite), which was expected to average a vanadium content equivalent to 4 per cent vanadium pentoxide. Of course, it was not expected that a low-silicon ferrovanadium would result from direct smelting of this ore, although the experimental work with ore of this grade had shown that a ratio of vanadium to silicon in the alloy could be obtained which would probably not preclude a market. Imagine the disappointment when the average vanadium pentoxide content of the one hundred-ton lot was found to be only a little over one-half of 4 per cent. Working with an ore that was very largely silica, the effect of a difference between a 4 per cent and a 2 per cent vanadium pentoxide content on the cost of production and on the ratio of vanadium to silicon can be readily appreciated. At all events, the work of direct electric smelting progressed, conditions being changed from time to time for experimental reasons, with the result that high-silicon ferrovanadium was produced in which the silicon varied considerably. Silicon was greatly diminished in some of this alloy by refining processes, and all the ferrovanadium finally found a market. The difficulty in obtaining a 4 per cent vanadium pentoxide vanadiferous sandstone in appreciable quantities from Colorado came to my knowledge later.

In the spring of 1904, Stephen T. Lockwood equipped a small plant on the outskirts of Buffalo for the treatment of Utah carnotite, operating under the name of Welsh-Lofftis Uranium Rare Metals Company, which later became the Rare Metals Reduction Company. Lockwood's primary interest was the production of radium salts, and he claims the earliest preparation in this country of high-activity barium-radium sulfate in appreciable quantity. The occasional small lots of calcium vanadate and iron vanadate furnished by this little plant throughout the years 1904 to 1907 afforded additional opportunity for experimentation at the Niagara Research Laboratories.

The discovery in 1905 of the huge, rich deposits of vanadium sulfide in the Andes Mountains of Peru marks the beginning of intensified effort towards the commercialization of vanadium and vanadium steels. These deposits were acquired by the American Vanadium Company, and the greater part of the world's supply of vanadium has come from this source. Early in 1906 the American Vanadium Company entered into an arrangement with the Niagara Research Laboratories for the reduction of these Peruvian ores. The first small lot of ore received was a high-vanadium coal, which of course necessitated the burning out of carbon before direct smelting could be applied for production of the desired low-carbon ferrovanadium. Extremely high-grade sulfide ores were later received, and still later the oxidized ores of vanadium. Whether from the sulfide or the oxidized ore, all the ferrovanadium was produced by the silicon reduction process in one or more of its modifications. This work in 1906 and 1907 entailed many exasperating experiences and the expenditure of much hard manual labor, but the product enabled the American Vanadium Company to have many heats of vanadium steel made at the plants of various steel manufacturers. Through the thoughtfulness of J. J. Flannery and J. M. Flannery, I had the pleasure and valuable experience of witnessing a number of the early heats of vanadium steel. Well I remember the first instance—a small heat of armor plate at the Homestead Steel Works—and the great disappointment of the metallurgists over the results until proper heat treatment had been later applied to the steel; also the last case, particularly because I not only saw the first commercial heat of chrome-vanadium automobile steel, made in the spring of 1907 at the plant of the United Steel Company, Canton, Ohio, but because I then had the pleas-

ure of meeting Henry Ford and his companion, C. H. Wills. Later in 1907 the American Vanadium Company started the manufacture of its own ferrovanadium at a plant in Bridgeville, Pa., utilizing the alumino-thermic process of reduction.

Returning to the serious efforts being made to commercialize the vanadiferous sandstone, it should be noted that a chemical plant at Newmire, Colo., owned by the Vanadium Alloys Company started the production of iron vanadate in 1906. The Niagara Research Laboratories produced ferrovanadium from the small lots of vanadate turned out that year and the year following. And how harrowing the work on the early material! Loaded with volatile vanadium oxychlorides and still larger amounts of volatile sodium salts, the furnacing of this product in the absence of adequate hoods and other auxiliary equipment was a sacrifice; and I remember on one occasion in the early hours of the morning the surprise of the fire department in answer to a call from some friend with good intentions. The work at Newmire progressed, and the vanadium properties in addition to the plant were later acquired by the Primos Chemical Company, which subsequently marketed ferrovanadium in substantial quantities until purchased by the Vanadium Corporation in 1920.

The Standard Alloys Company, of Pittsburgh, has been marketing for several years in the form of ferroalloy the vanadium obtained from the operations on carnotite of the Standard Chemical Company, well-known manufacturers of radium and uranium compounds.

So within the United States has been held substantial control of the vanadium industry, a point of considerable economic importance during the war. Within the past three or four years there have appeared in the world's markets vanadium concentrates from the east and west coasts of Africa. Although of the lead vanadate family, these ores are of exceedingly complex nature, and they have presented in their commercial reduction a marvelous array of problems in chemistry, metallurgy, and economics. A relatively small amount of ferrovanadium has been produced in the United States from these ores.

The development of vanadium steels was undertaken in business-like fashion following the advent of the American Vanadium Company. A prominent metallurgist of England, J. Kent Smith, who in conjunction with Captain Sankey had previously accomplished so much with vanadium steels, came to this country for the American Vanadium Company and contributed immensely to the success of the introductory work. One early hope of the Flannery brothers has not yet materialized—the general use of vanadium in rail steel; on the other hand, an indispensable use has been established concerning which I never heard them venture a prediction—the addition of vanadium to high-speed steel in relatively high percentage. John A. Mathews, in discussing modern high-speed steel developments of the past twenty years, said not long ago:

\* \* \* the most noteworthy change is in the introduction of vanadium which is now used in practically every high-speed steel; in fact, it is the only general addition that has been made to the earlier types which seems to afford universal improvement in quality.

Vanadium appreciably enhances the dynamic qualities of steel, particularly in conjunction with chromium, nickel, or chromium and molybdenum. This is its principal attribute. So vanadium steels find their chief applications where resistance to shock and vibration is the desideratum, which explains their use in automobiles and aeroplanes, in locomotives and marine engines, in ordnance and cutting tools, and in numerous other devices.

#### Ferrotitanium

Many of us cannot think of this alloy without associating Auguste J. Rossi. With establishment of a successful titanium industry at Niagara Falls as a result of his many years of arduous work, his remarkable perseverance, and his never-failing confidence in the merits of titanium, Rossi did not rest. His astonishing vitality and enthusiasm are still manifest in his daily work, which continues to bear fruit, at more than four-score years, in the development of titanium compounds for various applications.

Ferrotitanium is a valuable deoxidizing and scavenging agent, possessing also the property of inhibiting segregation of sulfur and carbon.

Rossi fully described the development and applications of titanium alloys in his address of acceptance of the Perkin Medal delivered in this room on January 18, 1918.

#### Zirconium Alloys

It may be presumptuous even to mention zirconium with the metals I have discussed, all of which have contributed to our safety, convenience, or formidability, whereas zirconium has not been accepted generally as valuable; but I will venture to make a few statements concerning this remarkable element and leave its possibilities to your imagination.

How an intensive program of experimentation with zirconium in steel for light armor was undertaken by the Ford Motor Company in 1918; how a simultaneous development was started by us at the request of the War Industries Board for the production of a variety of zirconium alloys; how after the armistice the Bureau of Mines and the Bureau of Standards experimented with zirconium steels and drew conclusions not encouraging; and how the peculiar properties of zirconium gleaned during production of the alloys appealed to me sufficiently to institute an elaborate investigation of zirconium in steel—all these points are referred to more fully in a paper I contributed to the American Electrochemical Society in May, 1923.

Nearly four hundred electric furnace heats of steel running between two hundred and three hundred and fifty pounds each have been made under conditions approximating commercial practice. Several specific effects of zirconium have been determined as a result of this work.

Zirconium is one of the most versatile and effective of the known steel-treating elements in its reactions with dissolved impurities. It is unique in metallurgy, being a deoxidizer more potent than silicon and a corrective of the injurious effects of nitrogen, sulfur, and phosphorus.

Considerable analytical data are in our possession to show that zirconium-silicon alloy is much more effective than ferrosilicon in eliminating both oxygen and nitrogen from steel. Zirconium-treated steels are unusually free from the dispersed slag particles that characterize so-called dirty steel.

Ingots of zirconium-treated steels containing 0.31 per cent sulfur and only 0.14 per cent manganese have been rolled under commercial conditions into entirely satisfactory plate, while complete failure on the first pass through the rolls resulted with ingots of equal sulfur content in which it was attempted to overcome the effects of sulfur through the agency of manganese instead of zirconium. Many successful demonstrations have been made of the effect of zirconium in overcoming the hot-working difficulties with high-sulfur steels.

Zirconium has a marked effect in counteracting the embrittling property of phosphorus, at least in steels containing 0.75 per cent and higher carbon. Experiments have shown that steels having 0.75 per cent carbon and phosphorus up to at least 0.14 per cent can be rendered as shock-resisting as normal low-phosphorus steels by the permanent addition of moderate amounts of zirconium.

Ordinary carbon steels in which a small percentage of zirconium has been incorporated possess, when properly heat-treated, physical characteristics approaching those of the more expensive high-grade alloy steels; and, furthermore, some of the well-known alloy steels may be improved through the use of zirconium.

While effect of zirconium on the shock-resisting qualities of high-phosphorus steels has not been investigated on a steel

works basis, all the other effects I have described have been corroborated in actual commercial practice, so it is well to contemplate the future of zirconium in relation to the manufacture of steel.

### CONCLUSION

While it would not be entirely proper to say in these days of resourcefulness that anything is indispensable, it is nevertheless true that without ferroalloys certain of our major industries would be set back at least a generation in their development. An analytical study of the enormity of the wage earnings and capital investment in the innumerable kindred trades which rely for their existence on special steels forces a further realization of the dependency of this country on an adequate supply of these alloys, and in their absence we would be deprived of many of the articles which affect our everyday convenience and even govern our efficiency. Indeed, such deprivation would be a tremendous calamity.

Such is the importance of the ferroalloy. And happily the American industry is sufficient to the need. Surely the industry will go forward because it is full of

\* \* \* men who have not been content with knowledge sufficient for the present need, but who have sought additional knowledge and stored it away for the emergency reserve.

Are not alloys the "emergency reserve" of our swiftly moving world?

. . . . . . .

Acceptance of the Perkin Medal and the honor associated with it affords me a rare opportunity to acknowledge the unfailing support of the men responsible for the business policies of the earlier years, when optimism was needed to appreciate the technical possibilities which have since been commercially realized. To their continued liberality I owe the provision of exceptional facilities for experimentation and development work. Because of his leadership in these things, of his fruitful application of engineering judgment, and of his continuous faith in the future of ferroalloys, the electric furnace industry is especially indebted to E. F. Price.

Equally welcome is the opportunity to express appreciation of my younger associates, who have contributed to our work through timely suggestion and intelligent execution.

It has been my good fortune to be occupied in a field of technical endeavor still rich in opportunities for the advancement of metallurgy and the benefit of civilization.

Fully realizing the large share in this honor to which my associates are entitled, I am happy to receive this evidence of the regard of my fellow workers in chemical industry.

# NOTES AND CORRESPONDENCE

## Analysis of Soap Powder

*Editor of Industrial and Engineering Chemistry:*

Kindly accept my criticism of the article entitled "A Rapid Method for the Analysis of Soap Powder," by Fred F. Flanders and Anna D. Truitt, appearing in THIS JOURNAL, **15**, 1232 (1923).

In the authors' method for the determination of anhydrous soap, the factor 0.0306 is selected, representing a soap which has a mean molecular weight approximately that of sodium stearate. A very incorrect result will be obtained, however, where the mean molecular weight of the soap used varies from the above arbitrarily selected value—i. e., a soap made from cottonseed oil foots.

I would suggest that after titrating the fatty acids with sodium ethylate the resulting soap formed be evaporated to dryness *in vacuo* and the soap weighed. The mean molecular weight of the soap can be accurately determined from the titration and the weight of soap (corrected for unsaponified and unsaponifiable matter). This value can be used for similar soap powders coming from the same source, provided the mean molecular weight is checked occasionally.

BENJAMIN JOACHIM

745 EAST 175TH ST.
  BRONX, N. Y.
December 8, 1923

. . . . . . . . .

*Editor of Industrial and Engineering Chemistry:*

Several letters have been received commenting on our "Method for the Analysis of Soap Powder."

The formula for the calculation of sodium carbonate was incorrectly stated; naturally the whole volume of half normal acid must be multiplied by the factor 5 to bring it to tenth normal. From this is taken the back titration and also the ethylate titration, both being first reduced to tenth normal. The final result is then multiplied by the factor 0.0053, divided by the weight of sample taken, and of course finally multiplied by 100 to express the result in per cent.

We have tried various ways of checking up the factor 0.0306 for anhydrous soap. By determining the acid number of the fatty acids a corrected factor may be calculated. This will give better results in some cases, but not in all cases. Again, we have evaporated off the chloroform after titration, dried and weighed the residue, and calculated the correct factor as suggested by Joachim. Here also one may fall somewhat into error unless correction for unsaponified and unsaponifiable matter is made. In factory practice on the same type of samples this would undoubtedly be the best procedure.

As we generally know nothing at all about the origin of our samples and may have a dozen at the same time, each from a different manufacturer, we prefer to determine moisture and test the correctness of our result by adding up the constituents, as stated in our paper. A large majority of the samples sum up around 98 to 99 per cent; some, however, fall as low as 94 per cent, others go as high as 106 per cent. Such samples, of course, should be checked by the gravimetric method. It should be noted also that when much sodium silicate is present there will be a slight error in the results of the sodium carbonate calculation. Such samples are recognized by failure to clear up after boiling with the excess of half normal acid.

FRED F. FLANDERS

DEPARTMENT OF PUBLIC HEALTH
  BOSTON, MASS.
January 14, 1924

## Calendar of Meetings

American Ceramic Society—Atlantic City, N. J., February 4 to 9, 1924.

American Institute of Mining and Metallurgical Engineers—New York City, February 18 to 21, 1924.

American Concrete Institute—20th Annual Convention, Chicago, Ill., February 25 to 28, 1924.

American Chemical Society—67th Meeting, Washington, D. C., April 21 to 25, 1924.

American Electrochemical Society—Spring Meeting, Philadelphia, Pa., April 24 to 26, 1924.

# Internal Treatment of Boiler Waters

*Editor of Industrial and Engineering Chemistry:*

I have read the article by D. K. French on "Internal Treatment of Boiler Water" [THIS JOURNAL, 15, 1239 (1923)] with great interest, and believe that this article would be of greater benefit to the engineer if the information contained therein were of more specific data, of which the engineer could make actual use.

Mr. French mentions the soda-lime process only—but what about the zeolite water purification? This omission leaves the impression that zeolite systems are the greatest competitors of his compound.

I also feel that Mr. French would render greater service to the engineer by specifying such organic compounds, reactions of which form bulky, amorphous precipitates and have coagulating and clarifying actions, and mentioning such chemicals which will offset the corrosive action of magnesium chloride, magnesium sulfate, and calcium nitrate.

Castor oil "properly compounded" no doubt means to change its chemical and physical character by sulfonation to that of a soluble oil. Sulfonated oils—Turkey red, soluble castor, etc.— have long been known and used as antifoam agents in various industries, but so have other fatty oils, such as coconut oil (unchanged), and I wonder if Mr. French is not mistaken in his valuation of castor oil alone and other oils as antifoam agents.

There are, without question, a great many worthless, fake compounds on the market, but the same is true of compounds entering other industries, including patent medicines. Only the ultimate consumer can remedy this condition. By giving quantitative analysis, however, without mentioning the *exact* names of *all* the ingredients, great harm may be done to a good compound. Most all compunds, including such as have recognized merits and are distributed by large companies with research laboratories, etc., would stand a very poor show if their analyses were given and a comparison were made of actual costs of manufacture and selling prices. It is very difficult to analyze correctly a compound having organic matter as a constituent, and the analysis is generally given as containing a certain percentage of pectic or gelatinous matter without further investigating its true nature, taking it for granted that their only purpose is to cover up the large percentage of water present.

But there is a certain gelatinous sodium salt that has distinct beneficial action on scale. The acid belongs to the protein family and forms insoluble, bulky, amorphous precipitates with any calcium salt and most all alkaline earths and heavy metals. The benefits of such bulky precipitates Mr. French describes. There is no compound known that will prevent scale formation entirely, but a compound which will prevent crystalline scale and only leave a soft precipitate is of great benefit to the engineer, even if such compounds show large percentages of water.

OTTO F. ANDERSSON

THE CHEMISTS' CLUB
NEW YORK, N. Y.
December 24, 1923

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*Editor of Industrial and Engineering Chemistry:*

The article which appeared in the December issue of your journal on "Internal Treatment of Boiler Water" has just been brought to the writer's attention.

Frankly, it is indeed regrettable that the author did not make a more intensive study of the subject, because while we realize that Lieutenant Commander Lyon might have made some *laboratory tests* in regard to the treatment of boiler waters, the tests were not made under actual working conditions. In other words, it has been actually demonstrated that there is no electrolytic action in a boiler providing graphite is used for a scale remedy.

We are still selling large quantities of Mexican boiler graphite, which demonstrates beyond a doubt that some of the biggest manufacturing companies in the United States are securing excellent results from the use of this product and which in our mind refutes the very damaging report published by Lieutenant Commander Lyon in 1911.

A. S. HARVEY

THE UNITED STATES GRAPHITE COMPANY
SAGINAW, MICH.
December 27, 1923

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*Editor of Industrial and Engineering Chemistry:*

In reply to the letters from Mr. Andersson and Mr. Harvey, I will take up Mr. Andersson's first and consider the questions in order.

We did not discuss either the lime-soda process or the zeolite method, because they had already been compared in papers previously published. The objections to the two, roughly, are incomplete treatment in the first case and unnecessary soda in the second. The latter point is one which is fairly well known and emphasized whenever zeolite water purification is considered.

It is with regret that we cannot place on record the various special organic materials which are so effective in producing the noncrystalline precipitate, save to state that tannins, organic sugars, and starches play an important part in their make-up. Liquid extracts have properties entirely different from the same extract in the powdered form, and the extracts from different trees and sources have varying efficiencies. Certain protective colloidal properties also come from the organic sugars and starches in vegetable extracts, as well as a definite retarding action on the electrolytes in the slowly concentrating boiler water.

Regarding castor oil, it might be stated that there is no question but that some distinct property exists in this oil, which we feel we understand to a slight degree, as it is not true that sulfonated oils have equal efficiency in the control of foaming. During the war period, when the Government took over the castor oil supply for their aeroplanes, we endeavored to duplicate physically, chemically, and in every other way, castor oil by the use of sulfonated as well as blown oils, but were never able to obtain the same results in practice that castor oil seems to give.

Certain types of organic acids are much more effective than fatty or other types of oil, and it is my personal opinion that the oil itself has no bearing upon the control of foaming, which is due rather to certain organic compounds produced in the oil's breakdown which affect the surface tension conditions of the boiler water.

With reference to the giving of the names and amounts of materials present in formulas supplied, we have found that this is never advisable, as these formulas are derived with a background of observation and experience and are subject to change as operating conditions vary. They mean a great deal to one who understands them, but not very much to a nontechnical user, and it has been our practice to withhold such information; although I have never hesitated to give in full detail the exact composition of any material supplied, to a directing, consulting, or controlling chemist who could understand the reasons as well as the materials.

With regard to Mr. Harvey's letter, I am very sorry that we gave the impression that our sole objection to graphite was based upon Lieutenant Commander Lyon's paper of 1911. This paper explained to us a great many things that had been observed in actual practice, and it might be well to state at this time that in all probability there is no company supplying water treatment as extensively in the United States, or in fact in the world, as the company with which we are connected, and the opportunity to observe the action of the materials is very great.

Time and again we have incorporated graphite in preparations which we have supplied for the purposes of determining its effect and influence, finding at all times that there is absolutely no sci-

entific reason for its having any effectiveness so far as control of scale is concerned.

Regarding the electrolytic phase, however, it is generally accepted and can be easily demonstrated that powdered zinc, a strong electropositive metal, if introduced into the feed water in a boiler, will soon be converted into carbonate or oxide while retarding or preventing corrosion in the boiler. Why is it not as reasonable to assume that carbon, one of the most electronegative of chemicals, will act in the reverse way and stimulate corrosion?

Getting away from tradition and considering graphite, or impure carbon, with a cold and questioning air, it is impossible to conceive of the slightest chemical action upon water which could influence scale formation or its prevention.

There is no question but that graphite has a distinct corrosive action. Although not always the case, it is generally true that, following the first use of graphite, old scale in a boiler becomes loosened and drops in enormous quantities. Many samples of scale so removed have been brought to our attention, with the request to note the black coating of graphite on the tube side of the sample. In all our experience, however, analysis has failed to detect the slightest trace of carbon or graphite, but the coating has invariably turned out to consist of oxides of iron—part of the boiler removed by the carbon. Chemically, graphite is inert; physically, its action is very little greater than that of suspended matter in a slightly turbid water.

Mr. Harvey objects to placing faith upon laboratory tests made by Lieutenant Commander Lyon. It is unfortunate that the influence of laboratory tests upon science is given so little consideration. The laboratory, with scientific theory, must point the way, and while the results rarely work out in practice as is expected from the experimental study, they invariably point the way and prepare the ground for the practical side.

Unfortunately, until the present time no one has been sufficiently interested in checking up the action of the many materials used in the steam boiler, and for this reason there is little on record save the experience of those who have had a wide contact with that particular field.

We cannot but feel that Mr. Harvey's consideration of the effects of graphite is influenced to a very large extent by the interest of the seller.

<div align="right">D. K. French</div>

DEARBORN CHEMICAL COMPANY
    CHICAGO, ILL.
    January 8, 1924

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# A Successful Experiment

*Editor of Industrial and Engineering Chemistry:*

On Saturday, January 12, 1924, an intersectional symposium was held at Boston in which the Connecticut Valley Section, the New Haven Section, the Rhode Island Section, and the Northeastern Section coöperated. The meeting was admittedly somewhat of an experiment in this part of the country, but in view of its success some of the things learned may be of interest to the members of other sections who have not tried the idea.

In the first place it was demonstrated by an attendance of over five hundred that there is a distinct place in the scheme of the AMERICAN CHEMICAL SOCIETY for intersectional meetings, and in this instance at least the symposium type of meeting met with enthusiastic approval. One of the comments most frequently heard among those in attendance was the great advantage that a meeting of this type offered for a program of a few well-selected papers, with ample time for complete discussion of each. While it is true that the program on the first day of our national meeting is arranged somewhat along this line, there does not seem to be the atmosphere, even if there were the opportunity,

for the unusually free and stimulating discussion which followed all the papers on our local program.

For the success of such a meeting several things seem to be necessary. First, of course, is the selection of the general subject for the meeting, and, no less important, the selection of the speakers who are to handle the various subdivisions of it. Another important point is the selection of the presiding officer. The degree to which those present will take part in the discussion depends largely on this person, and he should by all means be one thoroughly familiar with the subject of the meeting.

One of the popular features of the New England meeting was the fact that there was no registration fee. A buffet lunch was provided before the afternoon meeting and a dinner between the afternoon and evening sessions. These meals were furnished at cost. The other expenses of the meeting were divided among the coöperating sections. In other words, as far as this meeting is concerned, at least, there appeared no reason why the national officers of the SOCIETY need be troubled with the details of arranging intersectional meetings, nor does it appear that any appeal need be made to the treasury of the national SOCIETY to help finance such gatherings.

If properly fostered, the intersectional meeting idea should very soon find a permanent place in our chemical activities. An intersectional meeting should provide a program of sufficient interest to warrant the attendance of chemists within a range of one hundred and fifty miles. It will then afford an opportunity for those men who do not find it possible to attend the national meetings to get the stimulation which comes from associating with fellow chemists. It will also afford an opportunity for the chemists in any given section of the country to become better acquainted, to say nothing of the benefit which is bound to accrue to those who have the privilege of hearing authorities present the latest results of their investigations and then to participate in, or at least follow, an enthusiastic discussion. From one who was only lukewarm toward the idea of intersectional meetings, our New England experience has changed me to one who is decidedly enthusiastic about their possibilities.

<div align="right">GUSTAVUS J. ESSELEN, JR.</div>

BOSTON, MASS.
January 15, 1924

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# The Lubricant and Asphaltic Hydrocarbons in Petroleum
## (Correction)

The following corrections should be made in the article under this title, THIS JOURNAL, **15**, 1233 (1923):

Page 1235, second column, first line under Table II, after "hydrocarbons," insert "the series $C_nH_{2n}$, the naphthene hydrocarbons, and the ethylene hydrocarbons in small amounts."

Page 1235, second column, second paragraph, second line, should read "Table III" instead of "preceding table."

Page 1237, first column, last paragraph, insert after first sentence, "Nitric acid attacks them with almost explosive rapidity, but if the first violent reaction is controlled by cooling and heat is applied, the change proceeds quietly."

<div align="right">CHARLES F. MABERY</div>

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# Notes on the Oil from Kauri Copal
## (Correction)

In the article by Gill and Nishida, under this title [THIS JOURNAL, **15**, 1276 (1923)] the sentence under the second table in the second column should read: "The refined oil had the same drying property as the raw oil and gave the color reactions of rosin oil with the Lieberman-Storch test."

# WORLD-WIDE CHEMISTRY

## Canadian Letter

### By S. J. Cook

140 BROADWAY AVE., OTTAWA, CANADA

### MINERAL PRODUCTION IN 1923

The mineral production of Canada advanced about 12 per cent in 1923 to a total of $214,102,000, as compared with $184,297,242 in 1922 and the record value of $227,859,665 attained in 1920, according to a statement recently issued by the mining branch of the Dominion Bureau of Statistics, Ottawa. It is pointed out that commodity prices, which reached a peak in 1920, have since receded, and this fact must be borne in mind when production is computed in terms of values. A weighted index showing the volume of production would undoubtedly mark 1923 as the banner year in Canada's mineral industry.

New output records were established for coal, lead, zinc, asbestos, and the total value of cobalt. Copper production was more than double the tonnage produced in 1922, and nickel increased practically three and one-half times. Gold and silver were slightly lower than in 1922. A group of nonmetallic minerals, including about twenty commodities, increased $2,000,000 to a total of $19,000,000. Structural materials and clay products, including portland cement, showed little change in the aggregate value, the total for the year being estimated at $38,900,000.

Employment in metal mining industries increased approximately 27 per cent to a maximum at the close of the year, and all mining industries, considered as a group, showed a gain of 6 per cent during the year.

### GOVERNMENT ASSISTED RESEARCHES

Forty-five persons are at work in the graduate schools of the various Canadian universities under fellowships, studentships, and bursaries awarded by the Research Council of Canada. Twelve fellowships, having a value of $1200 each, 8 studentships, with a value of $1000 each, and 25 bursaries having a value of $750 each, have been granted by the Research Council for the present year, and these awards are being held in nine departments of science at nine universities. Members of the scientific staffs of the various universities are coöperating with the Research Council in the supervision of the work being carried out by these graduate students.

During the six years ending March 31, 1923, the Research Council awarded 27 fellowships, 65 studentships, and 54 bursaries. These 146 awards were held by 96 persons at 15 universities in 12 departments of science. Forty-nine members of the scientific staffs of the universities coöperated with the Research Council in supervising the work carried out by the holders of these awards. According to returns furnished to the Research Council, 119 scientific papers have been published by these grantees, 56 of whom have received the degree of M.A., 28 the degree of M.S., and 19 have received the degree of Ph.D.

Of the grantees who have finished the training which they proposed to take under the auspices of the Research Council, 18 are continuing their post-graduate studies either in Canada or abroad; 25 are engaged in the teaching profession, 21 of these having accepted positions in Canadian universities; 10 have gone into industrial work; and 10 have accepted positions in the technical branches of the federal and provincial Governments.

### BRITISH EMPIRE FORESTRY CONFERENCE

The importance of forest research in Canada was emphasized recently when the second British Empire Forestry Conference was held. Delegates representing the forest administrations or timber trade attended from Great Britain, Australia, India, Ireland, New Zealand, South Africa, the Colonial Office, Nigeria, Kenya, Ceylon, Federated Malay States, and British Guiana, as well as from the various Canadian Forest Services.

The principal purposes of the conference were to secure definite information as to the extent and nature of the forest resources, to promote trade between different parts of the Empire, to encourage the better handling of the forests with the view of insuring continuous production, and to consider the progress of silvicultural and forest products research. Papers were presented on the softwood situation in Europe, Canada, and the United States. Fire protection and silviculture were also leading subjects of discussion. Other papers presented dealt with forest entomology and pathology, Empire trade in forest products, forestry education, the function of the Empire Forestry Association, and silvicultural and forest products research.

Resolutions were passed urging the importance of each part of the Empire laying down a definite forest policy, surveying its resources, and conserving and augmenting its own resources in growing coniferous timber; that the Empire's requirements of timber and other forest products be supplied to the greatest possible extent from sources within the Empire; that a central institution for post-graduate and specialized forestry training and research be established at Oxford University; that the *Empire Forestry Journal* be the medium for the publication of official and technical information; that a standing committee representing the various forest authorities be appointed to maintain continuity of action in respect to the meetings of the British Empire Forestry Conference; that the scope of the Forest Products Research Board in Great Britain be extended; that the forest authorities be given full public support and requisite assistance from the Governments in the protection of the forests from fire; and that more effectual silvicultural methods be applied to Canadian forests.

It was decided to accept the invitation of Australia to hold the next conference there in 1928.

### FOREST PRODUCTS RESEARCH

At the Forest Products Laboratories of Canada, which are operated in coöperation with McGill University at Montreal, much work of a chemical nature is being conducted in the division of pulp and paper. Investigations in progress include the pulping of Jack pine by the sulfite process, the chemistry of cellulose, and a fundamental study in connection with certain chemical tests for pulps. At this writing details regarding these projects are not available, however, as results are to be published later. Work has just been completed on the pulping qualities of fire-killed wood, and a bulletin reporting the findings is now in course of publication.

### HALF A CENTURY OF PROGRESS

In 1871, three years after the Confederation of the Dominion of Canada, the first census of the united country was taken. It is interesting and illuminating to compare the figures of that year with those of 1922, and to note the remarkable progress which the young country has made in the ensuing half-century.

|  | 1871 | 1922 |
| --- | --- | --- |
| Land area under cultivation | 10,000,000 acres | 60,000,000 acres |
| Value farm property | $1,787,102,630 | $3,196,876,000 |
| Wheat crop | 16,700,000 bushels | 400,000,000 bushels |
| Agricultural exports | $13,000,000 | $453,622,826 |
| Value agricultural production | $364,906,866 | $1,420,170,000 |
| Total exports | $74,100,000 | $932,229,443 |
| Total imports | $86,947,000 | $802,457,043 |
| Invested in manufactures | $80,000,000 | $3,230,686,368 |
| Manufacturing production | $221,000,000 | $4,019,371,869 |
| Fisheries production | $6,577,000 | $41,908,076 |
| Mineral production | $20,000,000 | $180,622,000 |
| Fur production | (1881) $987,555 | $16,458,621 |
| Lumber production | $100,000,000 | $207,163,577 |
| Pulp and paper production | ...... | $151,003,165 |
| Dairy production | $1,601,738 | $250,618,000 |
| Population | 3,485,761 | 8,778,483 |
| Railways | 2695 miles | 39,196 miles |
| Telephones | ...... | 902,090 |
| Bank deposits | $37,000,000 | $537,340,000 |
| Immigration | 27,773 | 70,500 |

### TEXTILE LABORATORY FOR CANADA

The Canadian Woolen Manufacturers' Association has established a laboratory in Toronto for the purpose of dealing with the many problems which confront this rapidly growing industry. Especial attention will be given at first to problems in dyestuffs and chemicals.

## Model Fish Preserving Plant

For the purpose of improving methods of curing, salting, packing, and marketing fish, the Dominion Government has made an appropriation of $70,000 to establish a Fisheries Experimental Station, and it is stated that Halifax will probably be selected as the location, since it is the most central point to which men interested in the fishing industry of Nova Scotia might be brought. Should the new experimental station prove successful, it is expected that additional stations will be established in other parts of Canada.

## Sodium Sulfate Development

Two companies are now engaged in the development of the sodium sulfate deposits in the Province of Saskatchewan. The domestic salt is now being used in the manufacture of glass at Radcliff, and six deposits so far have been investigated by the federal department of mines. Other deposits not yet investigated by the department number close to ninety.

The largest development is near Dana, where $500,000 has been spent on the work, and a plant is being installed at Frederick Lake, New Mitchellton. There are also large deposits near Ceylon and Lake Johnston, the products of which can be used in the manufacture of paper and glass, the textile industries, dyeing, etc. The Saskatchewan deposits have been cited by experts as likely in time to be able to supply the needs of the whole Dominion.

January 9, 1924

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# Washington Letter

## Meeting of the American Engineering Council

James Hartness, former governor of Vermont and past president of the American Society of Mechanical Engineers, was elected president of the American Engineering Council to succeed Mortimer E. Cooley, dean of the University of Michigan, at the annual meeting of the Council held in Washington, January 10 and 11. Addressing the Council, President Hartness declared that his administration would be characterized by an effort to aid the American people in making the best use of the Nation's energies and resources through the engineering profession. Vice presidents elected were L. P. Alford of New York and Charles R. Gow of Boston. Other vice presidents are Calvert Townley of New York and Gardner S. Williams of Ann Arbor, Mich. H. E. Howe of Washington was reëlected treasurer, and L. W. Wallace of Washington was again chosen executive secretary.

An outstanding feature of the Washington assembly was the national Public Works Conference, held on January 9 and attended by representatives of sixty-three engineering and allied organizations. The conference adopted resolutions favoring a reorganization of Federal departments. The Brown plan was not indorsed specifically, that part of the resolutions embodying the aims of the Nation's engineers, architects, contractors, and kindred bodies reading:

This conference particularly indorses grouping and coördinating within an existing department, preferably renamed a Department of Public Works, the construction and administration of all nonmilitary public works.

It was voted again to set in motion the nation-wide movement for the establishment of a Department of Public Works, which, it is believed, would save millions annually to the Government and promote efficiency and stability in the conduct of Federal affairs. The movement will be directed by the American Engineering Council from its national headquarters in Washington. In association with the Engineering Council, an advisory council composed of one representative from each participating organization will function. Philip N. Moore, of St. Louis, former chairman of the War Minerals Relief Commission, and one of the original sponsors of the public works project, was chairman of the conference, which was addressed by Secretary Hoover. The American Construction Council, headed by Franklin D. Roosevelt, pledged its support to the public works movement. General Richard C. Marshall announced that the Associated General Contractors of America would aid. Similar assurances of support were received from numerous other national and local organizations.

Indorsing the recommendation of its executive board, the Council passed a resolution urging that sanitary engineers in the U. S. Public Health Service be made commissioned officers.

Another notable event of the meeting was the annual dinner on the evening of January 10 at the Chevy Chase Club. Secretary Hoover, President Nicholas Murray Butler of Columbia University, Assistant Secretary Dwight F. Davis of the War Department, President Hartness of the Council, and the Italian Ambassador, Don Galasio Benedetto Anatolio Caetani, were among the distinguished visitors present. Both Secretary Hoover and Dr. Butler emphasized the need of broader engineering education and of greater engineering participation in the social, economic, and political life of the country. The ambassador outlined a plan by which young graduates of Italian technical schools will be brought to America and provided employment in the industries. Assistant Secretary Davis described the industrial mobilization plans of the War Department. He appealed for the coöperation of the engineer, which was unanimously tendered at a business session of the Council. President Charles F. Loweth assured Mr. Davis of the assistance of the American Society of Civil Engineers. Dean Cooley presided at the dinner, reviewing, in a brief address, the achievements of the Council, whose work, he predicted, would develop substantially during the coming year. In his farewell address to the Council, Dean Cooley said that progress of industry and social well-being were so intimately bound up with engineering that this profession could no longer be held back.

Foremost among the Council's activities for 1924 will be the direction of the public works enterprise and the development of closer working contacts with the member societies.

## National Research Council Activities

In a statement of the activities of the National Research Council for the year July 1, 1922, to June 30, 1923, the secretary stated that the Council has had a year of much activity and creditable achievement. The Council maintains a very wide contact with the scientific organizations and men of this country and of various foreign countries, these organizations and men representing both fundamental science and its applications. The actual membership of the Council is composed chiefly of accredited representatives of more than seventy national scientific and technical societies. Relations with foreign workers and organizations are closely maintained through the International Research Council and its affiliated International Unions, representing different special fields of science. Certain of the National Research Council's special divisions of science and technology are the officially recognized American sections of the International Unions.

Contact with the colleges and universities of the country is maintained by the Council especially through its division of educational relations; with the Government's various scientific bureaus through the division of Federal relations; and with the activities of the various State scientific boards and bureaus through the division of States relations. Relations with the industrial research laboratories of the country, and with applied science in general, are maintained through the Council's divisions of engineering, research extension, physics, and chemistry and chemical technology.

During the year the Council was entrusted with the responsibility of expending considerable sums of money given by various foundations, industrial concerns, and individuals for the support of special undertakings for the promotion of scientific work and research.

Perhaps the most outstanding new undertaking of the Council was the establishment of a series of post-doctorate research fellowships made possible by an appropriation from the Rockefeller Foundation.

## Hardness Changes of Metals

For some time the Bureau of Standards has been investigating the changes in hardness which accompany the severe cold working of metals. At a recent meeting of the Advisory Committee on Nonferrous Metals several suggestions were made for further work on this problem, and during the past month several of these suggestions were followed. The results indicate that the hardness changes of metals after severe cold working, as measured on the surface of cold-rolled strips, are of the same nature as the changes within the strips—that is, as measured on sections through the strips perpendicular to the surface. There do not appear to be any pronounced directional properties in the hardness of severely cold-rolled metals. The effect of the temperature of rolling on zinc and copper was also investigated. When the rolling was carried out at rather low temperature, produced by cooling both the rolls and the specimen with ice water, it was found that the hardening of the metal, particularly of the zinc, during the initial stages of deformation, was greatly increased. The tendency of the metal to crack and split during the initial stages of deformation was very marked. After the metal had been reduced to a strip, however, softening occurred as before, and with further deformation the low temperature appeared to have but little, if any, influence.

## C. W. S. Reserve Officers Organize

The reserve officers of the Chemical Warfare Service residing in the District of Columbia are organizing an association, which, it is planned, will soon become a national organization. The first meeting will be held on Monday evening, February 4, at the Raleigh Hotel. Captain Frank B. Gorin will preside at the meeting, and Brigadier General Amos A. Fries, chief of the Chemical Warfare Service, will be the honor guest. There will be motion pictures showing recent chemical warfare developments and an exhibit of gas warfare material.

## Soil Important Factor in Forest Growth

C. G. Bates, of the Fremont Forest Experiment Station, has found that the very small and minute particles in the soil may have an important effect upon the rate of growth of forest trees. For example, a very large proportion of alkali may be held in an absorbed condition by the clay and may not become soluble even when there is abundant water. Since the clay is as important in soil as the soil water itself, this absorbed alkali has a far-reaching effect upon the tree's rate of growth.

## Exploration of Alaska's Petroleum Reserve

A midwinter start in the examination of the Navy's largest petroleum reserve is being made by the Interior Department in sending geologists and engineers of the Geological Survey to Arctic Alaska. The area to be examined is somewhat larger than the State of Maine, covering about 35,000 square miles, but it is a practically uncharted wilderness that includes rugged mountain chains and vast silent stretches of tundra. The reserve is an irregular tract that extends for nearly 300 miles along the coast of the Arctic Ocean, with Point Barrow as its northern point, and runs inland in places for more than 200 miles.

The technical members of the party who will explore the naval reserve are Philip S. Smith, geologist in charge; J. B. Mertie and William T. Foran, geologists; Gerald Fitzgerald and R. K. Lynt, topographic engineers, and several assistants.

## Starch Plant Explosion

The disastrous explosion in the starch plant of the Corn Products Refining Co., Pekin, Ill., January 3, in which 42 persons were killed, 21 injured, and property damaged to the extent of approximately $1,000,000, was caused by a fire originating from an overheated bearing in a starch conveyor, according to the report of David J. Price, engineer of the Bureau of Chemistry, who, with two assistant engineers, H. R. Brown and P. W. Edwards, coöperated with the State fire marshal and officials of the company in making a study of the wreckage.

The engineers found unmistakable evidence that the hot bearing had set fire to the inside of the conveyor box in the basement of one of the buildings. The progress of the explosion indicates that it started when one of the wagons loaded with dry starch in the kiln house was dumped into the conveyor. The dust cloud produced by the dumping was set off when it reached the fire in the conveyor box. The rapidly burning fire traveled through this conveyor to a cross conveyor and finally was communicated to the hoppers of the starch-packing house, where the most violent explosion occurred, resulting in the complete wrecking of this building. In the first building affected by the explosion little damage was done because of the large window area, a type of construction recommended by the Department of Agriculture for buildings in which such explosions are liable to occur. In this case the windows were blown out and little damage was done to the walls and floors.

As a result of the thorough study of conditions producing this disaster and the behavior of the explosion, the investigators have obtained new information which will make possible the adoption of new control measures in all kinds of industrial plants where combustible dusts are produced. In the opinion of the engineers, operations in which such dusts are produced in large quantities should be conducted in buildings set well apart from other buildings, and such operations as starch dumping and packing should be performed in buildings with large window area and remote from the rest of the plant.

January 22, 1924

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Corrections—On page 99 in the January issue of This Journal, in the section on "Use of Liquefied Sulfuric Acid in Industry," *sulfurous acid* should be substituted for *sulfuric acid* in the heading, and also in lines 8, 11, and 14 of the section.

In the paragraph entitled "Spain Offers Market for Fertilizers," on page 101 of the January issue of This Journal, the sixth line should read: "18 per cent *phosphoric* acid," etc.

## Motor Fuel Investigations in Switzerland

**Motor Fuel Investigations in Switzerland**—The Swiss Government has been making persistent efforts to find a successful process whereby alcohol can be used as a substitute for gasoline. Thus far experiments under the joint direction of the Swiss Federal Department of Alcohol and the Technical Section of the Military Department have failed to discover a motor fuel better or cheaper than gasoline.

**German Consumption of Raw Copper Wanes**—Assistant Trade Commissioner W. T. Daugherty, Berlin, states that the November consumption of raw copper in Germany was estimated to be 3000 tons, compared with approximately 3500 tons in October, and a monthly average of 10,000 tons in 1922. The copper industry is consuming about one-third of the amount of copper used in 1922 and is operating only part time. The occupied area is not importing copper. The receipts of raw copper into Germany from the United States for September and October are estimated at 2500 tons monthly, compared with the monthly average of 7500 tons for the first seven months of 1923.

**Production of Benzene in India**—The Bararee Coke Company has announced that it has placed in operation what is believed to be the first plant for the recovery of benzene in India. This is regarded as a further step forward in the country's industrial development. The installation of this modern benzene plant makes an important addition to the company's ammonium sulfate plant and battery of thirty-five waste heat ovens, which are producing a high-grade coke for the local blast furnaces. From the coke oven gases, tar, ammonia in the form of ammonium sulfate, and crude benzene are recovered. The tar is put through the tar distillation plant to yield carbolic oils, creosote oils, anthracene oils, and pitch. The benzene vapors are recovered from the gases by scrubbing with creosote oil obtained from the tar distillation plant, and crude benzene is then separated from the creosote oil by distillation. It is anticipated that the rectified benzene can find a ready market in India as motor fuel.

**Swedish Oil Shale Possibilities**—As Sweden's annual coal bill is nearly $25,000,000 and its oil bill approximately $10,000,000 (sums which are paid principally to English exporters, and to a lesser extent to American principals), much interest is aroused by the work carried on by scientists and engineers among Swedish shale deposits, particularly those in western Sweden.

Alum shale is found in the Goteborg district in considerable quantities, chiefly in the hills of Kinnekulle, Halleberg, Hunneberg, and Billinger. At Kinnekulle the shale is about 12 meters thick and very rich in combustible oils—the shale containing up to 8 per cent oils. The problem of separating this oil from the shale has been investigated for several years in Sweden, and the experiments have been subsidized to a considerable extent by the Swedish Government.

**Alcohol Industry in Cuba**—Scarcity of exhausted molasses (black strap) in Cuba has been growing more and more serious since the early summer, and with it the shortage of alcohol for industrial purposes. Of the more important distilleries, thirteen are practically shut down, and several of these have been closed for a number of months. The scarcity of molasses is charged against foreign exportation, particularly to the Netherlands, where the Government especially favors alcohol production and offers manufacturers an export bonus, also giving subvention to ocean carriers of alcohol from the Kingdom. Refiners of petroleum are also said to be promoters of this outward movement of molasses, because of the inroads made by alcohol motor spirit and fuel upon the gasoline and kerosene consumption in Cuba. It is alleged that the Republic's former sales of refined petroleum products used for stoves and motors—70,000 gallons daily—have materially dropped, and that motor gasoline sales have fallen off about 30 per cent, owing to substitution by alcohol. The Cuban Government has been called upon for immediate relief through measures designed to restrict exportation from Cuba of residual molasses in order to assure a sufficient supply remaining in the country from year to year for the distilling industry.

**Motor Alcohol Deliveries in France**—The French Government's plans for forcing the sellers of motor fuel to take certain quantities of the national alcohol stocks to be mixed with motor fuel are developing slowly. A *comptoir* has been created among the sellers of gasoline, and began actual work early in November. This body receives the alcohol deliveries from the Government and arranges for the mixing of the so-called *carburant national* and its delivery to the oil interests in such proportion as their purchases require.

**Production of Borax in Chile**—A steady decline has been taking place in the Chilean borax industry in spite of an almost inexhaustible supply in deposits, while in the United States a contrary situation has developed, according to a recent article in the *Riqueza Minera de Chile* (combined September and October issue).

# BOOK REVIEWS

**Marine Products of Commerce.** By D. K. Tressler and others. 762 pages. The Chemical Catalog Co., New York, 1923. Price, $9.00.

Someone has said that the products of an acre of sea are as valuable as those from an acre of land. It is not difficult to believe this when glancing over the contents of this admirable book—a real treasure house of scientific data on every product of the water. The subjects run from sea salt to whales, and from edible algae to pearls of great price, not to mention the ordinary products of the fisheries. It all reminds one of the magic benzene tree that used to grow and fruit so marvelously in the walls of the chemical lecture halls in our college days.

Dr. Tressler, in arranging his material, begins with chapters on the inorganic materials from the sea, such as salt, iodine, and potash; then the kelp products, like agar-agar; then pearls, pearl essence, mother of pearl, precious coral; then the food fishes, their food value, methods of catching and preserving them, and their by-products such as fish meal, oil, and glue, through the edible shell fish; then whaling, seals, porpoises, walruses; and finally, the important and interesting sponge industry. To mention these subjects takes but a moment, but each one of them has been treated in an authoritative and comprehensive way by a specialist in that particular field. It was a revelation to the reviewer to learn that so many chemical and economic data were available. They have been collected for the first time in one handy volume. Chemical composition and industrial application, as well as statistical material, are all presented in an attractive way.

From a mechanical standpoint "Marine Products of Commerce" is very satisfactory. The use of paper, printing, and handling of the illustrations are all well done. The numerous illustrations are attractive and bring out important and interesting points, thus adding a great deal to the value of this work. In passing it should be noted that on page 19 the picture of salmon jumping falls in Alaska has enough action to satisfy any devotee of the movies. It also shows why most of the salmon are so bountifully provided with fuel oil for their long and arduous trips from salt water to their spawning areas, which may be hundreds or more than a thousand miles up stream.

The subject of the handling of the by-products of the fisheries is well treated. This is an important question both from the standpoint of realizing values now wasted and also of eliminating what in many places is a nuisance. There is a great field here for the chemical engineer to develop units that will operate satisfactorily and economically in inaccessible places without requiring skilled labor. The Indians taught the Pilgrim farmers in Massachusetts to bury a small fish or two near each hill of corn, so our fish fertilizer industry is a gradual development from the earliest colonial days.

The copious references in nearly all the chapters should prove very valuable to investigators who wish to follow subjects back to earlier authors. On page 553 in the chapter on The American Shrimp Industry, Table 71, giving the composition and food value of shrimp, was taken from *Bulletin* 538, U. S. Department of Agriculture, and it should have been so indicated.

The presence of vitamins and of indispensable amino acids in fishery food products is important and is adequately treated in various sections. Recently it has become fairly certain that the fish absorb the vitamins from plankton and other vegetable food in the sea, and thus act as storers and not synthesizers of vitamins. Owing to the increasing interest in goiter and its apparent causation by lack of iodine in certain parts of the United States, it would have been well to include in this work some data on the amount of iodine present in common sea foods. The use of sea foods has been suggested as a probable aid in combatting goiter in districts where drinking water and the local foods are deficient in iodine.

Besides agriculture, our fisheries constitute our only supply of certain essential foods, and Dr. Tressler very aptly closes his introduction with the following significant sentence: "Thus while the ocean is, and is likely to remain, an unconquered wilderness, as man learns more concerning its animal and vegetable life, it may be made to contribute more than it now does to the welfare of man."

E. D. Clark

**The Chemistry of Paints, Pigments, and Varnishes.** By J. Gauld Bearn. 277 pages. Ernest Benn, Ltd., London, 1923. Price, 30 s. net.

The author states in the preface that the book has been written in the hope that it will be of assistance to works managers and to students in obtaining both a general survey of the industry as a whole and an account of the modern technical processes and of the chemistry of the raw materials employed. Necessarily this book represents the English viewpoint, which is quite different from the American, and for this reason it should be of special interest to American paint and varnish technologists.

The arrangement of the subject is admirable, the book being divided into three parts.

Part I treats of the composition, properties, and uses of paints. If a specific criticism were to be made, it would be the brevity of treatment accorded to this phase of the subject, it being limited to twenty-six pages including chemical analysis and physical testing. Presumably, this reticence in treatment may be traced to the prevailing idea of secrecy relative to the processes of manufacture and the composition of their products which still obtains with English manufacturers.

Part II deals with the various pigments, both organic and inorganic. Their preparation, properties, analysis, and valuation are discussed with considerable detail and in a very comprehensive manner. Considerable information has been included regarding the newer white pigments, such as titanium white and antimony white. Many of the processes given for the manufacture of the colored pigments are quite different from those used in this country and are of interest from a comparative standpoint.

Part III describes the principal materials used in the manufacture of varnishes, lacquers, and japans, together with a brief treatment as to the manufacture of oil and spirit varnishes and black japans. Again the divergence between the English and the American manufacturing practice is evident. Numerous analytical methods as to the valuation of varnish materials are given. A two-page bibliography is given at the end of Part III. This bibliography could with advantage have been materially enlarged to include many original references dealing with the valuation and analysis of paint and varnish materials.

The book undoubtedly serves the purpose for which it was written, and has much that is of interest and value to any one who has contact directly or indirectly with the paint and varnish industry.

C. D. Holley

**Science Remaking the World.** Edited by Otis W. Caldwell and E. E. Slosson. 288 pages. Doubleday, Page & Co., New York, 1923. Price, $2.50.

This is a collection of lectures presented during the summer of 1922 in Teachers College, Columbia University, for the purpose of providing interesting information about the achievements of modern science. To this collection has been added a chapter on Our Present Knowledge of Tuberculosis by L. R. Williams, and one on Insect Sociology by Vernon Kellogg, so that the volume presents sixteen chapters covering a very wide field of applied science, presented in that fashion which we term "nontechnical" or "popular."

It is a book that all those engaged in disseminating a knowledge of applied science to lay readers will want to study at length, for not only are the various subjects, such as electrons, achievements and applications of modern science, international public health, the meaning of evolution, and the chemistry and economy of food, presented in a complete and engaging fashion, but each chapter concludes with a guide to further reading which is indeed valuable. There is the variation in style which one must expect in a book written by so many authors, but this is in no way detrimental and for some may prove an added attraction. The chemists who are accustomed to and appreciative of the characteristic style of Dr. Slosson will at once recognize his work in the chapters for which he is responsible. We recommend the book for general as well as special reading, and chemists may here find information slightly outside their own fields presented in a manner that cannot fail to hold the attention.

**Chemistry of Rubber.** By B. D. W. Luff. 232 pages. Ernest Benn, Ltd., London, 1923. Price, 25 s. net.

This book comprises a detailed survey of the more important literature on the chemistry of rubber, together with enough of the author's own experience and ideas to make it interesting and readable. It is apparently the first attempt to correlate such literature. Mr. Luff, owing to his long experience as research chemist for the North British Rubber Co., Ltd., is well fitted for the authorship of such a book. It is well illustrated with photographs showing the preparation of plantation rubber and some manufacturing methods.

The book contains fourteen chapters, which may be divided into the following six groups: Chapter 1, Historical; Chapters 2 to 7, Chemistry of Latex and Crude Rubber; Chapter 7, Chemical Properties, Constitution, and Synthesis; Chapters 8 to 11, Vulcanization; Chapters 11 and 12, Compounding Ingredients and Accelerators; Chapters 13 and 14, Methods of Manufacture and Analysis.

The work is exceedingly well planned, each subject being allotted the amount of space which the author feels is due it, looking at the subject from a broad scientific rather than specialized point of view.

The chapters dealing with latex and crude rubber are good. The subject is treated from a historical point of view to show the development of the rubber plantation industry.

The chapter on Chemical Properties, Constitution, and Synthesis and that on Vulcanization are particularly good. Synthetic rubber is discussed, but, as the author states, the space allotted to this subject is only commensurate with the technical importance of the subject at the present day.

The chapter on Compounding Ingredients gives a comprehensive discussion of the recent work on this subject, particularly as carried out in America, and furnishes an interesting picture of the possibilities offered by this field of research. The same may be said of the chapter on Accelerators.

The book is of convenient size, well printed, and comparatively free from errors. Its reading should furnish pleasure and inspiration to all interested in this subject.

<div align="right">R. P. Rose</div>

**Coke and Its Use in Relation to Smoke Prevention and Fuel Economy.** By E. W. L. Nicol. 32 pages. Ernest Benn, Ltd., London, 1923. Price, 19 s. 6 d. net.

This book offers a much needed presentation in nontechnical language of the arguments for using coke instead of soft coal in domestic and industrial furnaces. The properties of coke and the various methods of carbonization are very briefly described in the first three chapters. The remaining seventeen discuss the use of coke as fuel for steam raising in hand and stoker-fired furnaces, as fuel for electric power stations, as fuel for motor road transport, marine boilers, and for domestic purposes, such as hot water boilers, room heaters, and cooking ranges.

The author is the inventor of the Sandwich system, in which coke breeze and bituminous slack coal are fed in layers onto a chain grate or underfeed stoker. The bottom layer of incandescent coke is claimed to prevent the bituminous coal from falling through the grate and to burn all the volatile matter practically without smoke.

The chapters on evaporative capacity of coke-fired boilers, influence of excess air, forced draught, coal smoke, smoke prevention, fuel value, and grading of coke are replete with test data and practical suggestions for industrial fuel engineers seeking to introduce the use of coke in place of bituminous coal.

It must be said, however, that the author's enthusiasm in a worthy cause has led him in several cases to quote incomplete results of tests comparing the fuel efficiency of coke and coal which are unduly favorable to coke. For example, on page 4 comparisons are made indicating that the coke and tar from carbonizing a ton of bituminous coal will evaporate the same amount of water as a ton of coal. Kreisinger and others have shown, in *Technical Paper* **315** of the Bureau of Mines, that in house-heating furnaces bituminous coal gives a thermal efficiency of approximately 55 per cent as compared with 68 per cent for coke. This difference in efficiency does not entirely compensate for the heat lost in carbonization and heat in the gas.

Although the book is more applicable to British conditions, which are quite different from American, it should prove very useful to the coke sales department of American gas companies in their efforts to educate the public to the advantage and method of using this fuel in place of high-priced anthracite or smoke-producing bituminous coal.

The printing, illustrations, and quality of paper are excellent.

<div align="right">A. C. Fieldner</div>

**Coal-Tar Distillation and Working Up of Tar Products.** By Arthur R. Warnes. 3rd edition. 511 pages. Ernest Benn, Ltd., London, 1923. Price, 45 s. net.

The third edition of this book is a very decided advance over the second, and gives a very clear and complete picture of the industry as it exists in Great Britain.

The addition of the first two chapters on coal is useful, particularly that portion which deals with the chemical nature of coal substances, concerning which so much has appeared in the technical literature in the last decade. Happily, the purely geological side has been made brief, as any extended exposition would have been out of place here.

In the third chapter, dealing with the composition of coal tar, there is a wealth of useful data. Those dealing with the percentages of distillate obtained from various types of tar would be much more informative if in all cases, as was done in Table 47, the melting points of the pitch residues were stated numerically. Moreover, the method of distillation in these tests is not stated, and the way in which tar is distilled has, within certain limits, a great influence on the oil yield obtained to a given pitch hardness.

Chapters 4 and 5 contain many useful suggestions for the general layout of a plant and storage tanks, with many useful concrete suggestions.

Chapters 6 to 8, inclusive, describing tar stills and settings, are exclusively British, as the only type described is the vertical still largely used in England. This description is very complete and detailed, but it is to be regretted that the author did not see fit to mention that the standard batch stills in the United States are all horizontal and have been built up to 20,000 gallon capacity, while the largest stills he mentioned are the 30 ton size, or about 6000 gallons. The descriptions of the Hird continuous still given in the eighth chapter are excellently written and amply illustrated.

Chapters 9 to 18, inclusive, which cover tar still operation and plants and processes for the production of phenol, cresylic acids, benzols and naphthas, pyridine, naphthalene, and anthracene, are very well written with respect to the selection and general arrangement of the subject matter.

In Chapters 19 and 20, however, on pitch and creosote oil, it seems as if the subject could have well been expanded to go into further detail as to the uses of pitch. The same, to a lesser extent, is true of the section on creosote oil. Some of the space given to Chapter 21 on gas stripping could well have been devoted to these subjects. Chapter 21 is unusually complete and detailed but seems somewhat outside the general scope of the book.

The final chapter, on testing methods, is quite extensive and is very useful as a general reference to British specifications and methods of test. The appendix, covering health methods particularly applicable to tar works, is extremely valuable and indicates that British industry is giving minute attention to specific industrial hazards.

In the writer's opinion, the index could be extended to advantage and made much more detailed. The book as a whole is a very fine piece of work and represents a real and useful addition to the literature.

<div align="right">J. M. Weiss</div>

**Electrochemistry Related to Engineering.** By W. R. Cooper. Part of a "Treatise of Electrochemistry," edited by Bertram Blount. xiv + 134 pages. D. Van Nostrand & Co., New York, 1923. Price, $3.75.

This book is written for the engineer who desires some acquaintance with developments in electrochemistry that may be useful to him in his professional work.

The first third of the volume is devoted to electrolytic corrosion. The general theory is well presented, but in giving specific examples the emphasis could be better placed. Thus, only three pages are devoted to electrolytic corrosion of reinforced concrete, a very important plant problem, whereas nine pages are taken with a discussion of superimposing alternating on direct currents, which is of doubtful interest. The chapter on corrosion of brass condenser tubes gives an interesting presentation of their protection by means of an e. m. f. externally or internally applied.

It is doubtful whether the twenty-two pages on electro-osmosis and cataphoresis will be of great value to the engineer except as general information.

The subject of the electrical precipitation of dust, smoke, and fume occupies forty-five pages, a good general presentation of

this important problem being given. However, this is really a chapter on electrostatics, not electrochemistry.

About twenty-four pages are devoted to the effect of electric discharges on the growth of plants, the reason for the inclusion of which is not apparent. The book closes with a short discussion of the relative importance of cheap power and cheap freights to the manufacturer of electrochemical products.

The chief criticism of this book is concerned with the relative emphasis given to the different topics presented. These would seem to have been rated more by the authors' interest therein than by a desire to have the presentation complete and evenly balanced.

The typography of the book is to be highly commended, the various topics are presented in an interesting manner, and the volume is well worth the perusal of any engineer.

G. PRESCOTT FULLER

**Systematic Survey of Rubber Chemistry.** By C. A. BEDFORD AND H. A. WINKELMAN. 385 pages. The Chemical Catalog Co., Inc., New York, 1923. Price, $7.00.

It is generally recognized that there is today no real good book on rubber. To cover this broad and interesting subject properly would require something of the nature of a Beilstein or of "Allens' Commercial Organic Analysis." There are simply too many data for any one book or any one writer to describe properly. In lieu, then, of this deficiency, the chemical engineer or chemist who is interested in rubber must refer almost entirely to the periodical literature. The task of compiling a complete review of the literature of rubber is so great that no one can really estimate the enormous amount of careful, painstaking, and extremely exhausting effort required. For attempting this task Bedford and Winkelman should be given the thanks of everyone interested in rubber.

The book is divided into five parts. The first part contains a discussion of organic accelerators of vulcanization by L. B. Sebrell, which portrays a rather good picture of the Bedford-Bruni theories of acceleration. For one well conversant with accelerator technic it will be found quite interesting, but there is a question if it is elementary enough to be of great use to the novice. While it is to be regretted that such an important subject is condensed to such a small volume, there is no question but that Dr. Sebrell has done the work well.

In the second chapter W. J. Kelly has adequately summarized our present theories of vulcanization in 21 pages. In the reviewer's opinion it is the best discussion of this subject that has ever appeared.

The main portion of the work consists of an authors' index of 158 pages, a subject index of 154 pages, and a patent index of 9 pages. The authors' index lists the articles of each investigator in rubber under his name, with the exceptions noted together with discussions of the same. While there are probably some errors, on the whole the work has been very well done. The subject index contains references to the various authors who have written on the subjects listed. By the use of these indexes, an investigator can rather quickly locate the various articles on on almost any subject related to rubber chemistry.

One criticism of the work is based on the fact that there is so much in the literature which is really valueless that merely having a list of articles on a subject without a chart and a compass to inform the traveler as to which is right and which is wrong, is of questionable value. The reviewer is of the opinion that the authors could very easily have given a sentence or so of criticism on the different articles which would have greatly enhanced the value of the book.

It is to be regretted that the authors have limited their search to the chemistry of rubber, and that such subjects as the analysis of rubber, synthetic rubber, the physical properties of rubber, rubber testing, rubber botany, the diseases of rubber trees, and reclaimed rubber have not been considered. In so limiting the scope of the book, the authors have considerably decreased its value; in other words, there is a demand and a real need for a complete index for the literature of rubber. However, it is recognized that getting out an index even as broad as this one was a very great task, and it is hoped that Bedford and Winkelman will complete their work in the next edition.

One of the most important aspects of this publication is the fact that it indicates a changed attitude on the part of industrial concerns when they permit the publication, by their employees, of a compilation of this kind, apparently entirely financed by the company's money. It is hoped that this example may be followed by other companies, and that in this way our technical literature may be built up by publications otherwise impossible because of the amount of time and money necessary for their completion.

C. O. NORTH

**Konduktometrische Titrationen.** By I. M. KOLPHOFF. 94 pages. Theodor Steinkopff, Dresden and Leipzig, 1923. Price, 62 cents.

This book gives in the first two chapters a good summary of the laws of electrolytic conduction and the theories of dissociation and equilibrium between electrolytes. In the subsequent chapters many applications of the laws of electrolytic conductance to quantitative and analytical problems are treated in detail.

The method used is to plot the electrical conductivity as ordinates against cubic centimeters of reagent added as abscissas. The point in the curve where the slope changes suddenly represents the completion of some particular reaction.

Though conductivity measurements of this kind can give interesting information about what takes place in solutions of electrolytes, there are few practical determinations which can be done in this way any better than by the use of electrode potential measurements to determine the concentration of particular ions such as hydrogen, silver, and lead. Where either method can be used the latter is preferable, for a small addition near the end point of the reaction will usually produce a much greater change in the concentration of some particular ion than in the conductivity of the solution.

A good list of references is given, as well as a table for calculating conductivity from slide wire bridge readings. The language is less involved than most German.

W. T. BOVIE

**Notes on the Composition of Scientific Papers.** By T. CLIFFORD ALLBUT. 3rd edition. 192 pages. Macmillan & Co., Ltd., London, 1923. Price, 6 s. net.

We commend this book, written by a professor in the University of Cambridge, to all our readers and particularly to our contributors. The volume, although intended chiefly for medical students, is well worth the attention of any writer, and could be read with profit many times by authors of technical papers. This edition has been divested of the peculiarly scientific features of the first edition, and many of the medical illustrations have been exchanged for others of a pleasanter kind. The writer concerns himself, not with letters as a whole, but with so much of the form and correctness of scientific papers as in his experience is perverted or neglected by the average scientific writer. The volume is divided into two parts—the first being more general and having to do with the selection of subjects for scientific papers and the method of handling the subject matter when once a subject has been chosen. The author describes his own method of composing, which we would quote in detail if space permitted. His method of procedure is so logical and at the same time so simple that we heartily recommend it. The second portion of the book has to do with composition in all its detail. The section on misused words is particularly helpful.

Throughout the author insists on the qualities of clearness, precision, and definition, and in setting forth the common literary errors and defects he stresses the point that "it must not be supposed that 'mere literary form' is but a toilette, a skin-deep quality," but agrees with Pope in that

> True ease in writing comes from art not chance,
> As those move easiest who have learned to dance.

**Strength and Structure of Steel and Other Metals.** By W. E. DALBY. xii + 176 pages, 9 × 5³/₄ inches. Cloth. Longmans, Green & Co., New York; Edward Arnold & Co., London, 1923. Price, $6.00 net.

The general plan of the book is to compare methods of testing and correlate the results by means of the load-extension diagram, and in conjunction with this to record the results of the author's researches on the strength and structure of metals.

The subject matter comprises seven chapters. In Chapter I, Quality Tests, practically all the ordinary and a number of the less usual tests are described, together with the instruments for carrying them out. These include tensile, shock, hardness, wear, fatigue, microstructure, and so on, but exclude chemical tests. This chapter describes the Dalby recorder and includes automatic and autographic records of tests by it. Chapter II deals with load-extension diagrams as applied to the inner structure of certain metals in common use. Chapter III is a comparison of tabulated records of strength and ductility, with observation and deductions therefrom. Chapter IV is devoted to the inner structure of metals. Chapter V presents some new

phases of considering the elastic and plastic states of metals. Chapter VI deals with strength of screw threads.

The most unique feature is the author's optical recorder. In this instrument the tracing point is a spot of light which draws the load-extension diagram on a photographic plate. By the aid of two mirrors mechanically connected so as to function as optical levers, the motion of the test piece is magnified so as to make a highly sensitive and accurate record on the camera plate.

In physical make-up the book is admirable. The illustrations are of excellent selection, quality, and quantity. The arrangement of the subject matter is clear and concise. It is written so that it will appeal particularly to the engineering student and profession. At the same time it is attractive to those in other fields who know the ground it covers, and is of inestimable value to those who do not already know the field but are students of the subject.

The book represents a large amount of earnest labor and is distinctly a contribution in making available the information it brings.

<div align="right">Geo. M. Berry</div>

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol IV—Ra and Ac Families, Be, Mg, Zn, Cd, Hg. By J. W. Mellor. 1074 pages. Longmans, Green & Co., London, 1923. Price, $20.00.

Volume IV of the "Comprehensive Treatise" continues the standard set by the earlier volumes. [See This Journal, 15, 764 (1923).] The first chapter is devoted to a general discussion of the structure of matter. This is followed by a chapter on the radioactive elements, and the latter by a chapter on the architecture of the atom, the whole occupying 200 pages. These chapters give in much detail the modern views, which were entirely omitted from the theoretical discussion of valency and allied subjects given in Volume I. The discussion is apparently brought very well up to date, and the references are numerous. Little attempt is made to reconcile the various theories of the static atom with the ideas of Bohr and others, but almost all the worth-while work is quoted and the reader may judge for himself, cautioned from time to time by the author's pungent interjections concerning the speculative nature of many conclusions. The three chapters make interesting reading, and represent a valuable addition to the literature of the subject.

The remainder of the volume follows the more or less conventional lines adopted in Volumes II and III. Beryllium and magnesium are given separate treatment; zinc and cadmium are discussed together. A very large amount of material is given, frequently in extreme detail. Thus six pages are given to the solubility of magnesium carbonate, followed by about one hundred references.

Mercury is given more exhaustive treatment (about 350 pages) than has been accorded thus far to any other element. As in the earlier volumes, in the endeavor to include *everything*, many older qualitative statements of doubtful value appear, making the task of locating exact data somewhat more difficult than might have been the case if a more critical attitude had been taken.

Altogether, Volume IV contains a wealth of information on the subjects treated, and is an important addition to the earlier volumes.

<div align="right">Graham Edgar</div>

General Chemistry. An Elementary Survey Emphasizing Industrial Applications of Fundamental Principles. By Horace G. Deming. xii + 605 pages. Illustrated. John Wiley & Sons, Inc., New York, 1923. Price, $3.50.

As the author sets forth in the preface, "A special effort has been made to give the present textbook flexibility. The purpose has been to encourage the instructor to teach what he wishes to teach, in the order that seems best to suit the past preparation and the future needs of his students."

To accomplish this purpose, there has been included in the text more material than is normally put into a textbook of general chemistry. One would realize even by a casual examination that the book contains more information than the student of even more than average preparation and capacity could be expected to amass in a one-year course. This forces the instructor to choose what parts he is going to present, and the author has suggested in the preface some of the things which, in his opinion, should be omitted. He has further aided the plan by placing "material of secondary importance, or of the nature of a digression," in small type.

The book is well cross-referenced and generously supplied with

good half-tone pictures and figures. The exercises at the end of each chapter and the general reviews in the latter part of the book should aid the student materially in seeing how to apply the information which he has gained. They should also be of help to the younger instructor, as they bring to his attention the more important points in the chapters.

The appendix contains much useful information in readily available shape. Although there are some errors in the industrial information given, the book can be said to be equally as good in this respect as others on this subject. In the opinion of the reviewer, the book should serve, not only as a textbook for general chemistry, but also as a condensed reference book, especially for those who have had the advantage of using it as a textbook in a course in general chemistry.

The quality of the paper and the press work are as good as usual, and the general appearance of the volume is pleasing.

<div align="right">L. I. Shaw</div>

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## NEW BOOKS

An Advanced Course in Quantitative Analysis. Henry Fay. 2nd edition. 115 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $1.50 net.

Chemistry and Physics of Clays and Other Ceramic Materials. A. B. Searle. 695 pp. E. Benn, Ltd., London. Price, 55 s. net.

Clouds and Smokes. W. E. Gibbs. 240 pp. J. & A. Churchill, London. Price, 10 s. 6 d.

Dangerous Goods. J. Abby. 2nd edition. 319 pp. Crosby Lockwood & Son, London. Price, 30 s.

Des Essais des Fils et Cables Isolés au Caoutchouc. A.-R. Mathis. 128 pp. Dunod, Paris. Price, 14 fr.

Einfache und Fraktionierte Destillation in Theorie und Praxis. C. V. Rechenberg. 814 pp. Schimmel & Co., Leipzig. Price, paper, 17 gold marks; bound, 18 gold marks.

Elements of Engineering Thermodynamics. James A. Moyer, James P. Calderwood, and Andrey A. Potter. 2nd edition, revised. 224 pp. John Wiley & Sons, Inc., New York. Price, $2.50 net.

Essentials of International Trade. Simon Litman. 398 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $3.50 net.

Examination of Canned Salmon. E. D. Clark, R. W. Clough, C. R. Fellers, and O. E. Shostrom. 16 pp. Illustrated. National Canners Association, Seattle, Wash.

Financial Engineering. O. B. Goldman. 2nd edition, revised. 325 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $3.50 net.

First (Experimental) Report to the Atmospheric Corrosion Research Committee (of the British Non-Ferrous Metals Research Association). W. H. J. Vernon. 62 pp. Illustrated. The Faraday Society, London.

Foundations of National Industrial Efficiency. Vanderveer Custis. The Macmillan Co., New York. Price, $2.25.

Function of Vacuum in Canned Salmon. E. D. Clark, R. W. Clough, and O. E. Shostrom. 31 pp. Illustrated. National Canners Association, Seattle, Wash.

Industrial Alcohol, the Production and Use of Alcohol for Industrial Purposes, for Use as an Illuminant and as a Source of Motive Power. J. G. M'Intosh. 2nd edition, revised and enlarged. 400 pp. Scott, Greenwood & Son, London. Price, 12 s. 6 d.

Industrial Management. Richard H. Lansburgh. 488 pp. Illustrated. John Wiley & Sons, Inc., New York. Price, $4.50 net.

Keramik. E. P. Bauer. Fortschritte der Chemischen Technologie in Einzeldarstellungen. Part I. Edited by B. Rassow. 143 pp. T. Steinkopff, Dresden and Leipzig. Price, 4 s.

Lead, Its Occurrence in Nature, the Modes of Its Extraction, Its Properties and Uses, with Some Account of Its Principal Compounds. J. A. Smythe. 343 pp. Longmans, Green & Co., London. Price, 16 s.

Organic Syntheses. Vol. III. Hans Thacher Clarke, Editor-in-Chief, James Bryant Conant, Oliver Kamm, Roger Adams, Carl Shipp Marvel. 105 pp. John Wiley & Sons, Inc., New York. Price, $1.50.

Pharmaceutical and Food Analysis. Azor Thurston. 416 pp. Chapman & Hall, Ltd., London. Price, 21 s.

Proceedings of the American Society for Testing Materials, Vol. 23 (1923). Part I. 1006 pp. Part II. 683 pp. American Society for Testing Materials, Philadelphia. Price, paper, $6.00; cloth, $6.50; half-leather, $8.00.

Proceedings, National Lime Association. Twenty-first Annual Convention, June 13, 14, 15, 1923. 76 pp. National Lime Association, Washington, D. C.

Research Information Surveys on Corrosion of Metals. No. 2. Corrosion of Aluminum. Harold F. Whittaker. 8 mimeographed pages. National Research Council, Washington, D. C.

Second Year Book of the Institution of the Rubber Industry, 1923. 448 pp. Institution of the Rubber Industry, London. Price, 5 s.

Taschenbuch für Gerbereichemiker. H. R. Procter. 3rd edition. 283 pp. T. Steinkopff, Dresden and Leipzig. Price, 4 s.

Une Science Nouvelle: La Science des Vibrations Atomiques. Henri Mager. 50 figures. 141 pp. Dunod, Paris. Price, 16 fr.

# GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

## Bureau of Fisheries

Toxicities of Coal Tar, Creosote, Creosote Distillates, and Individual Constituents for the Marine Wood Borer Limnoria Lignorum. L. F. SHACKELL. *Bulletin of the Bureau of Fisheries*, 39, 1923–24, pp. 221–30. *Document* 952. Paper, 5 cents.

## Bureau of Foreign and Domestic Commerce

Dominican Republic. C. B. HOSMER. *Trade and Economic Review for 1923.* No. 32. 11 pp.

Foreign Commerce and Navigation of the United States Calendar Year of 1922. 672 pp. Cloth, $1.50.

Helping the Exporter. A Service Story Step by Step. 49 pp.

Madagascar. J. G. CARTER. *Trade and Economic Review for 1923.* No. 31. 4 pp.

Mexican West Coast and Lower California. A Commercial and Industrial Survey. P. L. BELL AND H. B. MACKENZIE with the assistance of F. J. DYER, B. F. YOST, AND W. E. CHAPMAN. *Special Agents Series* 220. 340 pp. Cloth, 85 cents.

Netherlands East Indies. C. L. HOOVER. *Trade and Economic Review for 1923.* No. 30. 26 pp.

Nitrogen Survey. Part I—The Cost of Chilean Nitrate. H. F. BAIN AND H. S. MULLIKEN. *Trade Information Bulletin* 170. 69 pp. Issued January 7, 1924. Prepared as part of the investigation of essential raw materials authorized by the Sixty-seventh Congress.

The London Market for American Textiles. H. D. BUTLER. *Trade Information Bulletin* 161. 16 pp. Issued November 5, 1923.

World Trade in Vegetable Oils and Animal Fats. J. E. WRENN. *Miscellaneous Series* 123. 214 pp. Paper, 25 cents.

## Bureau of Mines

Analytical Methods for Certain Metals, including Cerium, Thorium, Molybdenum, Tungsten, Radium, Uranium, Vanadium, Titanium, and Zirconium. R. B. MOORE AND S. C. LIND, J. W. MARDEN, J. P. BONARDI, C. W. DAVIS, AND J. E. CONLEY. *Bulletin* 212. 325 pp. Paper, 40 cents. Issued January, 1924.

Certain Interfacial Tension Equilibria Important in Flotation. W. H. COGHILL AND C. O. ANDERSON. *Technical Paper* 262. 55 pp. Paper, 10 cents. This report was prepared under a coöperative agreement with the University of Washington.

Explosives, Their Materials, Constitution, and Analysis. C. A. TAYLOR AND W. H. RINKENBACH. *Bulletin* 219. 188 pp. Paper, 20 cents.

Ferric Sulfate and Sulfuric Acid from Sulfur Dioxide and Air. E. S. LEAVER AND R. V. THURSTON. *Reports of Investigations* 2556. 5 pp. Issued December, 1923.

Gaseous Content of Ground Waters as an Aid to the Petroleum and Natural Gas Prospector. G. W. JONES, W. P. YANT, AND E. P. BUXTON. *Reports of Investigations* 2553. 15 pp. Issued December, 1923.

Methods of Decreasing Evaporation Losses of Petroleum. J. H. WIGGINS. *Technical Paper* 319. 57 pp. Paper, 15 cents.

Methods of Testing Detonators. C. A. TAYLOR AND C. E. MUNROE. *Reports of Investigations* 2558. 14 pp. Issued December, 1923.

Recovery of Gasoline from Uncondensed Still Vapors. D. B. DOW. *Technical Paper* 310. 53 pp. Paper, 15 cents.

Self-Contained Mine Rescue Oxygen-Breathing Apparatus, Handbook for Miners. D. J. PARKER, G. S. McCAA, AND E. H. DENNY. 139 pp. Paper, 20 cents.

The Effect of Silica in Iron Ore on Cost of Pig Iron Production. T. T. READ, T. L. JOSEPH, AND P. H. ROYSTER. *Reports of Investigations* 2560. 10 pp. Issued January, 1924.

## Bureau of Standards

Asphalt. *Simplified Practice Recommendation* 4. Accepted by Societies, Associations, Individual Concerns, and State Highway Officials as Listed on page 2. 6 pp. Original draft January 1, 1924. Paper, 5 cents.

Exposure Tests on Colorless Waterproofing Materials. D. W. KESSLER. *Technologic Paper* 248. Paper, 15 cents.

United States Government Specification for Vegetable Tanned Leather Belting. *Circular* 148. Paper, 5 cents.

## Bureau of the Census

Coke. *Census of Manufactures, 1921.* 11 pp. Paper, 5 cents.

## Congress

Adulterated Food. A Bill to amend an Act entitled "An Act for preventing the manufacture, sale, or transportation of adulterated or misbranded or poisonous or deleterious foods, drugs, medicines, and liquors, and for regulating traffic therein, and for other purposes," approved June 30, 1906, as amended. Introduced by Mr. Haugen, December 5, 1923. *H. R.* 762. 3 pp.

Same. A Bill to prohibit interstate shipments or transportation of certain food products; to define and to prohibit transportation and sale of adulterated or misbranded food products; to regulate traffic therein; to define and regulate cold storage; to regulate dealing in cold-storage food products; and to fix penalties for violation, and for other purposes. Introduced by Mr. McKellar, December 6, 1923. *S.* 429. 9 pp.

Agricultural Experiment Station. A Bill to establish an agricultural experiment station at Fort Mohave, in the County of Mohave, Arizona. Introduced by Mr. Ashurst, December 6, 1923. *S.* 496. 2 pp.

Alien Property Custodian. Resolution directing a select committee to be appointed by the President of the Senate to investigate the facts of the Alien Property Custodian and the administration of the Alien Property Custodian's office. Introduced by Mr. King, December 17, 1923. *S. Res.* 72. 2 pp.

Calcium Arsenate. A Bill to amend the Fordney-McCumber Tariff Act, by placing calcium arsenate on the free list. Introduced by Mr Collier, December 20, 1923. *H. R.* 4106. 1 p.

Same. A Bill to exempt from duty calcium arsenite and calcium arsenate. Introduced by Mr. Crisp, January 7, 1924. *H. R.* 4822. 1 p.

Same. A Bill to place all kinds of arsenate on the free list. Introduced by Mr. Crisp, December 5, 1923. *H. R.* 476. 1 p.

Same. A Bill to transfer calcium arsenate from the dutiable to the free list. Introduced by Mr. Clark, December 5, 1923. *H. R.* 464. 1 p.

Same. Introduced by Mr. Vinson, December 5, 1923. *H. R.* 583. 1 p.

Same. Introduced by Mr. Black, December 5, 1923. *H. R.* 629. 1 p.

Same. Introduced by Mr. McClintic, January 8, 1924. *H. R* 4974. 1 p.

Same. Resolution directing the Geological Survey to report to the Senate the location and amounts of arsenic deposits in the United States. Introduced by Mr. Harris, December 15, 1923. *S. Res.* 64. 1 p.

Department of Mines. A Bill to establish a Department of Mines. Introduced by Mr. Shortridge, December 11, 1923. *S.* 937. 12 pp.

Same. A Bill to establish a Department of Mines and for other purposes. Introduced by Mr. Oddie, December 6, 1923. *S.* 179. 8 pp.

Diploma Mills. Resolution authorizing the Committee on Education and Labor to inquire into certain abuses in medical education, and for other purposes. Introduced by Mr. Copeland, December 12, 1923. *S. Res.* 61. 2 pp.

Explosions. A Bill to enable the Secretary of Agriculture to carry out investigations of the causes and means of prevention of fires and dust explosions in industrial plants. Introduced by Mr. McKellar, December 6, 1923. *S.* 390. 2 pp.

Fertilizers. Resolution to print 1500 copies of the report of the Secretary of Agriculture concerning ammonia and nitrogen manufactured or imported for use in the United States as a Senate document. Introduced by Mr. Shields, December 20, 1923. *S. Res.* 104. 1 p.

Flaxseed. A Bill to increase the duties on wheat and flaxseed and their products. Introduced by Mr. Young, December 5, 1923. *H. R.* 594. 3 pp.

Same. Introduced by Mr. Ladd, December 6, 1923. *S.* 133. 3 pp.

Forest Experiment Station. A Bill for the establishment and maintenance of a forest experiment station in Arizona. Introduced by Mr. Ashurst, December 6, 1923. *S.* 497. 2 pp.

Same. A Bill to provide for the establishment and maintenance of a forest experiment station in coöperation with the University of California. Introduced by Mr. Raker, December 5, 1923. *H. R.* 152. 2 pp.

Same. Introduced by Mr. Raker, December 5, 1923. *H. R.* 153. 2 pp.

Helium Gas. A Bill authorizing the conservation, production, and exploitation of helium gas, a mineral resource pertaining to the national defense and to the development of commercial aeronautics, and for other purposes. Introduced by Mr. Kahn, December 5, 1923. *H. R.* 756. 5 pp.

Hydraulic Laboratory. Joint Resolution to establish a national hydraulic laboratory. Introduced by Mr. Ransdell, December 15, 1923. *S. J. Res.* 42. 1 p.

Labeling. A Bill to provide for proper labeling of bottles, receptacles, or containers containing poison which are shipped in interstate traffic. Introduced by Mr. French, December 5, 1923. *H. R.* 738. 2 pp.

**Metric System.** A Bill extending the use of metric weights and measures for certain purposes. Introduced by Mr. Ladd, December 6, 1923. *S.* 100. 3 pp.

**Same.** Introduced by Mr. Britten, December 5, 1923. *H. R.* 10. 2 pp.

**Mining.** Resolution to investigate oil leases issued under the Act approved February 25, 1920, entitled "An Act to promote the mining of coal, phosphate, oil, oil shale, gas, and sodium on the public domain." Introduced by Mr. Walsh, December 6, 1923. *S. Res.* 11. 5 pp.

**Muscle Shoals.** A Bill to authorize and direct the Secretary of War to sell to Henry Ford nitrate plant Numbered 1, at Sheffield, Alabama; nitrate plant Numbered 2, at Muscle Shoals, Alabama; Waco Quarry, near Russellville, Alabama; and to lease to the corporation to be incorporated by him Dam Numbered 2 and Dam Numbered 3 (as designated in House Document 1262, Sixty-fourth Congress, first session), including power stations when constructed as provided therein, and for other purposes. Introduced by Mr. McKenzie, December 5, 1923. *H. R.* 518. 16 pp.

**Same.** Resolution authorizing the Committee on Agriculture and Forestry to investigate charges in regard to lobbying against the resolution accepting the offer of Henry Ford to purchase Muscle Shoals. Introduced by Mr. McKellar, December 6, 1923. *S. Res.* 18. 2 pp.

**Same.** Joint Resolution relative to the offer of Henry Ford for the lease and purchase of the Government plants at Muscle Shoals. Introduced by Mr. McKellar, December 6, 1923. *S. J. Res.* 12. 1 p.

**Same.** A Bill to authorize and direct the acceptance of the offer of Henry Ford to purchase Muscle Shoals. Introduced by Mr. Vinson, December 5, 1923. *H. R.* 582. 1 p.

**Same.** A Bill to authorize and direct the Secretary of War * * to sell to Henry Ford or a corporation to be incorporated by him Nitrate Plant Numbered 1, at Sheffield, Alabama; Nitrate Plant, Numbered 2, at Muscle Shoals, Alabama; Waco Quarry, near Russellville, Alabama; steam power plant to be located and constructed at or near Lock and Dam Numbered 17 on the Black Warrior River, Alabama, with right-of-way and transmission line to Nitrate Plant Numbered 2, Muscle Shoals, Alabama, etc. Introduced by Mr. Madden, December 5, 1923. *H. R.* 8. 18 pp.

**Same.** Introduced by Mr. Ladd, December 6, 1923. *S.* 139. 18 pp.

**Same.** Resolution to investigate the legal right of the Secretary of War to dispose of the Gorgas Plant, Muscle Shoals. Introduced by Mr. McKellar, December 6, 1923. *S. Res.* 14. 2 pp.

**Nitrate.** Statement submitted to the Committee on Agriculture, House of Representatives, relative to the production of nitrates. Gray Silver. *Series H H (Second Supplement).* 75 pp.

**Oil.** A Bill relative to the acquisition of oil lands by foreign Governments. Introduced by Mr. McKellar, December 6, 1923. *S.* 424. 4 pp.

**Same.** Joint Resolution to cancel the lease of the Mammoth Oil Company. Introduced by Mr. Caraway, January 7, 1924. *S. J. Res.* 54. 2 pp.

**Paint.** A Bill for preventing the manufacture, sale, or transportation of adulterated, mislabeled, or misbranded linseed oil, turpentine, or paint. Introduced by Mr. Ladd, December 6, 1923. *S.* 136. 12 pp.

**Patents.** Resolution directing the Committee on Patents to investigate charges of alleged discrimination and favoritism in the Patent Office. Introduced by Mr. Shipstead, December 20, 1923. *S. Res.* 102. 2 pp.

**Petroleum.** Joint Resolution to cancel the lease of the Pan-American Petroleum and Transport Company. Introduced by Mr. Caraway, January 7, 1924. *S. J. Res.* 55. 2 pp.

**Pollution.** A Bill to improve the navigability of waters of the United States by preventing oil pollution thereof. Introduced by Mr. Edge, December 17, 1923. *S.* 1388. 4 pp.

**Same.** A Bill to protect navigation from obstruction and injury by preventing the discharge of oil into the coastal navigable waters of the United States. Introduced by Mr. Wadsworth, December 11, 1923. *S.* 936. 5 pp.

**Tests.** A Bill to authorize the Department of Commerce, by the national Bureau of Standards, to examine and test manufactured articles or products for the owner or manufacturer thereof, to issue a certificate as to the nature and quality of such manufactured articles or products, and to prevent the illegal use of such certificate. Introduced by Mr. Fletcher, December 10, 1923. *S.* 845. 6 pp.

## Department of Agriculture

**Action of Sodium Nitrite in the Soil.** R. H. Robinson. *Journal of Agricultural Research*, 26 (October 6, 1923), 1–7.

**Bordeaux-Oil Emulsion.** J. R. Winston, J. J. Bowman, and W. W. Yothers. *Department Bulletin* 1178. 24 pp. Issued November 21, 1923. Paper, 5 cents.

**Chemical Examination of "Chufa," the Tubers of Cyperus Esculentus Linné.** F. B. Power and V. K. Chesnut. *Journal of Agricultural Research*, 26 (October 13, 1923), 69–75.

**Directory of the Bureau of Animal Industry, corrected to October 1, 1923.** 107 pp. Paper, 15 cents.

**Effect of Autoclaving upon the Toxicity of Cottonseed Meal.** C. T. Dowell and Paul Menaul. *Journal of Agricultural Research*, 26 (October 6, 1923), 9–70.

**Investigations of the Manufacture of Phosphoric Acid by the Volatilization Process.** W. H. Waggaman, H. W. Easterwood, and T. B. Turley. *Department Bulletin* 1179. 53 pp. Paper, 15 cents. Issued December 1923.

**Soil Reaction in Relation to Calcium Adsorption.** C. O. Swanson. *Journal of Agricultural Research*, 26 (October 20, 1923), 83–123.

**The Auxotaxic Curve as a Means of Classifying Soils and Studying Their Colloidal Properties.** A. E. Vinson and C. N. Catlin. *Journal of Agricultural Research*, 26 (October 6, 1923), 11–13.

**The Constituents of "Chufa" Oil, a Fatty Oil from the Tubers of Cyperus Esculentus Linné.** W. F. Baughman and G. S. Jamieson. *Journal of Agricultural Research*, 26 (October 13, 1923), 77–82.

## Geological Survey

**Cement in 1922.** E. F. Burchard and B. W. Bagley. *Mineral Resources of the United States, 1922.* Part II, pp. 227–49. Published December 31, 1923.

**Forty-Fourth Annual Report of the Director of the United States Geological Survey to the Secretary of the Interior for the Fiscal Year Ended June 30, 1923.** 89 pp.

**Geology of the Tullock Creek Coal Field, Rosebud and Big Horn Counties, Montana.** G. S. Rogers and Wallace Lee. *Bulletin* 749. 181 pp. Paper, 50 cents.

**Gold, Silver, Copper, Lead, and Zinc in Idaho and Washington in 1922. Mines Report.** C. N. Gerry. *Mineral Resources of the United States, 1922.* Part I, pp. 217–56. Published December 18, 1923.

**Mineral Waters in 1922.** W. D. Collins. *Mineral Resources of the United States, 1922.* Part II, pp. 207–20. Published December 20, 1923.

**Sand and Gravel in 1922.** L. M. Beach. *Mineral Resources of the United States, 1922.* Part II, pp. 187–94. Published December 18, 1923.

**Surface Water Supply of the United States 1919 and 1920. Part II—South Atlantic Slope and Eastern Gulf of Mexico Basins.** N. C. Grover, G. C. Stevens, C. G. Paulsen, and W. E. Hall. *Water-Supply Paper* 502. 80 pp. Paper, 10 cents.

**Surface Water Supply of the United States 1919 and 1920. Part V—Hudson Bay and Upper Mississippi River Basins.** N. C. Grover, W. A. Lamb, and W. G. Hoyt. *Water-Supply Paper* 505. Prepared in coöperation with the States of Minnesota, Wisconsin, Iowa, and Illinois. 287 pp. Paper, 30 cents.

**Surface Water Supply of the United States 1921. Part IV—St. Lawrence River Basin.** N. C. Grover, S. B. Soule, A. H. Horton, C. C. Covert and C. H. Pierce. *Water-Supply Paper* 524. 112 pp. Paper, 10 cents. Prepared in coöperation with the States of Wisconsin, New York, and Vermont.

**Surface Water Supply of the United States 1921. Part VIII—Western Gulf of Mexico Basins.** N. C. Grover and C. E. Ellsworth. *Water-Supply Paper* 528. 96 pp. Paper, 10 cents. Prepared in coöperation with the State of Texas

## Navy Department

**Chemistry.** A Course Based on Foundations of Chemistry by Blanchard and Wade. Assignments 1 to 33. Syllabus prepared by Elliot Snow. *Navy Education-Study Courses.* 29 pp.

**Cholecystitis of Chemical Origin in Man Following Inhalations of Poison Gas.** H. M. Stenhouse. *United States Naval Medical Bulletin*, 19 (September, 1923), pp. 291–6.

## Public Health Service

**Biological Products.** Establishments Licensed for the Propagation and Sale of Viruses, Serums, Toxins, and Analogous Products. *Public Health Reports*, 38 (December 28, 1923), 3111–14.

**Effect of Acidification on Toxicity of B. Botulinus Toxin.** J. C. Geiger and W. E. Gouwens. *Reprint* 870 from *Public Health Reports.* 6 pp. Paper, 5 cents. Prepared in coöperation with the University of Chicago.

**Efficacy of Botulinus Antitoxin.** Note on "Studies on Organisms Concerned as Causative Factors in Botulism." (*Hygienic Laboratory Bulletin* 136.) *Public Health Reports*, 38 (December 14, 1923), 2966.

**Preliminary Note on Observations Made on Physical Condition of Persons Engaged in Measuring Radium Preparations.** R. C. Williams. *Public Health Reports*, 38 (December 21, 1923), 3007–28.

**Pyrotannic Acid Method for Quantitative Determination of Carbon Monoxide in Blood and Air.** R. R. Sayers, W. P. Yant, and G. W. Jones. *Reprint* 872 from *Public Health Reports.* 12 pp. Prepared in coöperation with the Bureau of Mines.

**Regulations for the Control of Manufacture, Importation, and Sale of Arsphenamine and Its Derivatives, Neoarsphenamine, Sodium Arsphenamine, Silver Arsphenamine, Neosilverarsphenamine, Phospharsphenamine, and Sulfarsphenamine, Referred to Collectively as Arsphenamines.** Supplementary to Regulations for Sale of Viruses, Serums, Toxins, and Analogous Products, Approved August 1, 1923. *Miscellaneous Publication* 22, revised. 3 pp. Paper, 5 cents.

**Studies on the Permeability of Living and Dead Cells. IV—The Penetration of Trivalent and Pentavalent Arsenic into Living and Dead Cells.** M. M. Brooks. *Public Health Reports*, 38 (December 14, 1923), 2951–66.

# MANUFACTURERS' TECHNICAL PUBLICATIONS

**Notice—***Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of* THIS JOURNAL, *on request to the firm issuing the publication. When writing for any of these items kindly mention* INDUSTRIAL AND ENGINEERING CHEMISTRY.

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**Riehlé. U. S. Standard Testing Machines.** *Catalog* "A," containing illustrations, descriptions, and particulars of operation on many types of testing machines. Indexed. 44 pp. $6 \times 9$ inches. RIEHLÉ BROS. TESTING MACHINE CO., 1424 No. 9th St., Philadelphia, Pa.

**"Technical Paints for Industrial Plants."** Booklet covering complete information on various types of paints for different classes of work. Conveniently arranged with marginal index and containing a technical article on "The Composition of Paints." Of particular value to those interested in the characteristics of different types of coatings. 28 pp. $6 \times 9$ inches. CHEESMAN-ELLIOT CO., INC., 23 Flatbush Ave., Brooklyn, N. Y.

**The Arnold Lining for Lime Kilns.** Interesting booklet giving questions and answers of general and valuable information about lime, its properties and uses. $3^{1}/_2 \times 6^{1}/_4$ inches. ARNOLD & WEIGEL, Woodville, Ohio.

**"The Reeves."** *Catalog* T-44, illustrating and fully describing uses and applications of variable speed transmissions. Prices, tables, and diagrams. 52 pp. $7 \times 10$ inches. REEVES PULLEY CO., Columbus, Ind.

**Viking Universal Pumps.** Bulletin describing and illustrating types for various purposes. 18 pp. $7^{3}/_4 \times 10^{3}/_4$ inches. VIKING PUMP CO., Cedar Falls, Ia.

**Westinghouse Underfeed Stoker.** Illustrated and descriptive of combustion equipment. 14 pp. $8^{1}/_2 \times 11$ inches. WESTINGHOUSE ELECTRICAL MANUFACTURING CO., Stoker Dept., South Philadelphia Works, Philadelphia, Pa.

**Water Softening and Filtration.** Bulletin completely covering this subject, with illustrations and descriptions of appropriate equipment. 32 pp. $8^{1}/_4 \times 10^{1}/_2$ inches. WAYNE TANK & PUMP CO., Fort Wayne, Ind.

**"Waste *vs.* Economy."** Illustrated bulletin on automatic refrigeration showing uses and applications of their system, and typical installations. 24 pp. $8^{1}/_2 \times 11$ inches. THE AUTOMATIC REFRIGERATING CO., INC., Hartford, Conn.

**Whitewash and Cold Water Paint.** *Bulletin* 304-B. Gives formulas and methods of preparation of whitewash and cold water paint. 8 pp. NATIONAL LIME ASSOCIATION, Washington, D. C.

# MARKET REPORT—JANUARY, 1924

IMMEDIATELY following the turn of the year broader activity in demand for chemicals was noted. About a week of good buying from spot stocks was followed by a slump back into inactivity for a week. Buying on the whole for the latter half of the month was steady, but apparently not up to the rate of activity reported by many of the consuming industries. The latter, it is believed, have been carrying on their operations with chemical supplies from stocks on hand. The belief that chemical stocks are being cut down in consuming quarters, and that, with greater activity, consumers will be forced into the market for some spot goods early in February, has caused a distinct hardening process in prices during the month. Sellers are considerably more bullish in their views at the close of the month than they were at its beginning.

Following the usual dullness of the holiday and inventory periods at the close of the old year and the beginning of the new, business in industrial chemicals began to take on better tone as trading became more active. A firmer undertone was noted and the tendency to shade prices for business became less noticeable. Deliveries on contract were slow in starting, but as the month drew to a close a better movement of goods was reported. After the first activity of the month, trading in chemicals dropped back into a routine demand for the usual small quantities for immediate delivery. Consumers had evidently allowed their stocks to become low and after a replenishing again dropped back into their former stride. .

One of the important developments during the month was the recovery in bleaching powder and chlorine. After gradually declining to the lowest levels in years during the last half of 1923 a stronger tone was noted in the market, which finally resulted in the announcement of an advance of 25 cents per hundred for contract and spot business at the works. Many consumers had taken advantage of the low prices and contracted for their requirements during the year, but others were caught in the higher prices. Chlorine was advanced $1/2$ cent a pound for business in tank cars. Caustic soda and soda ash have been well contracted for 1924 and deliveries are beginning to go out regularly. Current demand for heavy acids has not been important, while practically all contracts for the year have been closed. Demand for copper sulfate has been fair for future delivery and a steady improvement is expected during the next few months. Owing to the low prices for the metal, prices of copper sulfate are at low levels and little profit is expected at present selling levels. Ammonium sulfate is firmer under improved demand for spring consumption.

Potassium permanganate has been subject to keen competition between importers and domestic producers. Prices have declined steadily to 14 cents a pound for both domestic and imported material. Caustic potash has shown little improvement, while potassium carbonate is weak and prices are lower. Prussiates are holding fairly steady, though imported material is still offered at concessions in some quarters. Bichromates are slightly firmer, with some sellers asking higher prices for small quantities. Barium carbonate supplies have been increasing and imported material is considerably lower than the domestic material. Barium chloride has been fairly firm. Copperas has been subject to competition and is now quoted at lower prices. Ammonium chloride is firmer. Arsenic has been featureless during the month owing to the lack of interest, and prices have declined to $12^3/_4$ cents a pound. While some sales of calcium arsenate have been made, demand has been comparatively quiet and makers are proceeding cautiously in view of the high price of arsenic and the slow demand from consuming interests in the South.

Among the coal-tar products phenol and benzene have furnished the most interesting features. Producers of synthetic phenol have withdrawn from the market for the present, while the natural product is sold several months in advance. In the open market prices for odd lots have advanced to 36 cents a pound with very little available and difficult to obtain. After a steady decline to 18 and 19 cents per gallon, benzene has started on the upward trend. The recent advances in gasoline have strengthened coal-tar light oils and advances are recorded in benzene, toluene, and naphtha. The open winter has kept motor benzene moving steadily and producers are well sold ahead. Owing to the low prices in effect, production has been curtailed in some quarters and the total supply is somewhat below normal. Cresylic acid has become easier in view of a lessened demand and increased supplies. Pyridine is lower. Naphthalene demand for future delivery is increasing. Intermediates have been in routine demand with little in the way of price changes. Dyestuffs have been quiet but an improved demand is expected during the next month or two. Starches and dextrines have again been reduced.

Alcohol was expected to be advanced by leading producers, but no increase is expected now for at least three months owing to makers being covered for raw material over that period. Domestic manufacturers have reduced cream of tartar and now name 24 cents a pound. This price now compares favorably with the imported material, which is being held at $23^1/_2$ to 24 cents a pound.
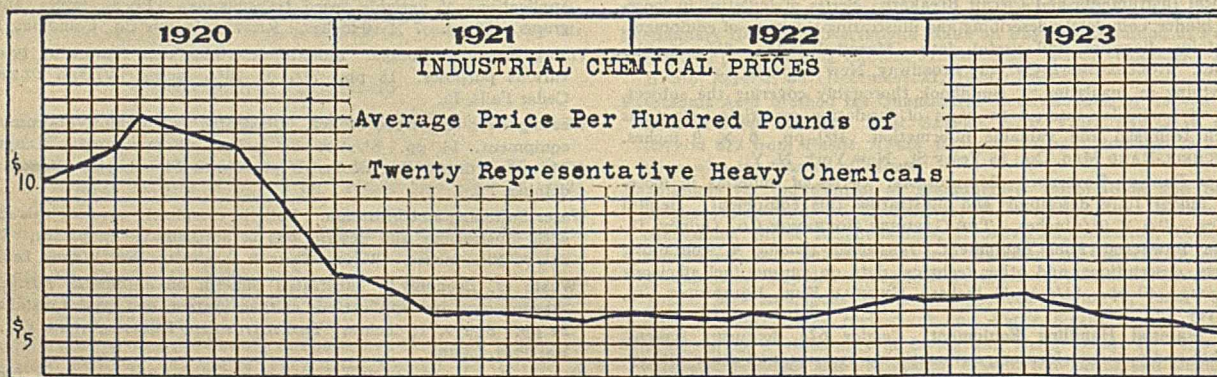
FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

## INORGANIC CHEMICALS

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Acid, Boric, cryst. bbls......lb. | .11 | .11 | .11½ |
| Hydrochloric, comm'l. 20°lb. | .01¼ | .01¼ | .01¼ |
| Hydrofluoric, 30% bbls...lb. | .07 | .07 | .06 |
| Hydriodic, 10% U. S. P...lb. | .73 | .73 | .65 |
| Nitric, 42°, cbys. c/1 wks.lb. | .06½ | .06½ | .06 |
| Phosphoric, 50% tech....lb. | .08 | .08 | .08 |
| Sulfuric, C. P..........lb. | .09 | .09 | .07 |
| 66° tks. wks.......ton | 15.00 | 15.00 | 15.00 |
| Oleum, 20%........ton | 18.00 | 18.00 | 18.00 |
| Alum, Ammonia, lump.......lb. | .03½ | .03½ | .03½ |
| Potash, lump...........lb. | *.03 | *.03 | *.03½ |
| Chrome............lb. | .05½ | .05½ | .05½ |
| Soda, ground...........lb. | .04 | .04 | .04 |
| Aluminum Sulfate (iron-free).lb. | .02½ | .02½ | .02½ |
| Ammonium Carbonate, pwd..lb. | .10½ | .10½ | .09½ |
| Chloride, white gran...lb. | .07½ | .07½ | .07½ |
| Ammonia, anhydrous.......lb. | .30 | .30 | .30 |
| Ammonia Water, drums, 26°.lb. | .07½ | .06¾ | .07½ |
| Arsenic, white..........lb. | .13¼ | .12¾ | .15½ |
| Barium Choride............ton | *85.00 | *85.00 | *92.50 |
| Nitrate................lb. | *.08½ | *.08½ | *.07½ |
| Barytes, white...........lb. | 33.50 | 33.50 | 33.50 |
| Bleaching Powd., 35%, works ................100 lbs. | 1.25 | 1.50 | 2.15 |
| Borax, cryst., bbls..........lb. | .05¾ | .05¾ | .05½ |
| Bromine, pure, wks..........lb. | .29 | .29 | .29 |
| Calcium Chloride, fused, f.o.b. N. Y.................ton | 24.25 | 24.50 | 24.50 |
| Chlorine, liquid.............lb. | .04½ | .04½ | .05¼ |
| Copper Sulfate........ 100 lbs. | 4.65 | 4.65 | 6.25 |
| Iodine, resublimed...........lb. | 4.55 | 4.55 | 4.50 |
| Lead Acetate, white crystals..lb. | .14 | .14 | .13 |
| Nitrate...............lb. | .22 | .22 | .22 |
| Red.............. 100 lbs. | 11.40 | 11.40 | 10.60 |
| White (Carb.)..........lb. | .09¾ | .09¾ | .08½ |
| Lime, live and hydrated, bbl..lb. | .01½ | .01½ | .01½ |
| Oyster shell..........lb. | .03½ | .03½ | .03 |
| Lime Acetate......... 100 lbs. | 4.00 | 4.00 | 3.50 |
| Magnesium Carbonate, tech..lb. | .08 | .08 | .08 |
| Magnesite, calcined......ton | 55.00 | 55.00 | 55.00 |
| Phosphorus, yellow..........lb. | .35 | .35 | .32 |
| Red................lb. | .75 | .75 | *.30 |
| Plaster of Paris, tech ......bbl. | 3.30 | 3.30 | 3.30 |
| Potassium Bichromate.......lb. | .09½ | .09½ | .10 |
| Bromide, imported......lb. | .17 | *.17 | .14½ |
| Carbonate, calc.,80–85%.lb. | .06 | .06 | *.05½ |
| Chlorate, cryst......lb. | *.07½ | *.07½ | *.05½ |
| Hydroxide, 88–92%....lb. | *.06¼ | *.06½ | *.08 |
| Iodide, bulk, U. S. P....lb. | 3.75 | 3.75 | 3.60 |
| Nitrate.............lb. | .06½ | .06½ | .06½ |
| Permanganate, U. S. P...lb. | *.14 | *.14 | *.16 |
| Prussiate, red..........lb. | *.42 | *.42 | *.90 |
| Yellow...........lb. | *.22 | *.21 | *.38 |
| Salt Cake, bulk..........ton | 24.00 | 24.00 | 28.00 |
| Silver Nitrate..............oz. | .44 | .44 | .44 |
| Soda Ash, 58%, bags....100 lbs. | *1.94 | *1.94 | *2.00 |
| Caustic, 76%, N. Y. 100 lbs. | 3.66 | 3.66 | 3.50 |

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Sodium Acetate............lb. | .05 | .05 | .07¼ |
| Bicarbonate....... 100 lbs. | 2.25 | 2.25 | 2.00 |
| Bichromate..........lb. | .07⅜ | .07⅜ | .07¾ |
| Bisulfite, powd........lb. | .04½ | .04½ | .04 |
| Chlorate...........lb. | .06½ | .06½ | .06½ |
| Cyanide, 96–98%.......lb. | .23 | .23 | .23 |
| Fluoride, tech........lb. | .09 | .09 | .09½ |
| Hyposulfite, bbls... 100 lbs. | 2.75 | 2.75 | 3.60 |
| Nitrate, 95%...... 100 lbs. | 2.52 | 2.48 | 2.57½ |
| Nitrite.............lb. | .08½ | .08½ | .08½ |
| Prussiate, yellow........lb. | .11½ | .11½ | .18½ |
| Phosphate (di-sod.), tech.lb. | .03½ | .03½ | .03½ |
| Silicate, 40°........lb. | .80 | .80 | .80 |
| Sulfide, 60%, fused......lb. | .04 | .04 | .05 |
| Strontium Nitrate...........lb. | *.12 | *.12 | *.08¾ |
| Sulfur, flowers........100 lbs. | 3.00 | 3.00 | 3.00 |
| Crude, mines......long ton | 14.00 | 14.00 | 14.00 |
| Tin Bichloride, 50% sol'n....lb. | .13½ | .13½ | .10¼ |
| Oxide................lb. | .51 | .51 | .43 |
| Zinc Chloride, U. S. P........lb. | .25 | .25 | .20 |
| Oxide, bbls.........lb. | .08⅛ | .08⅛ | .07½ |

## ORGANIC CHEMICALS

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Acetanilide, U. S. P., bbls....lb. | .32 | .32 | .35 |
| Acid, Acetic, 28 p. c.... 100 lbs. | 3.38 | 3.38 | 3.17½ |
| Glacial.........100 lbs. | 12.78 | 12.78 | 12.05 |
| Benzoic, U. S. P.........lb. | .72 | .72 | .72 |
| Carbolic, cryst., U. S. P., drums............lb. | .30 | .36 | .32 |
| 50- to 110-lb. tins...lb. | .32 | .32 | .34 |
| Citric, crystals, kegs.....lb. | *.48 | *.48 | *.48½ |
| Oxalic, cryst., bbls., wks.lb. | .12 | .12 | .13½ |
| Pyrogallic, resublimed...lb. | 1.55 | 1.55 | 1.55 |
| Salicylic, U. S. P........lb. | .35 | .35 | .45 |
| Tannic, U. S. P., bbls....lb. | .83 | .83 | .70 |
| Tartaric, cryst., U. S. P...lb. | *.31 | *.31 | *.32 |
| Acetone, drums.........lb. | .25 | .25 | .21 |
| Alcohol, denatured, complete. gal. | .48 | .48 | .45 |
| Ethyl, 190 proof, bbls..gal. | 4.83 | 4.83 | 4.70 |
| Amyl Acetate.............gal. | 4.65 | 4.65 | 2.50 |
| Camphor, Jap, refined, cases .lb. | .87 | .87 | .86 |
| Carbon Bisulfide, c/1........lb. | .06 | .06 | .06 |
| Tetrachloride.........lb. | .10½ | .10½ | .10½ |
| Chloroform, U. S. P., drums...lb. | .35 | .35 | .35 |
| Creosote, U. S. P...........lb. | .40 | .40 | .40 |
| Cresol, U. S. P...........lb. | .25 | .25 | .25 |
| Dextrin, corn...........100 lbs. | 3.64 | 3.49 | 3.09 |
| Imported Potato........lb. | .07½ | .07½ | .09 |
| Ether, U. S. P., 100 lbs........lb. | .13 | .13 | .13 |
| Formaldehyde, drums......lb. | .10¾ | .10¾ | .16 |
| Glycerol, dynamite, drums...lb. | .16½ | .16½ | .16½ |
| Methanol, pure, drums......gal. | .92 | .92 | 1.35 |
| Methylene Blue, med........lb. | 2.25 | 2.25 | 2.25 |
| Petrolatum, light amber......lb. | .04½ | .04½ | .03¾ |
| Pyridine ..................gal. | 3.75 | 3.75 | 2.75 |
| Starch, corn, pow'd.....100 lbs. | 3.22 | 3.07 | 2.47 |
| Potato, Jap............lb. | .06 | .06 | .06¾ |
| Sago..................lb. | .05 | .05 | .03½ |

* Resale or Imported (not an American maker's price).



MEDICINAL CHEMICAL PRICES
Average Price of Twenty Representative Fine Chemicals
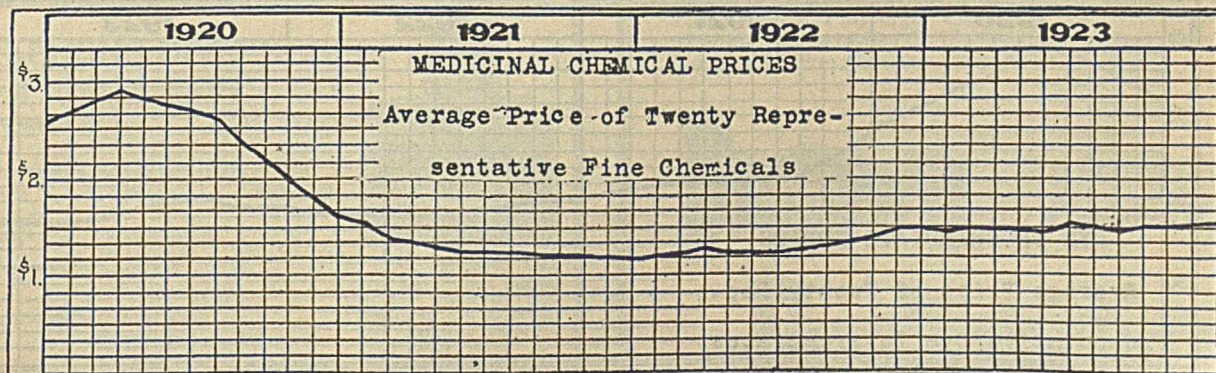
## OILS, WAXES, ETC.

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Beeswax, pure, white........lb. | .36 | .36 | .36 |
| Castor Oil, No. 3............lb. | .14 | .14½ | .13 |
| Ceresin, yellow.............lb. | .08 | .08 | .08½ |
| Corn Oil, crude, tanks, mills...lb. | .10 | .10 | .09¾ |
| Cottonseed Oil, crude, f. o. b. mill.................lb. | .09½ | .09½ | .09⅝ |
| Linseed Oil, raw, lc/l........gal. | .90 | .92 | .87 |
| Menhaden Oil, crude, mills...gal. | — | — | .53 |
| Neat's-foot Oil, 20°.........lb. | .17½ | .17½ | .18½ |
| Paraffin, 128–130 m. p., ref....lb. | .04 | .04 | .04 |
| Rosin, "F" grade, 280 lbs....bbl. | 5.80 | 6.00 | 6.25 |
| Rosin Oil, first run.........gal. | .43 | .43 | .45 |
| Shellac, T. N..............lb. | .63 | .63 | .80 |
| Sperm Oil, bleached winter, 38°.................gal. | .84 | .84 | 1.03 |
| Stearic Acid, double pressed...lb. | .12 | .12¼ | .12½ |
| Tallow Oil, acidless..........lb. | .10 | .10 | .11½ |
| Turpentine, spirits of.......gal. | .94 | 1.05 | 1.56 |

## METALS

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Aluminium, No. 1, ingots.....lb. | .28 | .28 | .23 |
| Antimony, ordinary......100 lbs. | 10.00 | 11.00 | 6.75 |
| Bismuth...................lb. | 2.75 | 2.75 | 2.75 |
| Copper, electrolytic..........lb. | .13 | .12⅝ | .14¾ |
| Lake..................lb. | .13 | .12⅞ | .14¾ |
| Lead, N. Y.............100 lbs. | 8.00 | 8.00 | 7.80 |
| Nickel, electrolytic...........lb. | .29 | .29 | .36 |
| Platinum, refined, soft........oz. | 125.00 | 125.00 | 118.00 |
| Quicksilver, flask......75 lbs. ea. | 61.00 | 60.00 | 73.00 |
| Silver, foreign...............oz. | .64¾ | .63 | .63 |
| Tin.......................lb. | .47 | .48¾ | .39 |
| Tungsten Wolframite....per unit | 8.50 | 8.50 | 7.50 |
| Zinc, N. Y.............100 lbs. | 6.70 | 6.75 | 8.25 |

## FERTILIZER MATERIALS

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Ammonium Sulfate, expt.100 lbs. | 2.75 | 2.90 | 3.90 |
| Blood, dried, f. o. b. N. Y...unit | 4.30 | 4.30 | 4.70 |
| Bone, 3 and 50, ground, raw..ton | 25.00 | 25.00 | 28.00 |
| Calcium Cyanamide, unit of ammonia................. | 2.25 | 2.25 | 2.25 |
| Fish Scrap, dried, wks.......unit | 4.75 | 4.75 | 5.35 & .10 |
| Phosphate Rock, f. o. b. mine: | | | |
| Florida Pebble, 68%.....ton | 3.25 | 3.25 | 3.00 |
| Florida, 70%...........ton | 3.55 | 3.55 | 3.55 |
| Florida, 74–75%........ton | 4.50 | 4.50 | 4.50 |
| Tennessee, 72%........ton | 5.50 | 5.50 | 5.25 |
| Potassium Muriate, 80%....unit | .68 | .68 | .68 |
| Tankage, high-grade, f. o. b. Chicago..............unit | 3.65 & .10 | 3.65 & .10 | 4.75 & .10 |

## COAL-TAR CHEMICALS

### Crudes

| | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Anthracene, 80–85%........lb. | .75 | .75 | .75 |
| Benzene, pure, tanks.......gal. | .20 | .22 | .30 |
| Naphthalene, flake.........lb. | .06½ | .06½ | .06½ |
| Phenol, drums.............lb. | .30 | .36 | .32 |

| Crudes (concluded) | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Toluene, pure, tanks........gal. | .22 | .24 | .30 |
| Xylene, 2 deg. dist. range, drums................gal. | .45 | .45 | — |

### Intermediates

| Acids: | Jan. 1 | Jan. 15 | Jan. 1923 |
|---|---|---|---|
| Anthranilic.............lb. | .96 | .96 | 1.10 |
| Benzoic, tech...........lb. | .70 | .70 | .65 |
| Cleve's...............lb. | 1.00 | 1.00 | 1.25 |
| Gamma...............lb. | 1.65 | 1.65 | 1.85 |
| H...................lb. | .75 | .75 | .80 |
| Metanilic.............lb. | .60 | .60 | .60 |
| Monosulfonic F.........lb. | 2.30 | 2.30 | 2.30 |
| Naphthionic, crude.......lb. | .62 | .62 | .60 |
| Nevile & Winther's.......lb. | 1.10 | 1.10 | 1.15 |
| Picric.................lb. | .25 | .25 | .20 |
| Sulfanilic.............lb. | .20 | .20 | .19 |
| Tobias'...............lb. | 1.00 | 1.00 | 1.30 |
| Aminoazobenzene...........lb. | 1.15 | 1.15 | 1.15 |
| Aniline Oil...............lb. | .16½ | .16½ | .17 |
| Aniline Salt..............lb. | .24 | .24 | .25 |
| Anthraquinone (sublimed).....lb. | 1.00 | 1.15 | 1.30 |
| Benzaldehyde, tech..........lb. | .75 | .75 | .65 |
| U. S. P..............lb. | 1.50 | 1.50 | 1.40 |
| Benzidine Base............lb. | .82 | .82 | .84 |
| Benzidine Sulfate..........lb. | .70 | .70 | .70 |
| Diaminophenol............lb. | 3.80 | 3.80 | 3.75 |
| Dianisidine..............lb. | 4.60 | 4.60 | 4.50 |
| p-Dichlorobenzene..........lb. | .17 | .17 | .17 |
| Diethylaniline.............lb. | .50 | .55 | .60 |
| Dimethylaniline............lb. | .39 | .39 | .41 |
| Dinitrobenzene............lb. | .19 | .19 | .19 |
| Dinitrotoluene............lb. | .19 | .19 | .20 |
| Diphenylamine............lb. | .48 | .48 | .50 |
| G Salt.................lb. | .55 | .55 | .60 |
| Hydroquinol.............lb. | 1.40 | 1.40 | 1.05 |
| Monochlorobenzene.........lb. | .10 | .10 | .10 |
| Monoethylaniline...........lb. | 1.00 | 1.00 | 1.00 |
| b-Naphthol, dist...........lb. | .26 | .26 | .26 |
| a-Naphthylamine..........lb. | .35 | .35 | .29 |
| b-Naphthylamine..........lb. | .76 | .76 | .95 |
| m-Nitroaniline.............lb. | .78 | .78 | .80 |
| p-Nitroaniline.............lb. | .74 | .74 | .74 |
| Nitrobenzene (Oil Mirbane)...lb. | .10 | .10 | .10 |
| p-Nitrophenol.............lb. | .75 | .75 | .72 |
| o-Nitrotoluene............lb. | .10 | .10 | .10 |
| p-Nitrotoluene............lb. | .55 | .55 | .65 |
| m-Phenylenediamine.........lb. | .96 | .96 | 1.00 |
| p-Phenylenediamine.........lb. | 1.45 | 1.45 | 1.50 |
| Phthalic Anhydride.........lb. | .25 | .30 | .35 |
| R Salt.................lb. | .55 | .55 | .55 |
| Resorcinol, tech...........lb. | 1.40 | 1.40 | 1.50 |
| U. S. P..............lb. | 2.25 | 2.25 | 2.00 |
| Schaeffer's Salt............lb. | .60 | .60 | .60 |
| Sodium Naphthionate........lb. | .62 | .62 | .62 |
| Thiocarbanilide............lb. | .30 | .30 | .35 |
| Tolidine (base)............lb. | .95 | .95 | .95 |
| Toluidine, mixed...........lb. | .31 | .31 | .30 |
| o-Toluidine..............lb. | .14 | .14 | .15 |
| p-Toluidine..............lb. | .85 | .85 | 1.00 |
| m-Toluylenediamine.........lb. | .90 | .90 | .95 |
| Xylidine................lb. | .50 | .50 | .43 |



DYE INTERMEDIATE PRICES

Average Price of Twenty Representative Dye Intermediates