Industrial and Engineering Chemistry

Vol. 18, No. 6

JUNE 1, 1926

Soil Conservation

IT IS doubtful if any one problem can be designated as the one of greatest importance before scientific men, but we believe it to be true that no problem exceeds in importance that of soil conservation, for it relates directly to the food supply. Agriculture is fundamental, although economics may occasionally mistreat it as if it were of no consequence.

The necessity of maintaining soil fertility has been recognized by the National Industrial Conference Board, a group composed of leading manufacturers. A report recently made to this board emphasizes the steady decrease in the vitality of our soil—the removal of necessary minerals at a rate greatly exceeding the restoration of such substances to the soil. The report states that in the United States the leading crops annually absorb about 17,000,000,000 pounds of ammonia, phosphoric acid, and potash, that the farms themselves return to the soil in plant food no more than 8,700,000,000 pounds, and that in 1925 another 2,400,000,000 pounds of plant food was supplied in the form of commercial fertilizer. This leaves a deficiency of some 5,900,000,000 pounds. Statistics compiled by other investigators show an even greater consumption of plant foods, and they therefore stress still more strongly the need for replacing the chemical compounds required for plant growth. In those years when the farmer's business is poor and the purchasing power of what he raises is very low, when considered in terms of what he must buy, an even smaller amount of plant food is returned to the soil as commercial fertilizer. The people generally, whether they realize it or not, are the ultimate losers.

Until recent years those studying soil fertility have made nitrogen, potassium, and phosphorus compounds the subject of their researches. There has been enough in these subjects to fully occupy their attention. Beginning with the experiment station at Rothamsted, England, a great number of agricultural experiment stations have been established in various parts of the world, and particularly in every State of the Union. Our Department of Agriculture has taken the lead, and the results are recorded in a voluminous literature and in greatly improved farm practice. Perhaps too little attention has been given to the general question of the physiological salt requirements of plants. Here and there we find information to show that other elements than those ordinarily listed as fertilizers are essential. Data have been published regarding calcium, sulfur, manganese, and iron and their relation to crops. But the surface of these problems has just been scratched. Nitrates, having been dragged into politics, have been emphasized before the public in such a way as to cause other factors in food production to be more or less neglected. Phosphoric acid is being intensively studied, both within and without government bureaus, principally to find some way of producing phosphorus in concentrated form for our phosphate requirements. The subject is far from exhausted. Potash is coming more and more to the fore in America, and elsewhere in this issue mention is made of the notable achievements at Searles Lake. Some attention has been given to the part the bacteria play, but here again we find further and more intensive study desirable.

Soil conservation, although receiving attention for many years, is still a question of commanding importance—of such importance that we believe the federal activities can be reorganized and the lines of attack coördinated to great advantage. The act providing appropriations for the Department of Agriculture brings the Fixed Nitrogen Research Laboratory into the Bureau of Soils. It will be recalled that heretofore this laboratory has done its work upon a lump sum appropriation, with which it was established at the close of the war. With the exhaustion of that sum this year it would have been necessary to have secured a special act of Congress for the continuation of the laboratory as a separate unit, had it not definitely become a part of one of the existing bureaus.

The present chief of the Bureau of Soils has a long record of service. He should now be relieved of the routine of administration and provided with facilities to enable him, while acting in an advisory capacity to the Department of Agriculture, to summarize his work and bring together his wonderful store of data on soils throughout the world.

We believe that all the lines of work having to do with soil conservation and soil fertility should be combined under a Bureau of Soil Conservation. The head of this new bureau should be a vigorous, well-trained scientist with authority to bring together the men best qualified to carry on the work. He should also be permitted to transfer elsewhere or dismiss any who cannot be fitted into a comprehensive plan of intensive work. Such a bureau would investigate all phases of soil fertility and would coöperate with those expert in field work, as well as with the state agricultural experiment stations, to which should be assigned much of the routine service work which the federal bureaus are now called upon to perform. Coöperation with the Bureau of Plant Industry would be essential, and in a new conception of the problems of today the valuable results of past work need not be discarded but, instead, will take on new significance. Concentrated fertilizers and their use, an instance of manufacture advanced beyond correct methods for application, presents a subject for immediate and intense study.

When one considers that the population of the United States may be expected to reach one hundred and fifty million by 1950, and that for its maintenance on the present basis an additional 38 million acres of agricultural land must be brought into production, the significance of soil conservation cannot be overemphasized. If one result of this work should be the production on present agricultural land of increased food supplies for a larger population, the saving in labor alone would be an economic item of great importance. Any objection to the creation of a business-like bureau of soil conservation should disappear in the face of our obvious duty. A new vision of soil conservation in relation to civilization must be caught.

An Ostrich Egg

YOU will recall the story of the rooster who laboriously rolled an ostrich egg into the hen yard, not in a spirit of criticism but merely to allow the hens to see what was being done elsewhere. What we shall say on the subject of scientific publication can be looked upon as an ostrich egg by those who feel that the ability of America to support scientific publication is greater than that so far demonstrated. Others will perhaps see in the record something worthy of congratulation and have a pride in being a part of an organization which, through conservative policy, well administered and with strength gained by unprecedented numbers, has been able to accomplish so much practically unaided.

If you sometimes feel that the publication facilities of the AMERICAN CHEMICAL SOCIETY are inadequate, please remember that we have to our credit the *Journal of the American Chemical Society, Chemical Abstracts, Industrial and Engineering Chemistry, Chemical Reviews*, the scientific and technologic series of monographs, the *Journal of Chemical Education* (the project of a division of the SOCIETY), and a share in the *Journal of Physical Chemistry.* To the best of our knowledge no other scientific society in the world undertakes such an ambitious program and none spends so large a proportion of its income—nearly 90 per cent in the case of the AMERICAN CHEMICAL SOCIETY—upon publication. At the present time the cost per member for the *Journal of the American Chemical Society, Chemical Abstracts,* and THIS JOURNAL is $19.20.

Chemists in other lands are not so fortunate. A correspondent in the *Scientific Worker* (a British publication) for February, 1926, points out that to receive literature which even undertakes to cover the same field as do the major publications of our SOCIETY an English chemist must pay the equivalent of $27.50. In Germany the field is covered by three publications at a cost of $30.25 to members and $48.55 to nonmembers. An examination of a price list of leading chemical journals published in England and on the Continent only serves to emphasize the fact that the American chemist is obtaining much more for his money than any other chemist in the world.

Notwithstanding this excellent record, it is apparent that a willingness to pay more would make it possible for the SOCIETY to perfect its publication service and that even small sums in addition to the present income would lead to great improvements, now that its journals are so well established.

So when you hear of what is being done elsewhere, answer with the facts concerning the accomplishments of our own SOCIETY, although of course if you are not satisfied with the size of the American egg you might try a feeding experiment.

Chemist Plus Man

PAST President L. H. Baekeland, addressing members of the Chemists' Club at the past presidents' dinner, emphasized that "A chemist, however able he may be in his science or his profession, is an awkward, undeveloped individual if he does not acquire those qualities that make of a man a real man, and not merely a specialist-freak. This addition of the man to the mere chemist has been frequently the beginning of a very successful career which otherwise might have miscarried. In this respect chemists, and especially young chemists, have much to gain by frequenting this club."

This is not only true of the Chemists' Club but local section meetings, regional meetings, symposia, and, in particular, the semiannual meetings of the AMERICAN CHEMICAL SOCIETY.

Gas in the Ascendency

AMONG the various anniversaries occurring in 1926 should be mentioned four of the gas industry. In 1796 a few citizens of Philadelphia assembled to watch an Italian maker of fireworks demonstrate the lighting qualities of the gas flame. In 1806 David Melville lighted his home and the street where his house was located in Newport, R. I., with gas. In 1816 the first gas company in the United States was founded in Baltimore. In 1876 an exhibition of cooking by gas was given at the Centennial Exposition at Philadelphia. That was the first time gas had been used for cooking and the feat was noted in the public press.

At times the early demise of the gas industry has been predicted, but we have no better example of the use of adversity and threatened danger as a stimulant. The electric light has proved one of this industry's greatest blessings. That chemistry saved the lighting industry by the perfection of the Welsbach mantle is an oft-told story, but it is doubtful whether the industry would have expanded so rapidly to its present size but for the necessity of finding new uses for gas, following its unequal competition with electricity in the lighting field.

The sales of gas for all purposes in 1925 established a new record of 421 billion cubic feet. This was an increase of 16 billion cubic feet over 1924 and of 100 billion in the last five years. In the past ten years gas sales have more than doubled. Not only has there been a large annual increase in the number of persons served by gas, but an increase in the average individual consumption. Figures made public by the American Gas Association show that approximately 52 million people in the United States now use gas, that there are 9,800,000 gas stoves, 3,400,000 water heaters, and 4,400,000 space heaters. At present about 400,000 new customers are being added annually.

In industry the gains are no less important. A few years ago gas engineers were proud of a list of one thousand different heating applications. This soon grew to five thousand, and now an English engineer states that gas is used in more than twenty-one thousand trade processes. Many look upon the use of gas as the real answer to fuel conservation and a vital factor in any superpower plan to utilize coal at the mines. The advent of the gas-fired refrigerator, the adoption of the temperature method of cooking food, the desire for homes automatically heated in winter and artificially cooled in summer—all point to continued expansion for the gas industry. Chemists who believe that true conservation simply involves efficient utilization will welcome this expansion in an industry peculiarly chemical in its characteristics, for they appreciate the loss incident to the burning of coal in the raw state and the value of an air unpolluted by smoke and soot.

The gas industry has reached its present state of affluence because it has been willing to apply science and to take advantage of any opening made by the application of new facts. A recent example of this is the scrapping by one gas company of a $100,000 ammonia-distilling apparatus and the spending of $250,000 for a new ammonium sulfate plant. This change was made in recognition of the fact that the fixation of atmospheric nitrogen makes possible the production of a purer ammonia at a lower price than can be made by the distillation of ammonia liquor, which is a by-product in gas manufacture, thus making it advisable for this particular gas company to make a product for the fertilizer trade.

The activities of the American Gas Association and of many companies which maintain research laboratories indicate that in this chemical industry there is still much to be done and that gas should be looked upon as an industry that is in every sense progressive.

Commodity Acceptance Testing

DO YOU buy on specifications which clearly state the properties of the article, or do you continue to specify a particular brand "or equal?" The latter practice belongs to the days of the windpost of the Northwest Indians, but it is still followed by the great majority of purchasers, whether they be manufacturers buying materials for resale after the application of their processes, or the ultimate consumer.

The Department of Commerce is convinced that the wider use of sane specifications would go a long way toward eliminating waste in manufacture, and as a first step in that direction urges the simplification and unification of specifications. To this end a subject index of some 407 U. S. Government Master Specifications will soon be sent to more than ten thousand purchasing agents. The index will indicate methods whereby copies of these specifications can be secured. These specifications have not been set up as necessarily ideal or the ones which should take precedence over those established in industry, but they are offered as the ones used by all government bureaus and as indicating one basis upon which others buying similar materials may specify what they want. Since but few items in commerce are bought on specifications, it may easily follow that many will adopt these master specifications, at least until experience shows a better way.

The wider use of specifications leads in two directions: first, the more extensive testing of commodities prior to final acceptance; and second, the extension of the certification list now being compiled by the Bureau of Standards.

The bureau is already in position to furnish considerable information regarding the equipment of various testing laboratories and this information will doubtless be greatly extended. Manufacturers and other purchasers, therefore, who desire to purchase on specifications but have no facilities for testing commodities may thus learn channels through which such testing can be satisfactorily done. Since the present work was undertaken by the bureau at the request of state and municipal purchasing agents, it seems reasonable to expect that the testing done officially for such states and municipalities will be carried on in laboratories in institutions supported by such organizations. Where a state educational institution lacks adequate equipment, the official bureaus requesting the test and the institution in position to provide the personnel will undoubtedly coöperate, so that adequate testing facilities may be available in such laboratories. This increases facilities for research, provides extensive experience for students, and enables state institutions to extend their service to the supporting public. On the other hand, there are temptations which the directors of these departments must resist. Their departments must not become testing laboratories to the detriment of research and the neglect of teaching. It is a service that can be properly performed without such emphasis as to detract from the fundamental work of an educational institution.

So far as the manufacturers and other purchasers are concerned, the adoption by them of specifications should not only lead immediately to lower costs but bring home to them the advantages of the testing laboratory, with the employment of science on more perplexing problems the next step. Well-established commercial laboratories with a reputation for reliable and careful work are certain to profit.

Some purchasing agents will not look upon this plan with approval. We still meet the familiar P. A., who regards the chemist as a man who seeks to displace him and who fails to realize that the advances made in methods of manufacture make it humanly impossible to purchase to advantage without the aid of laboratory guidance. The purchasing agent can no longer depend wholly upon his five senses or his simple faith in a salesman whom he knows personally. Both may be fooled through some unique treatment of materials with which they are unfamiliar. The number of these old timers is gradually diminishing.

The certification plan as now being applied by the Bureau of Standards calls for the listing of those firms which, upon request, are placed on the list of manufacturers willing, when requested, to certify to purchasers that material supplied by them is in accordance with a particular U. S. Government Master Specification. These lists, which already comprise the names of more than five hundred manufacturers, will be classified by commodities and specifications relating thereto.

This project will commend itself to our readers. A unification and simplification of specifications is needed. Experience tells us that the gains can be large. We believe purchasers, and manufacturers as well, will heartily support the plan when it is thoroughly understood and given a fair trial.

Fortune Favors the Brave

IF YOU had been told back in war days that by 1927 the United States would possess one of the two or three largest potash refineries in the world, you would probably have expressed skepticism, just as we all were doubtful about many other eventual developments. The present construction work of the American Trona Corporation will make it possible for the plant at Searles Lake to produce 90,000 tons of potassium chloride and approximately 45,000 tons of borax in 1927. This potash production will be greater than that of any single mine in France or Germany, while the borax refinery will be the largest in the world, producing more than half the world's requirements. The maximum production of all the American plants during the war did not exceed 55,000 tons of K_2O, while the 1927 production of the Trona plant will be equivalent to about 56,000 tons of K_2O.

Potash is cheaper in the United States now than before the war and a potash monopoly is a thing of the past, for today we have three potash producers. The German exports are slightly more than double those of France. Germany exports all the sulfate and about five-eighths of the other potassium salts. France exports no sulfate and three-eighths of all other potash compounds. American production in 1927 will amount to from 17 to 20 per cent of the American requirements, but it is still capable of further enlargement. It is gratifying that the feeling between French, German, and American producers is friendly and that recently no difficulties have been encountered. It is also a pleasure to note that the fertilizer manufacturers whom we once had occasion to criticize on account of their policy toward American-made potash are now buying the entire American output before arranging for the remainder from abroad.

This noteworthy growth in the American potash industry has taken place without tariff protection, and is due to the belief in fundamental research and to the bravery of the directors in investing large funds in maintaining the American Trona Corporation until it is now able to show a profit and sell its product in a highly competitive market. The fact that this company is expanding under conditions fatal to its American rivals can be explained only by the excellence of the research work done in developing the process and the fact that the money back of the enterprise did not "get scared."

The great outlet for potash in American agriculture makes this a favorable time for the expansion of this industry, as well as for any others who may engage in potash production, having special reference to the recent prospects uncovered in Texas. Searles Lake has been an interesting story full of thrills, adventures, and victories through chemistry.

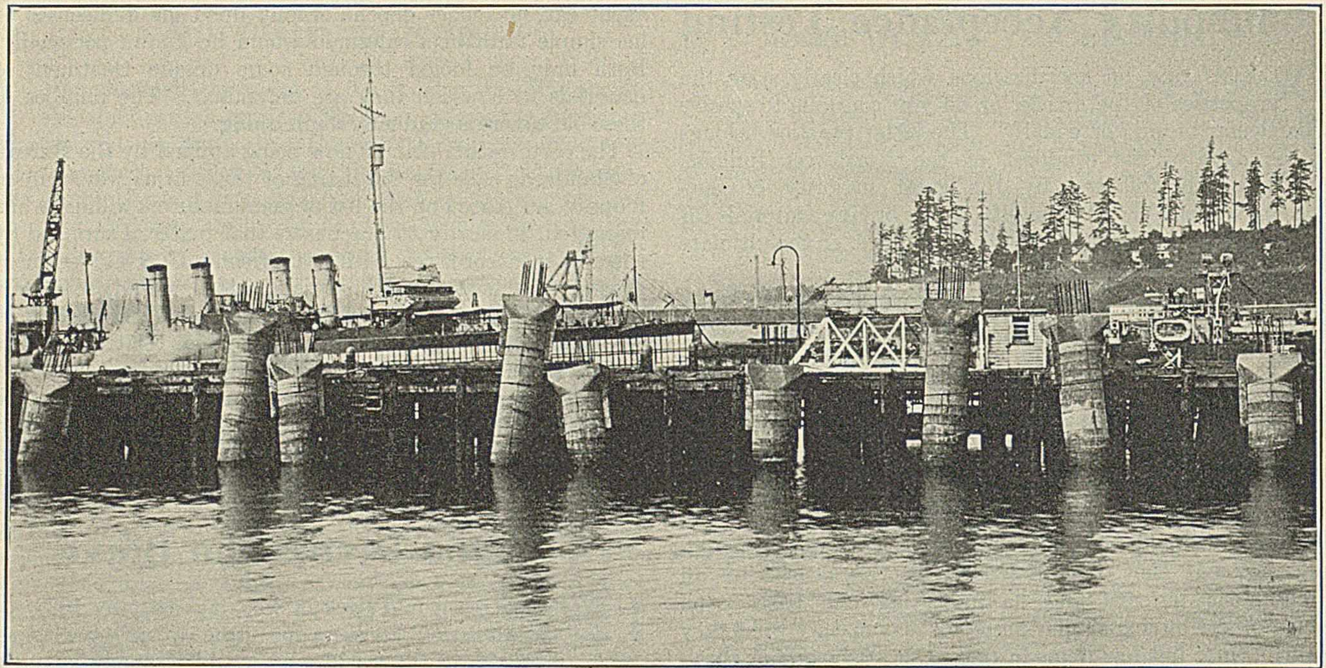

Figure 1—High-Alumina Cement Concrete Cylinders, as Shown in the Process of Making in Figure 5, Placed in Water Pending Final Placing

High-Alumina Hydraulic Cements[1,2]

By P. H. Bates

Bureau of Standards, Washington, D. C.

A GREAT deal of interest has been aroused recently by the appearance on the market of a new hydraulic cement characterized by the rapidity with which it attains strength. While Portland cement, the hydraulic cement so well known to all, will develop at the end of 28 days a strength of 2200 pounds per square inch when tested in a concrete of fair quality, composed of one part of cement to six parts of aggregate of good selection and grading, a concrete of this new cement will develop the same or greater strength at 24 hours when made of the same materials.

It is natural that there should be some interest as to wherein this cement differs from Portland cement. This, so far as composition is concerned, can be answered by referring to the following table:

Portland Cement

	Per cent
SiO_2	22.0
Al_2O_3	6.5
Fe_2O_3	3.0
CaO	63.0
MgO	3.0
SO_3	1.5
Impurities	1.0

High-Alumina Cement

	Per cent
SiO_2	5.0
Al_2O_3	42.0
Fe_2O_3	10.0
CaO	42.0
Impurities	1.0

These new cements are, therefore, distinctly high in alumina and consequently are frequently called high-alumina cements. Portland cements are made from either limestone and clay or any other naturally or artificially occurring materials such as will give the composition required after mixing and burning, while on the other hand to make the new product limestone and bauxite are needed.

The process of manufacture of both cements is identical with two slight exceptions. The raw materials are finely ground together after careful blending to secure the needed composition, then calcined to a clinker to bring about the needed reaction between the basic and acidic oxides of the raw materials, and the resulting mass is ground to the fineness shown by the finished cement as it reaches the market. The first distinct but slight difference is that whereas in this country Portland cement is always clinkered in a rotary kiln—and even when otherwise burned, as it is frequently abroad in kilns resembling a lime kiln, it is again burned to a clinker—the new cements, though they may be burned in a rotary kiln, are fused to a liquid or semipasty mass. Abroad they are produced either in a cupola from mixtures of fuel, limestone, and bauxite and the resulting cement tapped off as a slag, or they are produced in an electric arc furnace and again the product is obtained as a fused mass. Hence we have the origin of another name used especially abroad—*ciment fondu*, fused cement. The second difference is that before grinding the clinker of Portland cement it is necessary to mix it with 3 per cent of gypsum to retard and regulate its tendency to very quick setting (but not hardening) which characterizes these cements, whereas the high-alumina cements are slow setting (but quick hardening) and consequently do not require the addition of any foreign materials before grinding.

Note—It is necessary to distinguish between setting and hardening. The former is the stiffening of the mass of cement, aggregate, and water so that it can no longer be readily molded, while the latter more properly comprises the rate of acquiring strength.

Early Developments

Although the high-alumina cements have aroused new commercial interest they are not new. In 1883 Roth[3] took out a patent covering the use of bauxite in the manufacture

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[1] Received March 29, 1926.

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

[3] U. S. Patent 270,608 (1883).

of a cement. In this patent he limits the alumina content to "from 6 to 10 per cent or more." Apparently he covered the high-alumina cement from this one clause. However, he unfortunately also places limits upon the lime and silica content, the minimum limits in both of these cases being such that the maximum alumina content would not permit of making a true high-alumina cement.

Later patents were taken out by Spackman and Lazell,[4] which cover the making of true high-alumina cement. At the time Spackman and Lazell were doing their work Bied,[5] at that time technical director of the Lafarge Cement Company (Société Anomye Chaux et Ciments des Lafarge et du Teil) of France, took out patents in France. The commercial development to any extent did not follow immediately. Spackman, whose original purpose seems to have been the making of an accelerator for lime and natural cement, placed on the market an aluminous accelerator under the name of "Alca," some of the properties of which he described before the American Society for Testing Materials.[6] During 1916 the Bureau of Standards produced a number of high-alumina cements in its experimental cement plant and as a result of this work suggested their use for the placing of the large guns when this country entered the late war. At the end of the war it was announced that the French had actually produced and used these cements for this purpose during the war, but independently of any suggestions from this side. At the 1919 meeting of the American Society for Testing Materials a paper[7] was presented by a member of the Bureau of Standard's staff giving the first results which had been obtained in its laboratories in the making and testing of these quick-hardening cements. At the same time this paper was being presented before the American Society for Testing Materials, Endell read a paper before the German Cement Manufacturers,[8] giving data obtained from some cements which he had made of a composition very similar to those made at the Bureau of Standards. At this time also Bied formed a corporation in France for the commercial production of fused cements and at about the same time the Lafarge Company started commercial production. These represented the first commercial production of high-alumina cement anywhere. In 1921 appeared a paper by the Bureau of Standards[9] which gives in considerable detail general information covering the making and the properties of this material. In December, 1922, Bied read a paper[10] relating his early research work, but not giving any particular detailed data except that which he quoted from the Bureau of Standards paper.[9]

A new hydraulic cement high in alumina content has recently found commercial application on account of its high strength and resistance to sulfate-bearing water. It is difficult to overrate the importance of this cement, which attains the same strength in 24 hours that ordinary cements acquire in 28 days.

In this paper the composition and properties of this high-alumina cement, especially as compared with Portland cement, are described and its commercial uses are pointed out. The durability of these cements is still under discussion as no particular long-time tests or structures are available, but if durability tests fail to show this property, particularly in the presence of salt water, there is still an immense field for its use wherever a high early strength is desired.

Whereas Spackman was apparently seeking a quick-hardening product, Bied states that he was seeking one that would be immune to the attack of sulfate solutions such as sea water or the gypsum-bearing waters so common to many parts of France. These waters are particularly destructive to Portland cement products unless great care is taken in their manufacture. He states that he consequently bore in mind Vicat's research published in 1818, according to which *un ciment indecomposable* would be obtained if the ratio $\frac{SiO_2 + Al_2O_3}{CaO + MgO}$ was greater than 1. This ratio in Portland cement is about 0.5. Furthermore, he knew he could not increase the silica content to obtain this ratio because in so doing he would bring the composition into the field of metallurgical slags, which have little or no setting properties. He consequently increased the alumina content and obtained these new cements.

Nature of the New Cements

Investigative work[11] has shown that normal Portland cement is composed of a heterogeneous mixture of $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and unidentified compounds, largely glass, of iron and the other oxides which it may contain. In the Bureau of Standards paper[9] it is shown that the high-alumina cements are composed of $CaO.Al_2O_3$, $3CaO.5Al_2O_3$, $2CaO.SiO$, $2CaO.Al_2O_3.SiO_2$, and certain other unidentified compounds of iron, magnesia, and the other impurities. If the lime content is somewhat high there may be present $5CaO.3Al_2O_3$ in place of the $3CaO.5Al_2O_3$. In Portland cement the constituent active in the setting is the tricalcium aluminate, which in a pure condition hydrates in water as energetically as quicklime, with no hydrolysis and with no formation of compounds having any marked bonding properties. The constituent producing the early hardening is the tricalcium silicate, which breaks up into a hydrated lime and an amorphous silicate of a lower lime content. The dicalcium silicate reacts very slowly with water and has but little bonding properties at early periods. It also liberates a very small quantity of lime and an amorphous silicate somewhat higher in lime than the monocalcium silicate. The aluminates present in the new cement are decomposed by water into hydrated alumina and hydrated tricalcium aluminate. This is a slow reaction compared with that of the tricalcium aluminate and water, but it seems to proceed in the course of a few hours to a far greater completion than does the reaction of the silicates of Portland cement. But the different speed and type of reaction with water of the two cements is evidenced by the fact that unless a retarder—preferably and almost invariably gypsum—is added to Portland cement it reacts so energetically immediately that it cannot be used commercially, whereas no retarder whatsoever is added to the alumina cement. This retarder is added solely to control the rate of setting or initial stiffening of the mass and not the hardening or strength-gaining properties of the cement. Unretarded Portland cement of the composition used at present in commerce, while setting rapidly, never acquires sufficient strength to be of practical value.

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[4] U. S. Patents 903,018 (1908); 1,029,953 (1912).

[5] Bied mentioned these cements incidentally in a paper on "Various Chemical Phenomena Encountered in the Course of Industrial Investigations," *Proc. Intern. Soc. Testing Materials*, 2nd Section, XVIII-1 (1912).

[6] *Proc. Am. Soc. Testing Materials*, **10**, 315 (1910).

[7] Bates, *Ibid.*, **19**, 425 (1919).

[8] Endell, "Über Tonerdereiche Zements," Protokall Vereins Deutscher Portland Zement Fabrikanten, June, 1919.

[9] *Bur. Standards, Tech. Paper* **197** (1921).

[10] "Les Ciments a Haute Teneur en Alumine," Soc. d'Encouragement des Sciences, January, 1923.

[11] Rankin, *Am. J. Sci.*, **39**, 1 (1915).

The separating of lime in the hardening of Portland cement and of alumina in the hardening of alumina cement, the slow hardening of the former and the quick hardening of the latter, have suggested to some the possibility of mixing the two, thus inducing the desired quick hardening of the Portland cements through a combination of the soluble lime liberated in its reaction with water with the alumina set free in the hardening of the alumina cements. Unfortunately, this possibility is not realizable commercially. When enough alumina cement is used to produce any great amount of quick hardening of the Portland cement, a very quick set is obtained and with it the relatively low strengths which characterize quick-setting cements. No retarder has been isolated which will delay the set of such mixtures to the extent of permitting the development of satisfactory strengths.

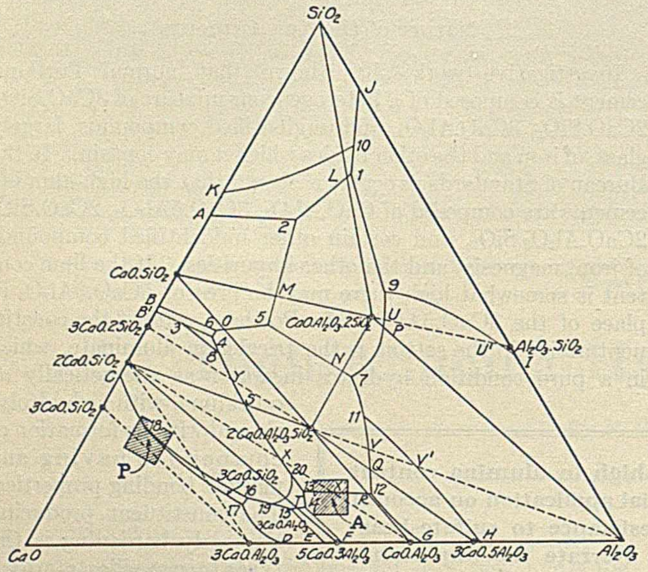

Figure 2—Diagram of the Ternary System $CaO-SiO_2-Al_2O_3$, Showing the Field of Portland Cement, *P*, and the Alumina Cement, *A* (after Rankin)

Figures 2 and 3, taken from Rankin's paper,[11] are presented in order that the reader may realize the relation between the constitution of Portland cements and high-alumina cements. The areas in the lime-alumina-silica system occupied by these two cements are indicated by the shaded areas. Work at the Bureau of Standards has shown that one can immediately determine what compounds would be present in cement by locating the composition as determined from the analyses on such a diagram as Figure 2, which shows the fields of stability of this system. Of course, as the amount of oxides other than lime, alumina, or silica becomes larger the possibility of error increases, but it is generally very surprising to note how a petrographic examination of cement clinker will corroborate such a procedure. It can be noted that, as the petrographic examination has shown, the dicalcium silicate is generally common to both of these cements, but in Portland cement it is seldom present to the extent of less than 40 per cent whereas in alumina cement it is present to but a very slight extent. All the other constituents of the two cements are different.

Figure 3 indicates to those familiar with the meaning of such models why the alumina cements are preferably fused and not clinkered as is Portland cement. In this figure the vertical distances indicate relative temperatures, and hence it is immediately noted that Portland cement is present in a region in which the compounds are formed at a high temperature where slight changes in composition require relatively marked changes in temperature to bring about the needed reaction, whereas the alumina cements occur in another region where the temperature at which the compound is formed is considerably lower and also where slight changes in composition will require marked changes in the temperature needed to bring about the desired reaction. Portland cement has what is known to ceramists as a wide firing range. Alumina cements have a very narrow firing range. Hence it is possible to clinker Portland cement readily but in the case of the alumina cements there is a very narrow range of temperatures at which they are a clinker and outside of which they are either a mass of uncombined raw material or a liquid. This fact, coupled with the fact that the temperature at which the fusion takes place is lower than the temperature at which clinkering takes place in Portland cement, is the reason for producing the alumina cements by fusion. It is not so generally understood on account of the high temperature required for the combination. The following data from Rankin[11] give the melting points of the compounds and eutectics which may occur in the fields of the two cements:

		° C.
	Portland Cement	
$2CaO.SiO_2$		2130
$2CaO.SiO_2$ $3CaO.SiO_2$	Eutectic	2065
$3CaO.SiO_2$	Dissociate	1900
$3CaO.Al_2O_3$	Dissociate	1535
	Alumina Cement	
$2CaO.SiO_2$		2130
$2CaO.Al_2O_3.SiO_2$		1590
$CaO.Al_2O_3$		1600
$3CaO.5Al_2O_3$		1720
$5CaO.3Al_2O_3$		1455
$CaO.Al_2O_3$ $3CaO.5Al_2O_3$	Eutectic	1590
$CaO.Al_2O_3$ $5CaO.3Al_2O_3$	Eutectic	1400
$CaO.Al_2O_3$ $2CaO.Al_2O_3.SiO_2$ $2CaO.SiO_2$	Eutectic	1505
$CaO.Al_2O_3$ $5CaO.Al_2O_3$ $2CaO.SiO_2$	Eutectic	1355

It should be remembered that the impurities such as iron and magnesia bring about the formation of low-melting compounds, which assist in the formation of the above compounds at lower temperatures. Work at the Bureau of Standards has shown that the average clinkering temperature of Portland cement is about 1435° C., whereas the alumina cements such as produced commercially fuse at 1425° C.

Table I—Physical and Chemical Characteristics of High-Alumina and Portland Cements

	High-Alumina Cements				Portland Cements			
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
	Tensile Strength 1:3 Standard Sand Mortars, Lbs. per Sq. In.							
24 hours	372	330	415	330	125	204	122	173
72 hours	425	310	...	...	200	320	242	255
7 days	435	330	280	690	255	415	323	327
28 days	425	310	335	540	330	460	383	375
	Compressive Strength 1:3 Standard Sand Mortar, Lbs. per Sq. In.							
24 hours	5615	5345	4410	2860	745	1900	475	400
72 hours	5120	5995	...	...	1435	3210	1315	1335
7 days	5085	5640	4880	8610	2140	4195	1635	2205
28 days	4835	6050	5285	7845	3150	5380	2650	3475
	Compressive Strength 1:2:4 Gravel Concrete, Lbs. per Sq. In.							
24 hours	2880	2160	3145	2930	...	215	...	...
72 hours	3330	3245	...	...	460	825	...	...
7 days	3260	3190	3570	6010	875	1905	1310	1655
28 days	2845	3480	3370	7060	1615	3030	2410	2640
	Chemical Analyses							
SiO_2	3.13	9.58	10.48	0.68	21.92	19.89	22.36	22.16
Al_2O_3	45.00	51.92	46.71	74.11	2.25	6.83	7.27	6.56
Fe_2O_3	10.11	2.45	2.13	0.40	6.88	3.22	2.44	2.46
CaO	41.19	33.82	39.79	23.82	60.92	62.93	64.48	64.89
MgO	0.33	2.57	1.04	0.81	3.40	2.60	1.96	1.98
SO_3	...	...	...	...	1.60	1.79	1.73	1.64
Ignition loss	0.78	0.04	0.14	0.38	2.30	2.19	0.30	0.43

Physical Properties

The data in Table I give some of the physical and chemical characteristics of four of each of these cements. Alumina cement *A* is a commercial cement of this type. The other three alumina cements were produced in the Bureau of Standards experimental cement plant. One of these is very close to the commercial cement in lime and alumina content, but higher in the silica and lower in the iron oxide content. However, in this respect, the Bureau of Standards product approaches very closely the composition of the fused cements made in France, which incidentally is the only country abroad where they have been produced over an extended period. Cements *B* and *D* are of higher alumina content than that now used commercially. *D* is of interest in that it approaches as closely to the composition $3CaO.5Al_2O_3$ as possible without the use of chemically pure raw materials. However, a petrographic examination showed it to contain considerable amounts of $CaO.Al_2O_3$ and a very small amount of $2CaO.Al_2O_3.SiO_2$. This particular cement can hardly be considered a commercial possibility.

The Portland cements given in the table are commercial domestic cements, except *F*, which is an imported "super Portland cement." With the marketing of the alumina cements in France, those countries not favored with their own source of bauxite were at a material disadvantage in their lack of a domestic source of quick-hardening cements. As a result Germany in particular began to study the possibility of improving the quick-hardening properties of Portland cement. Consequently, there have appeared throughout Europe certain quick-hardening Portland cements, very frequently referred to as super-cements, which do develop a higher strength at early periods than the usual material of this type. However, there is no particular new development in their production. The raw materials are more carefully blended, the lime increased to the maximum, they are more finely ground, and the burning is conducted more carefully and at a higher temperature as is required by the higher lime-silica ratio. The resulting clinker is also ground much finer, generally 90 to 95 per cent through a 200 sieve instead of the usual 78 per cent. This practice of fine grinding of the clinker also holds in the alumina cement industry, although the cements of this type prepared at the Bureau of Standards have not been ground any more finely than that required by the United States standard for Portland cement. It can be appreciated that the finer cement is ground the more surface is exposed to water and consequently the more readily is the reaction of hardening carried out.

The strengths given are typical of the two types of cement. It will be seen that the tensile strength of the alumina cement is from two to four times that of Portland cement at 24 hours, but that the gain in strength with age is minor whereas with Portland cements the gain is very considerable. The compressive strengths of the alumina cement as a mortar are from four to eight times that of the Portland cement—neglecting the super Portland cement—at the early periods, but again they do not maintain this advantage with age. Again neglecting the super Portland cement, at 24 hours the Portland cements had so little apparent strength as a concrete that the specimens were not tested, but the super-cements had only one-tenth the strength of the alumina cements, but again the latter do not maintain this advantage with age. It is distinctly seen, however, that the new cements do have the high early strengths accredited to them.

Another distinctive feature is that the relative compressive strength, especially as a concrete, of the two cements is much greater than is the tensile strength as a mortar. This is important in view of the very pronounced custom of evaluating the compressive strength of a cement as a concrete from its tensile strength as a mortar. If this procedure is followed in the case of the alumina cement using the ratio holding in the case of Portland cement between the two types of test pieces, there is obtained an entirely too low approximation of the concreting value. Putting these facts in another way, the Portland cement has a relatively high tensile strength and a relatively low compressive strength and the alumina cement the reverse. In this connection also note the high tensile strength of the imported super-cement, which compares very favorably with the alumina cement, but note again its low compressive concrete strength at 24 and 72 hours. The mistake should not, therefore, be made of trying to predict the early concreting properties of a Portland cement from the usual small tensile specimens, making use of the relation which holds for alumina cements between its tensile strength as a mortar and compressive strength as a concrete. The much desired quality of cements of having a high early compressive strength as a concrete suggests studies to see if this property cannot be developed in any manner in the more cheaply made Portland cements.

Sulfate Salt Resisting Properties of the Alumina Cements

It has been indicated above that Bied in his original work in developing the quick-hardening cements was following Vicat's suggestion for producing *un ciment indecomposable*—one not subject to attack by the naturally occurring sulfate salt solutions. It is a matter of much concern to Portland cement manufacturers and users that products made of it do not resist the disintegrating attack due to the presence of such solutions, to the extent of insuring the desired permanency of life. The cause of this lack of service is not generally understood. It is, however, a well-known fact that even naturally occurring materials such as building stone or such artificially produced commodities as brick and tile are not able to resist the expansive force resulting when such salts as sodium sulfate and magnesium sulfate crystallize from solution in their pores. One can see plenty of evidence of such failure in our country in the white alkali section of the West, which alkali is generally sodium sulfate and less frequently mixtures of this salt with magnesium sulfate and still less frequently calcium sulfate alone. In fact, an artificial freezing test (Brard's test) based upon the expansive force of crystallized sodium sulfate, has been in use for years to determine in an accelerated manner the resistance of building stone to normal freezing and thawing. Such a form of disintegration is physical and should the material subjected to such disintegration be free of voids no destructive action can result. But while it is conceded that at least part of the disintegration of concretes is due to the expansion of freezing salts in the voids, it has always been a well-grounded belief that possibly the major fault was due to a reaction of the cement or its products of hardening with the salts in the solution. Hence Bied's efforts along this line.

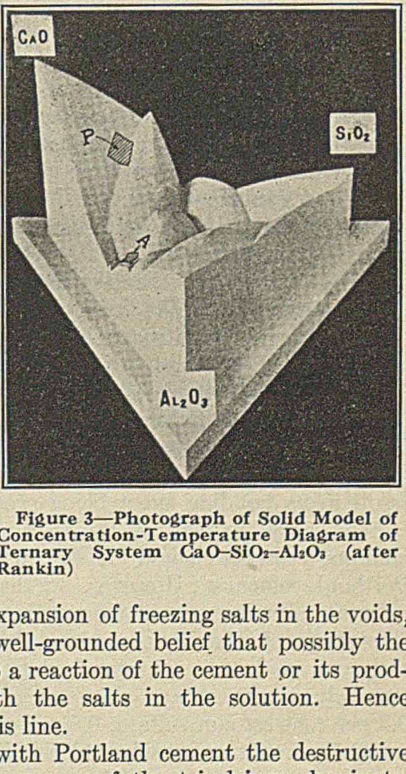

Figure 3—Photograph of Solid Model of Concentration-Temperature Diagram of Ternary System $CaO-SiO_2-Al_2O_3$ (after Rankin)

It is claimed that with Portland cement the destructive action is due to the presence of the tricalcium aluminate, which in the presence of soluble sulfate and lime solutions forms a compound $3CaO.3CaSO_4.Al_2O_3.xH_2O$. This is shown in Figure 4, wherein also is shown in the upper right-hand corner a transparent crystal of hydrated lime. In the absence of such sulfates the normal reaction is the formation of hydrated tricalcium aluminate. One of the reasons for the nonacceptance of this theory is the inability to find this calcium sulfo-aluminate in decomposed concrete. This inability is due to the fact, however, that the compound is unstable in solutions not almost saturated with lime, and this latter condition does not obtain except in excellent unattacked concrete. On the other hand, the high-alumina cements hydrate by the formation of the hydrated tricalcium aluminate and hydrated alumina being formed from the hydrolysis of calcium aluminates containing lime and alumina in a greater ratio than 3:1. There is not a sufficient concentration of lime in the presence of these latter cements resulting from the hydration of the minor amounts of silicates to permit the formation of the destructive complex sulfate, and consequently destructive chemical action should not result.

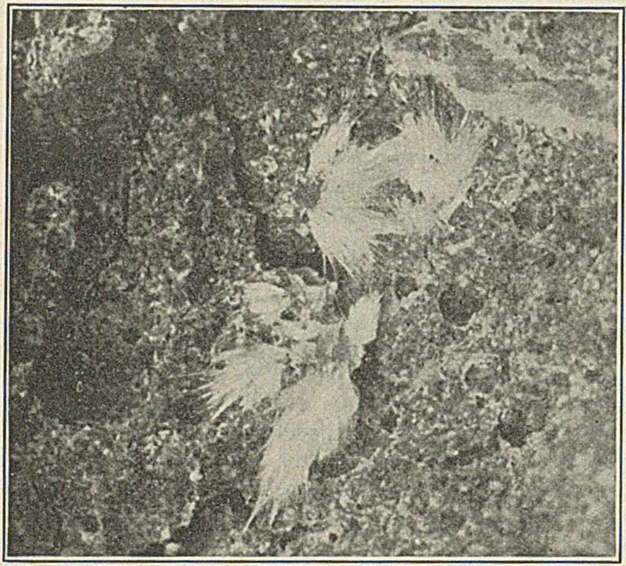

Figure 4—Broken Surface of a Portland Cement Mortar Briquet Showing the Acicular Development of $3CaO.3CaSO_4.-Al_2O_3xH_2O$ and in the Upper Right Corner a Crystal of $Ca(OH)_2$. Mag. 40 ×

Such an explanation of the different behavior of the two cements under adverse conditions is based partly upon the theory of the formation of the sulfo-aluminates, but more upon its destructive expansive force. Such an explanation, however, does not take into consideration the possibility that the harmful sulfate may cause a deviation from the normal process of reaction with water, which results also in the formation of a colloidal hydrated silicate in one case and hydrated alumina in the other. Such a possible departure from the normal course may result in an immediate flocculation of the colloids as they form, which consequently would result in no bonding agent being produced. But according to the theory advanced in the cases under consideration the alumina cements should be far more resistant than the Portland cements. However, we have been able to disintegrate alumina cement mortars in sulfate solutions in the laboratory of the bureau when these mortars contained sufficient voids. A 1:5 standard Ottawa sand mortar alternately immersed and dried in a solution composed of 0.5 per cent sodium sulfate, 0.5 per cent magnesium sulfate, and 0.5 per cent magnesium chloride began to disintegrate in less than one month. This, however, simply emphasizes the need of such careful grading of aggregates as will produce a dense product. Otherwise, the expansive force of the crystallizing salts contained in the solution will disrupt products made of alumina cement just as they will disrupt Portland cement products and such naturally occurring materials as limestones when they contain too great an amount of voids.

Water Control

It is well known that to obtain the optimum strength from Portland cement a certain maximum amount of water must not be exceeded. This has been very clearly shown in particular by Abrams,[12] but this optimum is somewhat below that which produces a fluid consistency which lends itself readily to working into forms or around reënforcing. Consequently, more water must be used than is advisable for best strength, but the tendency is to exceed even this conceded necessary excess, with the resulting loss of otherwise available strength.

When the alumina cements first appeared on the market abroad, the foreign manufacturers, in some way misled by the completeness of the hydration, suggested that more water be used than with Portland cement. But this has been found to be even more effective in reducing the otherwise available strength than has excess water with Portland cement. In fact, the effect of water is so marked that the too frequently used method with Portland cement concrete of obtaining a ready casting mixture by the use of excess water rather than by the choice of properly graded aggregates cannot be used with the alumina cements without a very serious strength reduction. In the design of Portland cement concrete it is assumed that the use of any particular aggregate will not so seriously affect the water-cement ratio that a satisfactory concrete will not be obtained, although it may not be so high testing as desired. Such an assumption will not hold, however, with the alumina cement. To obtain the high strengths for which it is purchased, the water-cement ratio which will give the best strength should not be much exceeded in order to obtain a workable mix from a particular aggregate. Should the latter be such that a marked excess of water is needed for a suitable mix, then if good results are desired it will be necessary to choose a different aggregate or grading of aggregates. In some work recently done at the Bureau of Standards[13] with one lot of aggregate in a 1:2:4 mix, each increase of 0.5 per cent of water, in terms of the weight of the dry mix, reduced the strength at 24 hours 11 per cent. With another lot of aggregate in a mix of the same proportions an increase of 1.5 per cent of water reduced the strength 40 per cent. In the latter case the use of 36.5 pounds of water in mixing 500 pounds of dry concrete gave a strength at 24 hours of 4440 pounds per square inch, while 44 pounds of water with the same dry mix gave a strength of but 2620 pounds per square inch. Furthermore, not only is the strength reduced but the concrete is of a porous nature and not able to resist a dissolving or disintegrating action of infiltrating solutions.

Heat Developed during Set

Those who are familiar with Portland cement know that during the process of setting and early hardening a certain amount of heat is developed. This is generally so slowly evolved that it is dissipated without causing any undue ill effects. On the other hand, the reactions with water resulting in the hardening of alumina cement are so rapid that any marked dissipation, particularly in large masses of concrete, cannot ensue. As a consequence such high temperatures may result that the concrete is permanently injured. This is particularly liable to happen if the custom of covering the

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[12] "Design of Concrete Mixes," Structural Materials Research Laboratory, Lewis Institute, *Bull.* 1.

[13] *Eng. News-Record*, **95**, 462 (1925).

concrete with wetted burlap or similar material to prevent evaporation is followed. In fact it has been found advisable in the case of masses of alumina cement concrete of fairly large section to have recourse to spraying with water at about the time the final set is taking place, which time will vary from 3 to 12 hours after placing the concrete. This time for wetting can be readily determined by noting the first rise of temperature as indicated by the feeling of warmth when placing the hand on the mass.

Reference to the work of Bied and to that of the Bureau of Standards[14] will show that the silicates and aluminates present in either Portland cement or alumina cement hydrate but slightly at 105° C. Of these compounds the one which shows the greatest, but far from complete, hydration at this temperature is the monocalcium aluminate. However, as one of the products of its hardening is hydrated tricalcium aluminate and since it is also shown that the latter is only very slightly hydrated at this relatively high temperature, it can be realized what would be the effect in a mass of slightly hardened concrete if a considerable amount of hydration of a compound such as tricalcium aluminate should take place. Undoubtedly, at higher temperatures of hardening the bonding is being done through the agency of dissociated hydrated alumina liberated from the partial hydration of the mono or 5:3 aluminate and inclosing considerable amounts of unhydrated or only very partially hydrated tricalcium aluminate. There would result low early strengths and after cooling the mass would be subject to disintegration as the unhydrated compounds came in contact with water with their resultant far more complete hydration.

Figure 5—One 50-Ton Reënforced High-Alumina Cement Concrete Cylinder Ready for Placing in Sea Water 24 Hours after Making, and Four Other Cylinders in Different Stages of Manufacture at the Puget Sound Navy Yard

Uses and Durability of Alumina Cements

The alumina cements have found commercial application based upon either their high strength or their resistance to sulfate-bearing water. Examples of such uses are the underpinning of structures, the paving of streets and roads, the making of foundations for machinery and of structures to be subjected to sea water. It has been found very advantageous in the paving of city streets since they may be opened to traffic immediately after completion. Thus, among many others may be cited several blocks of the Boulevard Haussmann in Paris and Tottenham Court Road in London, which were paved with alumina cements, the surfacing immediately placed thereon and the street immediately open to such traffic as the heavy passenger busses.

In the United States such concrete would be advantageous to use in the last portions to be completed of Portland cement concrete roads. Thus, if the last two weeks' work were made of alumina-cement concrete the entire road could be opened to traffic within 24 hours after the completion of the job, by which time those portions constructed of Portland cement concrete would have aged sufficiently. It has also been found advantageous in constructing concrete for the intersection of a road being built with one left in service, for by using this cement it would not be necessary to detour traffic at such intersections more than one day.

Alumina cements also have been used in a number of marine structures. The United States Navy has used it in constructing a hydroplane runway at its Norfolk yard and another piece of construction at the Navy Yard at Puget Sound is of interest in having consumed more alumina cement (9000 barrels) than used in any one job to date. In this particular project, 240 hollow cylinders 60 feet high and varying from 6 to 16 feet outside diameter with 6-inch walls were cast and placed in Puget Sound as hollow piles to be filled with Portland cement concrete for supporting the deck of a wharf.[15] Some views of this work are shown in Figures 1 and 5. The use of the quick-hardening cement made it possible to make the cylinders faster than they could be permanently located. As these cylinders could be handled within 24 hours after making, any extended equipment or space for making any large number before the first could be handled was not required. Indeed, this saving of equipment alone justified the extra expense of using alumina cements, although it had to be transported from the Atlantic to the Pacific Coast. In addition, of course, the securing of a cement more resistant to sea water was sought.

The durability of these cements in service is a matter of some discussion. Of necessity no particularly long-time tests or structures are available. Those reported by the Bureau of Standards[9] extended over a period of three years and the data indicate that when not subjected to water there need be no cause for questioning serviceability. When subjected to the action of water there is a question of durability, but it is possible that a closer adherence to such methods of close mixing water control as later work has found necessary in using this cement would indicate permanency in even this respect. Furthermore, the use of Portland cement subject to the washing or infiltration of water is in the majority of cases now only attempted when protected by exterior waterproofing. Such a procedure with the use of alumina-cement concrete would entail no extra cost not encountered in the use of Portland cement concrete. Even though service would show that it does not have the predicted and hoped-for immunity from salt attack, there is still an immense field for its use wherever a high early strength is desired. It has also had a marked effect in stimulating interest in the possible improvement of Portland cement, having in mind the development of a cement having the characteristics of the high-alumina cement but made from the more readily accessible and widely distributed raw materials.

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[14] *Bur. Standards, Tech. Paper* **43.**

[15] *Pacific Builder and Engineer,* **32,** 12 (1926).

Can Corrosion and Blackening in Certain Marine Products[1]

By D. B. Dill and P. B. Clark

Food and Drug Inspection Station, U. S. Bureau of Chemistry, San Francisco, Calif.

IN ORDER to present this problem clearly the following somewhat arbitrary classification of canned marine products is offered: (1) those which may be held for years without evident change in appearance or palatability, such as many species of mollusks, and among teleost fishes, the salmons and the tunas; (2) those which corrode plain cans and which will turn black, even in lacquered cans, such as the crustacea; and (3) those which corrode plain cans but in which there is no blackening, such as representative selachians and many teleost fishes, including the basses (family *Serranidae*), the flatfishes, the codfishes, the red rock cod (genus *Sebastodes*) and the barracuda (*Sphyraena argentea*).

An investigation, extending over six years, has been made of some of the deteriorative changes which may occur in sterile marine products. Neither free oxygen nor volatile bases appear to be significant factors in can corrosion or in the blackening of the flesh. The content of sulfide sulfur is related to the blackening process. The sulfide-sulfur content of those marine products which do not blacken is small and does not increase during storage. The sulfide-sulfur content of crustacea, which do blacken, increases to relatively high values during storage. Those products which corrode cans are more alkaline than pH 6.5. Marine products more acid than pH 6.5 never blacken and for the most part do not corrode the container.

Previous Investigations

The undesirable changes which take place in canned crustacea have constituted the subject of many investigations. That the prolongation of the sterilization period favors these changes is indicated by the study of Buttenberg.[2] Bigelow and Bacon[3] concluded that the attack of canned shrimp on the container cannot be explained by the action of an acid. They isolated monomethylamine from shrimp and suggested that it might be the substance responsible for detinning in this case. Okuda and Matsui[4] related the blackening of canned crab meat to its content of volatile sulfur. They found that the alkalinity of canned crab meat increases with time, that the black substance is iron sulfide, and that the black flesh is higher in soluble organic matter, in volatile sulfur, and in ammonia.

In an investigation of Canadian lobster canning, Harrison and Hood[5] found that the blackening of spring-caught lobster is much less pronounced than that of fall-caught lobster. The addition to lobster meat of organic acids, such as citric or acetic, greatly postpones blackening. In a later study of Canadian lobster canning, Reed and Macleod[6] confirm the findings of Harrison and Hood. They also emphasize the relation between bacterial decomposition before canning and the processes of corrosion and blackening. They believe that such decomposed material, even though completely sterilized, is more corrosive because of a greater content of hydrogen sulfide and volatile bases.

Bigelow and Cathcart[7] found that the pH of wet-packed shrimp was 6.9 and that of lye hominy, 7.0 to 8.0. Both these products blacken in the can. Products which they found to be distinctly on the acid side of neutrality do not blacken in the can. Kohman[8] later proved that there is a relation between the alkalinity of lye hominy and its blackening tendency. When the outer portion of the grain was scrubbed off, it was possible to reduce the lyeing enough to prevent the product from becoming sufficiently alkaline to cause blackening.

On the basis of these results it appears plausible that there is a direct relation between high hydroxyl-ion concentration and the processes of corrosion and blackening. However, it has been shown by Wilson[9] that the rate of corrosion of iron or steel by natural waters does not vary significantly over the pH range of 6.0 to 8.0. It seems possible that the corrosive agency in neutral or alkaline food products is not the hydroxyl ion, but some other ion or substance, absent in natural waters, whose concentration increases with increasing hydroxyl-ion concentration. The sulfide ion falls in such a category.

The marked acidity of certain agricultural products is frequently the direct cause of corrosion. "Hydrogen swells" result from such corrosion and are not uncommon in acid fruits, particularly in berries. Kohman[10] demonstrated that oxygen is an important factor in the corrosion of cans by acid products.

Stumper[11] has found that with tap and chlorinated mineral waters corrosion of iron or steel was increased nearly 100 per cent at 17° C. when the metal was in contact with iron sulfide. In a 1 per cent sodium chloride solution and contact with iron sulfide, corrosion was increased more than 200 per cent. If iron sulfide has a similar effect on the corrosion of tin plate by food, the process would seem to follow a vicious circle in those cases in which blackening from iron sulfide formation takes place. This may be a catalytic effect or it may be the specific effect of the sulfide ion.

Experimental

The results of the writers' investigation of the part played in the can-corroding power of certain marine products by oxygen, by hydrogen or hydroxyl ions, by bacterial decomposition before sterilization, by volatile bases, and by sulfide sulfur will now be presented.

Oxygen

The presence of oxygen was eliminated as a cause of the corrosion of cans by lobsters. Three methods were employed in removing the oxygen. Cans were nearly filled with meat from the spiney lobster (*Panulirus interruptus*). They were then sealed and heated in steam at 100° to 101° C. for one-half hour. As soon as the cans could be removed from the autoclave each was vented and the small puncture immediately closed with solder. A very large proportion of the oxygen contained in the can must thus have been removed. Each of another series was sealed and before heating each can was punctured and the gas evacuated to about 2-cm. pressure. By means of a three-way stopcock, carbon dioxide was introduced into the can until atmospheric pressure was reached. After a half-hour interval the cans were

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[1] Received December 3, 1925.

[2] *Z. Nahr. Genussm.*, **16**, 92 (1908).

[3] *U. S. Dept. Agr., Bur. Chemistry, Circ.* **79** (1911).

[4] *J. Coll. Agr., Imp. Univ. Tokyo*, **5**, 325 (1916).

[5] Honorary Advisory Council for Scientific and Industrial Research, Ottawa, *Rept.* **12** (1923).

[6] *Contributions to Canadian Biology, New Series*, **2**, 1 (1924).

[7] *Nat. Canners' Assoc., Bull.* **17-L** (1921).

[8] *Ibid., Bull.* **2-L**; This Journal, **14**, 415 (1922).

[9] This Journal, **15**, 127 (1923).

[10] *Ibid.*, **15**, 527 (1923).

[11] *Compt. rend.*, **176**, 1316 (1923).

again evacuated and refilled with carbon dioxide. The vents were then soldered. To each of a third series about 1 ounce of sardine oil, well known for its oxygen-combining power, was added. These three series were sterilized along with a fourth control series in steam at 115° C. for 75 minutes. The cans were examined after having been 4 months in the incubator at 37° C. All the cans were corroded. No consistent difference in the extent of corrosion of the can or in the amount of blackening in these four series was evident to the eye. Supplementary to this experiment, examination of the gases contained in canned shrimp (species undetermined) and in canned crab (*Cancer magister*) failed to reveal oxygen except in products examined only a few days after canning.

Note—The writers are indebted to the Seattle Laboratory of the National Canners' Association (E. D. Clark, in charge) for the use of apparatus in this determination.

Hydrogen and Hydroxyl Ions

The hydrogen-ion concentration of the centrifuged liquor from a number of marine products has been determined. As soon as the container was opened, the liquor was drained into a centrifuge tube and covered with paraffin oil. After centrifugation the pH was determined colorimetrically. Comparison was made with the standards of W. M. Clark,[12] employing as indicators bromocresol purple, bromothymol blue, cresol red, and phenol red. The results are shown in Table I. All the products examined were at least one year old. Without exception the crustacea are slightly or distinctly alkaline; the salmons and the mackerel are distinctly acid; and the barracuda (which corrodes but does not blacken) occupies an intermediate position. These results are in line with those of Bigelow and Cathcart[7] and imply a relation, direct or indirect, between alkalinity and corrosion. Some additional observations, not recorded in the table, were made. The rock cod (*Sebastodes*) has a reaction ranging from pH 6.5 to 6.9. The Washington clam (*Paphia staminea*) has a pH of 5.9. The sardine (*Sardinea caerulea*), packed salmon style without sauce, has a pH of 6.0.

Bacterial Decomposition before Canning

The finding of Reed and Macleod[6] that a relation exists between the extent of bacterial decomposition of lobsters before canning and the rate of corrosion and blackening after canning applies also to crab meat. One of the writers has had occasion to examine a commercial shipment of canned crab meat (*Cancer magister*), which was known to have been packed from crabs many of which had been dead from 12 to 48 hours before they were boiled. The odor of many cans indicated that their contents had been decomposed when packed. One-third of the cans showed some blackening, although they were examined only a few weeks after they had been packed. The canner opened the entire lot and recanned that portion of the meat which seemed to be normal. Examination of the repack a month later showed that nearly half of these were blackened. Eventually the entire lot was destroyed. Possibly the second sterilization hastened the processes which had been initiated by bacterial decomposition. Other packs of crab meat from the same region which present no evidence of bacterial decomposition show a much slower rate of corrosion and blackening.

Apart from the influence of bacteria, it is certain that normal crustacean meat will blacken and corrode cans. The meat used in the writers' experimental packs had undergone no appreciable decomposition before canning. Live crabs (*Cancer magister*) and live spiney lobsters (*Panulirus interruptus*) were boiled in brine, cooled, shelled, and packed without delay. Yet within the course of 1 or 2 years blackening and corrosion took place (Tables I and II).

Table I—Sulfide-Sulfur Content and pH of Marine Products

No.	HISTORY OF SAMPLE	CONDITION OF SAMPLE	Sulfide sulfur as H_2S Mmg./100 grams	pH of centrifuged liquor
A—Spider crab (Paralithodes camtschatica). *Commercial pack which had been condemned on account of excessive blackening. Lacquered cans with parchment paper lining. Samples more than 2 years old.*				
1	Untreated	Slight blackening	1280	7.6
2		Much blackening	2288	8.2
3		Very slight blackening	1536	7.8
4		Slight blackening	2000	8.2
5		Very much blackening	2528	8.0
6		Normal; no blackening	1920	7.6
7		Much blackening	1920	8.0
8		Slight blackening	1560	8.2
9		Much blackening	2088	8.3
10	Heated 56 days at 37° C.	Very much blackening	2664	
11		Very much blackening	2912	
12		Slight blackening	1920	
13		Much blackening	3768	
14		Normal; no blackening	2784	
15		Very much blackening	4416	
16		Much blackening	2368	8.1
17		Slight blackening	2512	7.7
18	Heated 56 days at 37° C.	Normal; no blackening	1344	8.0
19	Heated 24 hrs. at 115° C.	Black; porridge-like	10,160	7.4
20		Black; porridge-like	13,120	7.5
21		Black; porridge-like	16,720	7.7
Average Nos. 1 to 9; untreated			1902	8.0
Average Nos. 10 to 18; incubated			2743	7.9
Average Nos. 19 to 21; heated at 115° C.			13,333	7.5
B—Spiney lobster (Panulirus interruptus). *Experimental pack. Samples 15 months old.*				
1	Plain can, untreated	Slight blackening; much corrosion	472	7.7
2		Slight blackening; much corrosion	264	7.4
3		Slight blackening; much corrosion	320	7.5
4	Plain can, heated 24 hours at 115° C.	Much blackening; very much corrosion	688	7.2
5		Much blackening; very much corrosion	624	7.5
6	Glass jar	Normal	50	7.2
7		Normal	12	7.5
C—Alaska shrimp (species unknown). *Experimental pack. Samples 3 years old.*				
1	Glass jar	Normal appearance and odor	570	8.0
2	Lacquered can	Lacquer intact; meat badly blackened; black deposit around seams inside the can	2200	8.4
D—Barracuda (Sphyræna argentea). *Experimental pack. Samples 15 months old.*				
1	Plain can	No blackening; some corrosion	67	6.8
2		No blackening; some corrosion	45	6.8
3	Plain can, heated 24 hours at 115° C.	No blackening; much corrosion	880	6.9
4	Glass jar	Normal	16	6.7
E—Mackerel (Scomber japonicus). *Experimental pack. Samples 15 months old.*				
1	Plain can	Normal	168	
2	Plain can, heated 24 hours at 115° C.	No blackening; slight corrosion	1312	6.0
F—Dog salmon (Oncorhynchus keta). *Experimental pack of spawning fish. Samples 3 years old.*				
1	Plain can	Normal	19	5.9
2	Plain can, heated 24 hours at 115° C.	No blackening; slight corrosion	800	5.8
G—Sockeye salmon (Oncorhynchus nerka). *Experimental pack of fresh, stale, and tainted fish. Samples 6 years old.*				
1	Plain can	Normal odor; slight corrosion	<5	6.1
2		Normal odor; slight corrosion	<5	6.1
3		Stale odor; slight corrosion	<5	6.1
4		Tainted odor; slight corrosion	34	6.1
5		Putrid odor; slight corrosion	130	6.2
6		Putrid odor; slight corrosion	70	6.1

While bacterial decomposition in crustacea hastens the corrosive and blackening processes, it appears to cause no corrosion of cans by salmon. A 6-year-old pack of salmon (*G*, Table I) was not blackened, and there was little visible evidence of corrosion. Yet cans 5 and 6 contained salmon which was putrid when canned. It may be added that the writers' organoleptic examinations of thousands of cans of commercial salmon have revealed no significant corrosion in cans containing putrid salmon.

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[12] "The Determination of the Hydrogen Ions." Williams & Wilkins, Baltimore, Md.

Volatile Bases

Volatile bases have long been considered an important factor in can corrosion. The writers have made a number of determinations using the following method: 25 grams of the finely ground sample are washed into a 5 by 30 cm. cylinder with 100 cc. of water. After the addition of 75 cc. of alcohol, 2 cc. of kerosene, and 2 cc. of 50 per cent potassium carbonate solution, vigorous aeration is carried out for 4 hours, the ammonia and amines being absorbed in 0.02 *N* sulfuric acid. Suitable correction is made for the blank.

Table II—Volatile Bases in Marine Products

No.	Age of Sample	Container	Condition	Volatile bases as NH_3 Per cent
		Shrimp		
1	Not canned		Freshly boiled meat	0.022
2	24 hours	Glass jar	Normal	0.042
3	15 days	Lacquered can	Normal	0.043
4	33 days	Plain can	Some blackening	0.047
5	33 days	Lacquered can	Normal	0.041
6	34 days	Lacquered can with parchment paper	Normal	0.047
7	2 months	Lacquered can	Normal	0.039
8	2 months	Glass jar	Normal	0.039
9	2 months	Plain can	Some blackening	0.043
10	9 months	Lacquered can	Normal	0.047
11	9 months	Lacquered can with parchment paper	Slight blackening	0.050
12	9 months	Plain can	Slight blackening	0.049
13	9 months	Glass jar	Normal	0.046
14	Unknown	Plain can	Some blackening	0.050
		Spiney lobster (Panulirus interruptus)		
15	Not canned		Freshly boiled meat	0.023
16	24 hours	Plain can	Normal	0.048
17	24 hours	Glass jar	Normal	0.048
18	>2 years	Plain can with parchment paper	Can badly corroded and contents blackened	0.127
19	>2 years	Plain can with parchment paper	Can badly corroded and contents blackened	0.177
		Atlantic lobster (Homarus americanus)		
20	Unknown	Lacquered can	Normal	0.043
		Dungeness crab (Cancer magister)		
21	Not canned		Freshly boiled meat	0.017
22	13 days	Plain can	Normal	0.052
23	7 months	Plain can	Slight blackening	0.055
24	14 months	Glass jar	Normal	0.064
		Spider crab (Paralithodes camtschatica)		
25	Unknown	Lacquered can with parchment paper	Normal	0.040
		Barracuda (Sphyræna argentea)		
26	Not canned		Fresh meat	0.014
27	24 hours	Glass jar	Normal	0.052
28	10 days	Lacquered can	Normal	0.040
29	4 years	Lacquered can	Normal	0.055
30	4 years	Plain can	Can badly corroded	0.067
		Rock cod (Sebastodes sp.)		
31	28 days	Plain can	Normal	0.059
		Mackerel (Scomber japonicus)		
32	Not canned	Plain can	Fresh meat	0.010
33	15 months	Plain can	Normal	0.068
		Sardine (Sardinea cærulea)		
34	28 days	Plain can	Normal	0.034
35	13 months	Plain can	Normal	0.039
		Sockeye salmon (Oncorhynchus nerka)		
36	6 years[a]	Plain can	Can slightly stained and corroded	0.055
37	6 years[a]	Plain can	Can slightly stained and corroded	0.066
38	6 years[b]	Plain can	Can slightly stained and corroded	0.071
39	6 years[b]	Plain can	Can slightly stained and corroded	0.074
40	6 years[c]	Plain can	Can slightly stained and corroded	0.083
41	6 years[c]	Plain can	Can slightly stained and corroded	0.085

[a] In good condition when packed.
[b] Stale when packed.
[c] Putrid when packed.

The results are shown in Table II. Samples 1 to 13 represent an experimental pack of shrimp. Evidently there was no increase in volatile bases during the 9-month aging period. The amount found was independent of the nature of the container and was of the same order of magnitude as that found in teleost fishes.

Sulfide Sulfur

"Hydrogen sulfide" is another possible factor in corrosion which deserves study. Since practically no free hydrogen sulfide can exist within the pH range of canned crustacea, it seems more logical to use the term "sulfide sulfur" to denote that portion of the sulfur which is liberated by the addition of cold mineral acids. Almy[13] has developed an excellent method for the determination of sulfide sulfur in proteinaceous material. He has shown that the normal flesh of meat and fish contains practically none. This method was not available until after our experimental packs had been prepared. However, the writers have applied the method to several matured packs, both experimental and commercial. The results, shown in Table I, are expressed in terms of micromilligrams of hydrogen sulfide per 100 grams of sample. This is the standard used by Almy.

The first nine samples shown in Table I were from an importation of crab meat from Japan which had been seized by government authorities on account of excessive blackening. None of these freshly opened cans had an odor suggesting bacterial decomposition. Yet the content of sulfide sulfur was found to be of the same order of magnitude as that found by Almy in putrid fish. If this high sulfide sulfur content is not to be explained by bacterial decomposition, it may be related either to changes occurring during sterilization or to slow-going chemical reactions, which continue during aging. The corrosion or the blackening process might, or might not, be an essential step in the formation of sulfide sulfur in aging.

Samples 10 to 18 were from the same lot and were examined at the same time. However, these nine cans had been incubated at 37° C. for 56 days immediately preceding their analysis. When opened they had no odor suggesting putrefaction. There seemed to be more blackening than in the first nine samples. Five of these cans had a higher content of sulfide sulfur than any of the nine cans in the first group. The nine incubated cans had an average sulfide sulfur content 44 per cent greater than that of the first group. Conclusive evidence is thus furnished that this incubation increased the sulfide sulfur content. These eighteen cans show some correlation between degree of blackening and relative content of sulfide sulfur. The four cans having a sulfide sulfur content below 1600 mmg. of hydrogen sulfide per 100 grams were blackened slightly, if at all. Eight of the nine cans having a sulfide sulfur content in excess of 2000 mmg. of hydrogen sulfide per 100 grams were much blackened.

Cans 19 to 21 were heated at 115° C. for 24 hours. The temperature is that commonly employed in sterilization. The time is from eighteen to twenty-four times that employed in sterilization. The result was a sevenfold increase in the sulfide sulfur content. The flesh evidently underwent a profound alteration during this treatment, becoming porridge-like and inky black.

Section *B* of Table I shows that only about one-fourth as much sulfide sulfur was found in the spiney lobster contained in plain cans as was found in the older, commercial pack of crab meat. It is especially interesting that Nos. 1 to 3, plain cans, contained about ten times as much sulfide sulfur as Nos. 6 and 7, glass jars. Yet all the lobster meat was handled in exactly the same manner. The cans and the jars (with glass lids and rubber gaskets) were sealed at the same time and sterilized together at 10 pounds steam pressure for 90 minutes. It is clear that the high content of sulfide sulfur in the contents of the cans in this case is not a result of bacterial action or merely of aging. The metal container plays a part in its formation. Sections *C* and *D* confirm this finding.

The prolonged heat treatment appeared to increase the

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[13] *J. Am. Chem. Soc.*, **47**, 1383 (1925).

sulfide sulfur in the plain can pack of spiney lobster only about 50 per cent. The two samples remained coffee-colored during the determination of sulfide sulfur. All other samples became colorless as soon as the hydrochloric acid was added. Evidently, in this case tin sulfide had formed. The prolonged heat treatment produced much sulfide sulfur in all the other species examined, but the alteration of the flesh was less marked than in crustacea. After this long heating salmon remained edible, although it had a slightly scorched odor.

Section *G* shows that good quality sockeye salmon can be processed and then matured 6 years in plain cans without increase in the sulfide sulfur content.

Confirmation of the finding that the metal container increases the rate of formation of sulfide sulfur is found in Section *C*. In the 3-year-old experimental pack of Alaskan shrimp the amount of sulfide sulfur found in the contents of the lacquered can was of the same order of magnitude as that found in the blackened commercial crab meat (*A*). Only one-fourth as much was found in the contents of the glass jar.

Iron and Tin Content

At this point it may be worth while to present the results of a study on the proportions of iron and tin found in two crustacean packs. One of these, a 15-month old experimental pack of the spiney lobster, had been held at room temperature until the time of examination. The contents of each container were dried, weighed, ashed at very low red heat, and the ash dissolved in hydrochloric acid and the tin determined by the tentative method of the Association of Official Agricultural Chemists (revised to July 1, 1924). The filtrate was treated with 5 cc. of strong sulfuric acid and evaporated to remove chlorides. Iron was determined by the volumetric permanganate method. Two of the containers were glass jars with glass lids; hence their contents represent normal lobster meat. Two containers were plain cans, each of which was badly corroded. The contents in contact with the can were blackened. The last two containers also were plain cans, but before being opened they were heated at 115° C. for 24 hours. As before, this 24-hour heat treatment softened the flesh to a porridge-like consistency and the contents became inky black.

Table III—Iron and Tin Content of Canned Crustacea

Description	Total Can Contents Iron Mg.	Total Can Contents Tin Mg.	100 Grams of Dry Can Contents Iron Mg.	100 Grams of Dry Can Contents Tin Mg.
Spider crab[a]				
Heated 24 hours at 115° C. before opening	180	2	458	6
	190	9	466	22
Badly blackened	195	3	449	7
	182	5	433	12
Normal	28	2	61	4
	26	10	60	47
Spiney lobster[b]				
Heated 24 hours at 115° C. before opening	231	189	610	499
	452	173	985	377
Much corrosion; badly blackened	309	146	681	322
	290	119	621	255
Normal	11	None	21	None
	10	None	18	None

[a] These were from an import shipment which had been seized by government authorities on account of excessive blackening. It was packed in lacquered cans which were lined with parchment paper. The pack was known to be more than two years old when examined.

[b] This was our own pack. The first four were in plain cans; the last two in glass jars. This pack was 15 months old when examined.

The other pack examined for tin and iron was the condemned Japanese importation already mentioned. Government records showed that this lot had been imported two years before the writers examined it. The cans were lacquered and lined with parchment paper. Of the number opened two which were wholly normal in appearance and two having badly blackened contents were selected. Two other cans before opening were heated at 115° C. for 24 hours with the same effect on the flesh as in the case of the lobster. Tin and iron were determined in the contents of each of these six cans.

The results of these iron and tin determinations (Table III) show a fair correlation between the amount of iron and the degree of blackening, but no apparent relation between the amount of tin and the amount of blackening. The relationship of iron to tin in the contents of lacquered cans was about 20 to 1; in the contents of plain cans, 2 to 1.

Discussion of Results

It appears that free oxygen and volatile bases are not significant in the corrosion of cans by marine products. The experiments of Weber, Houghton, and Wilson,[14] on the corrosion of cans by 0.05 *N* solutions of ammonia and alkylamines, do not appear to be significant. Their solutions should have been titrated to a pH of 7.0 in order to obtain fairly comparable conditions, for this approximates the reaction of crustacea and other marine products which corrode cans. It is possible that the volatile bases cause corrosion because of their contribution to the hydroxyl-ion concentration. However, in such a well-buffered system a great increase in volatile bases would be required to produce a notable increase in alkalinity.

Although oxygen and volatile bases are eliminated, the role in corrosion of sulfur and of the reaction remains obscure. There appears to be some relation between hydroxyl-ion concentration and corrosion, for all the products examined which corrode cans are on the alkaline side of pH 6.5. Those which do not corrode cans are on the acid side of this reaction. The tentative suggestion is offered that the sulfide ion may be a significant factor in corrosion. Its concentration increases through conversion of SH^- to S^{--} as the product becomes more alkaline.

The mechanism of blackening in crustacea seems to be dependent on a neutral or alkaline reaction in the presence of a fairly high concentration of sulfide sulfur. It is undoubtedly significant that of all the marine products examined only crustacea contain organic sulfur metastable at ordinary temperatures, and only crustacea blacken to any great extent. It is also worth noting that the conversion of organic sulfur to sulfide sulfur is accelerated, directly or indirectly, by the metal of the container. This acceleration may be due to the disturbance of an equilibrium between these forms of sulfur by the precipitation of ferrous sulfide. In this connection it is interesting that Becking[15] has noted that the black mud of lake bottoms, which is black because of the presence of ferrous sulfide and which is the milieu of the iron bacteria, never has an acidity greater than pH 6.6 to 7.0. The black color disappears when an acidity greater than pH 6.6 is produced.

One practical suggestion that may be made in the light of this investigation is that crustacean packs should be stored at as low a temperature as possible. The rate of blackening increases rapidly with increasing temperature. It is conceivable that storage below the freezing point might be economical under some conditions. It seems probable that if the contents of the can were frozen, no corrosion of iron, and hence no blackening, would take place.

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[14] *U. S. Dept. Agr., Bull.* **908** (1921).

[15] *Ann. Botany*, **39**, 613 (1925).

Mine Production of Crude Platinum—The total production of crude platinum in the United States in 1925 was 343 ounces, according to reports from mine operators compiled by the Bureau of Mines. This output is more by 92 ounces than the purchases by refiners reported in a recent statement by the Bureau of Mines.

The Life of Fuller's Earth Used in the Vapor-Phase Treatment of Cracked Distillates[1]

By M. R. Mandelbaum and P. S. Nisson

The Gray Industrial Laboratories, Newark, N. J.

Laboratory experiments conducted on the recovery of fuller's earth used in the vapor-phase treatment of cracked gasoline show that after the fifth reburning the earth has deteriorated but little, if at all, for vapor-phase use. Larger runs in steel equipment were checked against small runs in glass for each burning. Figures on yield, color, color stability and gums, copper and glass dish are given for the product of each run.

In view of the use of cracked gasoline in ever increasing proportions as motor fuel and the consequent development of interest in vapor-phase refining, this paper is intended to answer some of the questions raised since the first publication on the subject.[2] The process consists fundamentally in the passage of the cracked motor fuel in vapor form, at a temperature approximating the boiling point of the hydrocarbons present, through an adsorption catalyst. In this way the less stable hydrocarbons in the mixture are caused to polymerize, the polymers being removed by taking advantage of their much higher boiling point. As a result the objectionable hydrocarbons, to which the undesirable characteristics of cracked distillates are ascribed, are selectively removed, with a minimum loss of the valuable olefins and aromatics. Moreover, it is possible in this way to refine the vapors directly as they come from the cracking still, thus eliminating the necessity of rerunning the distillate. This is extremely important in the light of recent improvements in fractionation on pressure stills which make possible the production of end-point cracked gasoline without rerunning.

The catalyst most desirable for refinery use, despite extremely interesting results obtainable in the laboratory with other materials, is fuller's earth. This is primarily because it seems to possess, under ordinary conditions, the right degree of activity; because of its wide occurrence and comparatively low cost; and because it is a material which many refineries are already equipped to handle and with which they are fully acquainted.

The present paper is concerned briefly with the efficacy of reburned clay in the process. This point has been frequently discussed, especially as in many cases of the revivification of clays used for decolorizing lubricating oils by percolation there is a distinct drop in value for each reburning. The results enumerated in Table III show that, for vapor-phase refining, the fuller's earth is practically unaffected by reburning after use. The work has so far been carried out through five reburnings and six uses of a typical Florida clay. It is intended to carry the experiments further with this particular sample, as well as on other clays. The data already obtained, however, are so conclusive that they are published at this time.

For comparing fuller's earths as to their utility in vapor-phase refining, it has been found, in the course of hundreds of experiments, that it is correct to assume that their relative efficiency is the same for most cracked distillates. This makes it necessary, in order to determine the relative merits of any two clays, only to refine with them, in the laboratory apparatus such as is described in the article mentioned above, any convenient cracked product. The practice has been adopted of rerunning the selected distillate to the yield (expressed in barrels of gasoline per ton of catalyst) which has been found to give a product of satisfactory quality with the clay used as a basis of comparison. This yield will, of course, vary with the character of the product treated. For reasons not entirely clear, the yields obtained in the laboratory have always been found to be much smaller than those obtainable for the same distillate and clay on the plant scale. The products obtained with various clays in laboratory runs on the same distillate are compared by one or more of the best methods described below, according to the degree of precision desired in the comparison. Because of the difficulty of reproducing and interpreting results, yields within 5 per cent of each other may be considered the same for the purpose of the tests.

Tests for Refinement

In the absence of a recognized method of test in order to obtain criteria of the refinement of cracked gasoline, it has been necessary to select from the available test methods the determination of those properties which seem most closely related to the undesirable characteristics of cracked products. The chief one, in the authors' judgment, is the deterioration of color on standing.

Color Stability—Color instability, in addition to being of itself objectionable, seems to be closely associated with the tendency to deposit gums on standing, which is probably the most serious undesirable property of insufficiently refined cracked products. The authors have observed that in many cases gum deposition has been preceded by a darkening of color. In such cases, upon the deposition of the resinous material on the bottom or sides of the container, the supernatant liquid reverts to a color considerably less yellow than it has had for some time prior to the settling out of the gum, and is comparatively stable. As is well known, color stability is purely relative and depends entirely on conditions of test. For the present purpose, however, it was simply desired to make a comparison of the effect of treatment of a given distillate with various samples of clay. The products were accordingly subjected to the sunlight by putting them in specially designed racks in an unobstructed south window for one week, the color being observed in the Saybolt chromometer after 2, 4, and 7 days. By exposing the samples simultaneously, any differences in temperature, intensity of sunlight, and so on, which are known to affect the stability, were eliminated. With one of the samples—the twice reburned clay in Table III—it became necessary to determine the stability at another time; this was accomplished without detracting from the value of the comparison, by exposing at the same time a sample treated with unused clay as a control. Attempts to accelerate the tests by the use of ultraviolet radiation and quartz containers have not yet been carried to the point where the results can be interpreted in terms of sunlight stability, although samples with varying

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[1] Received March 30, 1926. Presented before the Division of Petroleum Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

[2] Gray and Mandelbaum, This Journal, **16**, 913 (1924).

degrees of instability have usually been found to rank in the same order under both conditions of test.

The gumming tests have been conducted by two methods—the copper dish tests of the U. S. Bureau of Mines,[3] and the glass dish tests according to the method of Smith and Cooke.[4] The results obtained in either case were not readily reproducible, since they seemed to vary with every possible change of conditions, including the number of samples subjected to test at the time and, in the case of the copper dish, with the method of polishing used. The gum tests are therefore included merely as a basis of comparison (Table III).

METHYLENE BLUE TESTS—In view of the success attained by Hill, Nichols, and Cowles[5] in using the adsorption of methylene blue from an acid solution of the dye as a measure of the efficiency of reburned fuller's earth used in percolation, this method was tried to see if it was applicable to reburned clays used in vapor-phase refining. It was found that, whereas the burned unused earth had a methylene blue number of 0.1, the revivified clays gave results ranging from 1.0 to 1.5. This difference seems larger than would be expected from the results obtained in actual use, especially since the spent clays, which are practically useless, have numbers ranging from 3 to 7. But, remembering that Hill, Nichols, and Cowles found that the unused clay was somewhat out of line when the adsorption of dye was compared with percolation efficiency, the similarity of readings and actual results on the reburned samples would seem to justify the hope that further investigation of the methylene blue method will lead to the development of conditions under which it can be applied to revivification of clays for vapor-phase refining. For a comparison of different fuller's earths the method seems to hold no promise whatsoever, as different samples of similar activity have given far different methylene blue numbers, and vice versa.

TURPENTINE TEMPERATURE REACTION—Attempts were also made to correlate the activity of fuller's earth in vapor-phase refining with the temperature rise obtained by the addition of turpentine or pinene, as described by Venable.[6] As can be seen from the tables, even less satisfactory results were obtained than was the case with the methylene blue numbers. The turpentine temperature reaction recorded in this paper is taken arbitrarily as the temperature rise obtained by adding 7 cc. of the same sample of redistilled turpentine to 5 grams of the fuller's earth in an insulated test tube, the bulb of the thermometer being just covered by the clay. The figures are intended to be regarded as of comparative value only. Here the difference between the burned unused and the reburned used clay is even larger, and the difference between the reburned used clays and the spent clays (which range from 2 to 3) is barely outside the experimental error of the rather crude method used (Table III). Slight differences in moisture content would affect the temperature rise seriously, reducing thereby the applicability of a method based on this reaction.

Table II—Résumé of Runs to Exhaust Clay between Reburnings

Condition of clay charged	Unused	REBURNED Once	Twice	3 times	4 times
Number of runs	4	5	3	3	3
Total weight of clay charged, grams	3000	2521	2250	1979	1790
Total charge to still, liters	150	131	114	99.3	83.6
Total distillate, liters	99.6	84.8	76.7	72.3	62.2
Yield of product, barrels per ton clay	192	193	197	210	199
Product range of gravity, ° A. P. I.	54.5–55.3	53.4–55.3	56.3–57.0	55.7–57.0	57.0–57.5
Product range of end point, ° F.	432–435	440–458	422–427	422–432	425–430
Product range of color, Saybolt	26–29	25–30	27–30+	26–28	25
Final weight of clay, grams	3625	2725	2579	2232	2058
Temperature of burning, ° F.	1020	1020	1020	1020	1020
Loss on burning, per cent	18	10	17.5	12.2	13.4
Further loss on ignition, per cent	0.5	0.4	1.4	0.5	0.6

Reburning of Clay

The reburnings were made by the laboratory of a manufacturer of clay-roasting equipment, so that there might be no doubt of the applicability of the results to large-scale revivification. A gas-fired assay muffle furnace was used, the muffle being open at one end. The clay was gradually brought up to the desired temperature and frequently stirred.

The temperature necessary to burn out the organic material left in clay which had been used for vapor-phase refining in order to make it fit for re-use had been determined in the case of spent Georgia clay from a commercial installation. The clay in question had been used to refine gasoline from Fleming pressure distillate, at a yield of 600 barrels per ton, and contained 13 per cent of carbonaceous material. On reburning it at maximum temperatures of 1180° F. (638° C.), 1100° F. (593° C.), and 1020° F. (549° C.), the result in each case was a clay that could be used efficiently for vapor-phase refining. In fact, each reburned sample seemed somewhat more efficient than the unused clay (Table I), but this might be explained by the difficulties involved in sampling.

Table I—Activity of Revivified Georgia Clay Burned at Various Temperatures

Max. temp. of roasting, ° F.	1020° F.	1100° F.	1180° F.	Unused clay
Methylene blue number	1.5	1.0	0.7	0.2
Turpentine temperature reaction, ° F.	12	4	22	229
Yield, barrels per ton[a]	127	134	128	129
Color of product (Saybolt):				
Original	30	30	30	28
After 2 days (south light)	30	30	30	28
After 4 days (south light)	30	30	29	27
After 7 days (south light)	30	28	28	25

[a] A Dubbs pressure distillate was used in these tests.

From these results it is apparent that the lowest temperature gave the best results. This was adopted as the temperature for reburning the Florida clay used in these tests, on the basis that it was high enough to remove the organic material sufficiently and safely below the fusion point of fuller's earth.

In order to have sufficient clay for several reburnings, with the inevitable losses in handling, and to allow for retaining samples at each step for comparison, it was necessary to start with a larger amount than could be handled in the equipment available for this work—a polymerizer of approximately 2 pounds clay capacity and a 10-gallon still. The clay (burned unused 60 to 90 mesh Florida fuller's earth) was therefore divided and several runs were made. The spent clay was then recombined and reburned, and the remainder divided and another group of runs made. This procedure has now been repeated through five reburnings. Consequently, the runs have been made at various times, and with a pressure distillate which, although from the same source (a tank and tube product from a nearby refinery) has, of course, varied considerably. On this account and because of various operating conditions, it was impossible to obtain significant results for purposes of comparison from these runs. They were therefore performed solely in order to expend the catalyst for reburning, and the comparison of the

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[3] *Bur. Mines, Bull.* **323A**.

[4] Leslie "Motor Fuels," p. 582.

[5] THIS JOURNAL, **17**, 818 (1925).

[6] *J. Am. Chem. Soc.*, **45**, 728 (1923).

clay at various steps is based entirely on the behavior of the retained samples.

Table II is an abstracted record of the work done by the clay after the various burnings. All the runs with clay of the same condition have been grouped together, and each column represents the total. The individual yield in barrels per ton varied only slightly in any case from the average for its group. The constants determined on the refined product for control—A. P. I. gravity, Engler end point, and color—are indicated by giving the highest and lowest of each in each group. The table also shows the gain in weight of the clay at each use, and the loss on burning.

Refining with Reburned Clay

The retained samples of clay from the various burnings were compared by refining with them the gasoline from a Fleming pressure distillate which was known to give a product of the desired characteristics with the unused clay, at about 450 barrels per ton in the glass apparatus. In running these tests, 11.5 grams of the clay were used in each case, 1220 cc. of the pressure distillate, which had a gasoline content of about 75 per cent, being charged. Table III shows the results obtained, as regards color, stability, and gumming tests, and gives for comparison the methylene blue numbers and turpentine temperature reaction.

From the above it is evident that, although there is a slight difference in the stability of the products from the burned clays as compared with that from the unburned, it is not large enough to be of practical importance, especially since reburnings after the first seem to leave the clay unaffected. There is, therefore, no reason to doubt that the reburning and re-use can be repeated practically indefinitely without further impairing the efficiency of the clay.

Table III—Comparison of Reburned Clays for Vapor-Phase Refining

		REBURNED				
Clay used	Unused	Once	Twice	3 times	4 times	5 times
Methylene blue number	0.10	1.0	1.5	1.0	1.0	1.5
Turpentine temperature reaction, ° F.	148	6	12	4	5	6
Yield, barrels per ton[a]	456	461	461	460	456	467
Product, initial boiling point, ° F.	108	110	118	104	116	110
Temperature, ° F.:						
20% off	210	208	212	208	216	216
50% off	288	282	286	282	284	288
90% off	384	384	381	380	380	382
End point	416	410	422	414	414	426
Gum mg. per 100 cc.						
Copper dish	23.9	19.6	21.3	18.6	13.6	16.2
Glass dish	6	6	8	9	6	7
Color (Saybolt):						
Original	30	30	29	30	28	30
After 2 days (south light)	29	27	26	26	27	27
After 4 days (south light)	26	25	25	25	25	25
After 7 days (south light)	25	23	24	23	24	23

[a] A Fleming pressure distillate was used in performing these tests.

Conclusions

Organic material left in clay used for vapor-phase refining can be burned out sufficiently at a temperature of 1020° F. to allow of efficient re-use of the clay. This has been found to leave the efficiency of a Georgia fuller's earth entirely unimpaired by one reburning.

Reburned Florida clay, revivified at 1020° F., is only slightly less active than the unused clay. After the first reburning its utility remains unimpaired by further burnings as far as the present experiments have been carried—that is, through five reburnings.

Effect of Various Carbon Pigments upon Rate of Oxidation of Linseed Oil[1,2]

By F. H. Rhodes and H. E. Goldsmith

CORNELL UNIVERSITY, ITHACA, N. Y.

Lampblack and carbon black markedly inhibit the oxidation of raw linseed oil. This effect is not due to the presence of an oily impurity in the pigment, but is due largely to the adsorption on the pigment of the intermediate oxidation product which is the true catalyst in the drying of linseed oil. When added to linseed oil containing drier, the carbon pigments adsorb some of the drier and for this reason also tend to retard the drying. The extent to which the oxidation is inhibited varies with the nature of the drier present.

THE effect of the carbon pigments upon the rate of drying of paints has been discussed by numerous authorities. It is generally agreed[3,4,5] that some carbon pigments, particularly lampblack, act as "retarders in the drying of paints and tend to inhibit the oxidation of the oil. The exact cause of this effect is not fully understood. Several authorities[3,4,5,6] attribute the retarding action of lampblack to the presence in the pigment of a certain amount of oily material. In none of this previous work on the effect of black carbon pigments on the rate of drying of paints has a quantitative study been made of the effect of such pigments upon the rate of oxidation of linseed oil.

The present investigation was undertaken to determine quantitatively the effects of the black carbon pigments on the rate of oxidation of linseed oil, and to establish the causes for these observed effects.

Materials

Pure linseed oil from North American seed was used. It showed the following analysis:

Specific gravity at 15° C.	0.9315
Refractive index at 15° C.	1.4820
Acid number	4.51
Saponification number	195.3
Iodine number	170.5

The driers were linoleate paste driers, showing the following analyses:

COBALT PASTE DRIER

Cobalt (calcd. as metal)	5.74 per cent
Manganese	Trace
Magnesium, copper, nickel	Spectroscopic traces only

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[1] Received January 19, 1926.

[2] This article is respectfully dedicated by the authors to Prof. L. M. Dennis, and will be reprinted as Article Number Two in the Louis Munroe Dennis Quarter Century Volume to be published in commemoration of the completion by Professor Dennis of twenty-five years of service as head of the Department of Chemistry at Cornell University.

[3] Toch, "Chemistry and Technology of Paints," 2nd ed., 1916, p. 99.

[4] Sabin, "Technology of Paint and Varnish," 2nd ed., 1916, p. 201.

[5] Hurst, "Painters' Colours, Oils and Varnishes," 2nd ed., 1901, p. 250.

[6] Morrell, "Rubber, Resins, Paints and Varnishes," 1920, p. 136.

MANGANESE PASTE DRIER

Manganese (calcd. as metal)	5.16 per cent
Iron	0.055 per cent
Aluminum, copper, sodium	Spectroscopic traces only

LEAD PASTE DRIER

Lead (calcd. as metal)	17.59 per cent
Iron	0.0605 per cent
Sodium, aluminum, arsenic, magnesium, silicon	Spectroscopic traces only

In making up the vehicles for the paints studied, a calculated amount of the paste drier was dissolved in a known weight of warm linseed oil. The vehicles were stored in sealed bottles until used. The amounts of drier used were sufficient to give the following concentrations of active material (calculated as metal) in the vehicles:

Vehicle No.	METAL	Per cent
1	Lead	0.275
2	Manganese	0.0732
3	Cobalt	0.0221

The carbon pigments were:

	Carbon black Per cent	Lampblack Per cent	Vine black Per cent
Ash	0.166	0.2028	8.516
Moisture	3.68	2.15	5.72
Soluble in benzene	Trace	5.82	None

Procedure

The procedure was similar to that described by Rhodes and Van Wirt.[7] Paints prepared from pigment and linseed oil were exposed to an atmosphere of pure oxygen at 30° C. and the rate of absorption of oxygen and the rate of evolution of volatile matter were measured. Unless otherwise specified, each paint contained one part by weight of pigment and nine parts by weight of vehicle. With each paint there were made at least two parallel determinations, giving results which agreed to within the limits of experimental error.

Results

The results are shown graphically by the accompanying charts, in which the amounts of oxygen absorbed and the amounts of volatile matter evolved, each expressed in terms of percentage by weight of the oil in the paint, are plotted against the lengths of time of exposure. A single curve is shown to represent the average results obtained in the two or more check determinations made with each sample.

Linseed Oil Alone

Chart I shows the rates of oxidation and the rates of evolution of volatile matter of raw linseed oil alone and of the mixtures of linseed oil with the various driers. The autocatalytic character of the reaction involved in the drying of linseed oil and the effects of the driers in accelerating the formation of the autocatalyst and thus increasing the initial rate of oxidation are clearly indicated.

Carbon Pigments Added

Chart II shows the results obtained in a series of experiments made to determine the rate of oxidation of paints made from raw linseed oil and carbon pigments. The addition of the carbon pigments markedly retarded the rate of oxidation of the oil. The paints were still somewhat tacky after 400 hours' exposure.

As a supplementary experiment, samples of carbon black paint and of linseed oil alone were painted in parallel strips on a glass plate and allowed to stand in the air at room temperature. The film of oil became tacky in 4 days and was dry to the touch in 7 days. The paint made from carbon black became tacky only after 22 days and was dry to the touch only after 28 days.

It has been stated that the oily impurities in lampblack are largely responsible for the action of this pigment in retarding the oxidation of linseed oil. In order to obtain further information as to the effect of oil-soluble impurities in the pigments, samples of paints made from carbon black and from lampblack were centrifuged and the rates of oxidation of the clarified oils thus obtained were determined. The linseed oil obtained from the carbon black paint was clear and of a lighter color than the original raw oil from which the paint had been prepared; the oil from the lampblack paint was dark red and somewhat fluorescent.

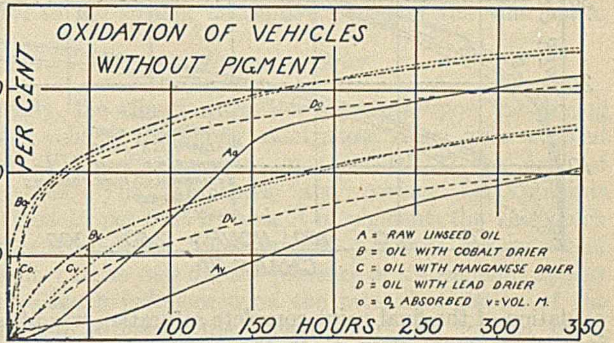
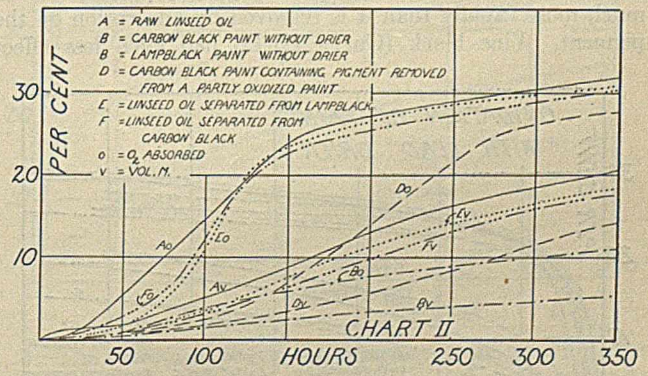


CHART I

The results of the oxidation experiments made with these oils are shown on Chart II. The oils separated from the paints oxidized a little more slowly at first than did the raw linseed oil, but after a short period of induction the separated oils took up oxygen at almost the same rate as did the fresh raw oil. These experiments prove that the effect of black carbon pigments in inhibiting the oxidation is not due to the presence in the pigment of impurities that are soluble in linseed oil. The action of the blacks in delaying the drying must, therefore, be due to some specific action of the pigments themselves. That the oils separated from the paints showed more marked periods of induction than fresh linseed oil suggests that the pigments may have adsorbed and removed the small amount of the autocatalytic intermediate oxidation product which is normally present in ordinary raw linseed oil. This, in turn, suggests that the slowness of drying of paints containing carbon pigments may be due to the fact that the pigments continuously adsorb and remove the autocatalyst as fast as it is formed.



Additional evidence in favor of this hypothesis is supplied by the following experiment: A paint made with carbon black was oxidized at 100° C. until it became thick when cooled. The pigment was separated from the vehicle by centrifuging, and was then washed with raw oil and again centrifuged to remove the wash oil. The resulting pigment was made up into a paint with raw linseed oil and the rate of oxidation of this paint was determined. Oxidation took

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[7] THIS JOURNAL, 15, 1135 (1923).

place very slowly for the first 150 hours, but after this period of induction oxygen was absorbed about as rapidly as by the raw oil alone. It will be observed that this paint made from pigment recovered from a partly oxidized paint dried much more rapidly than did paint made from the original pigment. The results indicate that during the preliminary treatment the carbon black had become almost saturated with the intermediate oxidation product, so that in the oxidation of the final paint complete saturation was attained in a short time, after which the autocatalyst remained in the oil to exert its normal effect in accelerating the drying.

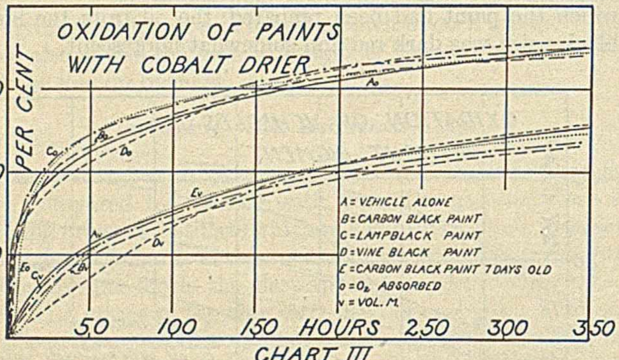

CHART III

Cobalt Drier

The effect of carbon pigments on the rate of oxidation of linseed oil in the presence of cobalt drier was next investigated. The paints were made up to contain 10 per cent of pigment suspended in linseed oil in which had been dissolved sufficient cobalt linoleate to contain an amount of cobalt equivalent to 0.0221 per cent of the weight of the oil. The results are shown by Chart III.

Curves III-B and III-C show the rates of oxidation of freshly prepared paints made from carbon black and from lampblack. These two curves are practically identical in form. In each case the presence of the pigment causes a very slight retardation of the initial rate of oxidation of the vehicle. In these experiments the effect of the pigments in inhibiting the oxidation of the oil was very much less than in the experiments made with paints prepared from linseed oil without drier. It appears that in the presence of the powerful cobalt drier the intermediate oxidation product that is the true catalyst in the oxidation reaction is formed much more rapidly than it is removed by adsorption on the pigment. Vine black (Curve III-D) had even less effect upon the initial rate of oxidation than had carbon black or lampblack. This is to be expected, since the vine black is relatively dense and gives relatively less adsorbing surface.

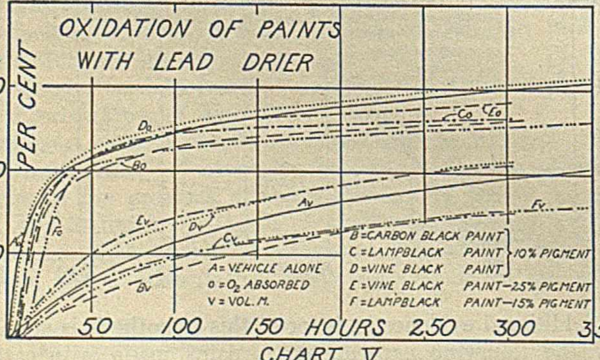

CHART V

It was observed (Curve III-E) that when the carbon black paint was allowed to stand for several days before being exposed to oxygen the initial rate of oxidation was appreciably less than the initial rate of oxidation of the freshly prepared paint. This appears to be due to the gradual adsorption of some of the cobalt drier by the pigment. In order to determine to what extent this adsorption of the drier occurs, freshly prepared and week-old samples of the carbon black paint were clarified by centrifuging and the resulting clear vehicles were analyzed for cobalt and tested to determine the rate of absorption of oxygen. The clarified vehicle from the freshly prepared paint contained 0.003 per cent of cobalt; that from the week-old paint contained only a trace of cobalt.

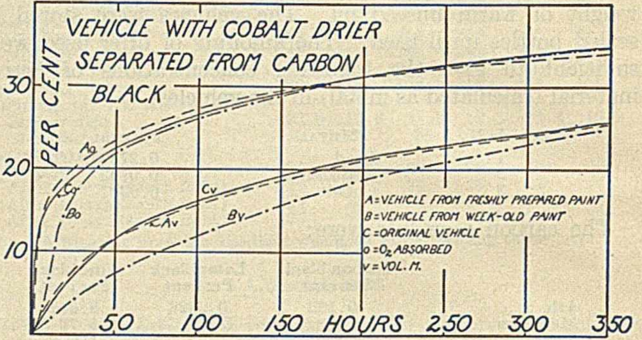

CHART IV

The rates of oxidation of the two clarified samples are shown by Chart IV. The clarified vehicle from the freshly made paint oxidized at almost exactly the same rate as did the original vehicle from which the paint was prepared. The vehicle recovered from the paint which had been allowed to stand for a week oxidized much more slowly. This was to be expected, since the concentration of drier in this sample was extremely low. From a comparison of Curves IV-B and IV-C it will be seen that the vehicle recovered from the week-old paint oxidized even more slowly than did the paint itself. It would appear that the cobalt drier still possesses some catalytic activity even when adsorbed in the pigment, although, of course, the adsorbed drier is less effective than drier in solution.

Lead Drier

In studying the effect of the pigments upon the rate of drying of linseed oil in the presence of lead drier, the vehicle used contained an amount of lead linoleate equivalent to 0.275 per cent of lead. The paints were made up to contain 10 per cent of pigment as before. The paint made from carbon black absorbed no measurable amount of oxygen during the first 5 hours' exposure. Oxidation then began and, after a short period of induction, progressed normally. The paint made from lampblack showed about the same characteristics as did the paint made from carbon

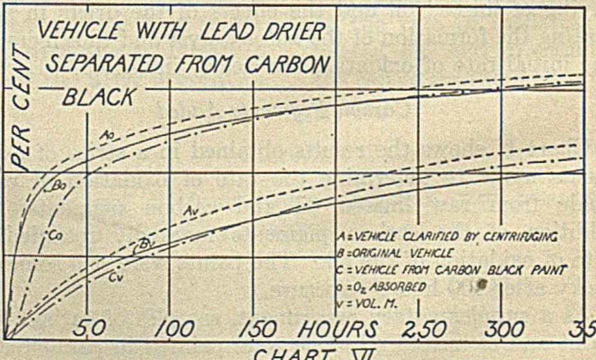

CHART VI

black, although the length of time during which no oxygen was absorbed was somewhat longer.

The effect of the pigments in retarding the oxidation of the vehicle may be due in part to the adsorption of the drier by the pigment. To determine the extent to which such adsorption occurs, a sample of the carbon black paint was centrifuged and the resulting clarified vehicle was analyzed for lead. For comparison, an analysis was made on a portion of the original vehicle which had been similarly centrifuged to remove any drier not actually in solution. The clarified original vehicle contained 0.097 per cent of lead, while the vehicle recovered from the paint contained only 0.0312 per cent of lead. Obviously, the carbon black had adsorbed and removed over two-thirds of the drier present in actual solution in the oil.

The progress of the oxidation of these clarified vehicles is shown by Chart V. In spite of the fact that the lead content of the original vehicle was reduced from 0.275 per cent to 0.097 per cent by centrifuging, the centrifuged vehicle oxidized at almost exactly the same rate as did the original. These results indicate that, under certain conditions at least, only a portion of the lead linoleate added to linseed oil actually passes into solution in the oil, and that only the comparatively small amount of drier in actual solution is effective in promoting the drying of the oil. The vehicle which was separated from the paint, and which contained only 0.0312 per cent of lead, showed a more pronounced period of induction and an appreciably slower rate of oxidation than did the original vehicle. This is the logical result of the lower concentration of dissolved drier.

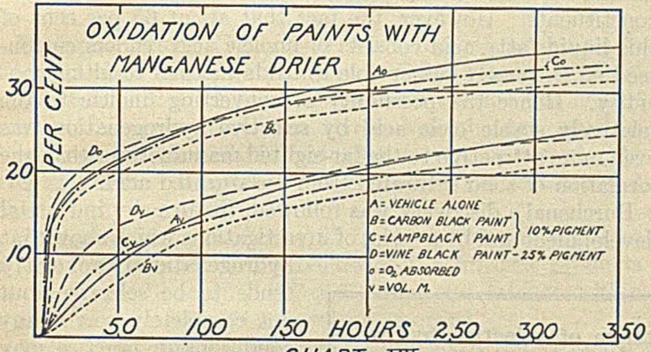

CHART VII

The adsorption of a large part of the lead drier by the pigment does not, however, explain all the phenomena observed in connection with the oxidation of the paints made with carbon black or lampblack. That practically no oxygen was taken up during the first few hours of exposure may be explained by the hypothesis that the pigment also adsorbed the small amount of autocatalyst which may have been present in the original oil or which may have been produced during this initial period. Only after several hours was sufficient unadsorbed autocatalyst produced to exert a marked effect in promoting the oxidation. It will be observed that in the case of the paint made up to contain 15 per cent of lampblack the initial period during which no oxidation took place was somewhat more pronounced than in the case of the paint containing only 10 per cent of lampblack. This is in agreement with the theory as outlined above.

That the effect of the pigment in inhibiting the oxidation continued for a few hours only instead of for many days, as in the case of the paint made from raw linseed oil, is due to the fact that in the present case the adsorption of the lead drier by the pigment very greatly decreased the adsorptive capacity of the pigment for the intermediate autocatalyst. It will be observed that in the case of the paints oxidation, when once started, took place somewhat more rapidly than in the case of the clarified vehicle separated from the paint (Chart VI). This provides additional indication that drier adsorbed on the pigment may still show some catalytic activity.

Paints made up to contain 10 per cent of vine black oxidized almost as rapidly as did the original vehicle. When the concentration of the vine black was increased to 25 per cent, a somewhat more pronounced effect was noted. That vine black is much less effective than carbon black or lampblack in retarding the drying of the oil is due, of course, to the smaller adsorptive power of the vine black.

Manganese Drier

Finally, the effects of carbon pigments upon the drying of the vehicle containing manganese drier were studied (Chart VII). The vehicle contained 0.0732 per cent of manganese. The lampblack and carbon black paints contained 10 per cent by weight of pigment; the vine black paint was made up to contain 25 per cent by weight of pigment. In no case did the presence of the pigment appear to have much influence upon the rate of oxidation of the linseed oil, although the paint made with carbon black showed a slightly longer period of induction than did the vehicle alone.

To determine to what extent the pigment absorbs and removes the manganese drier, samples of the original vehicle and of the carbon black paint were clarified by centrifuging. The centrifuged vehicle contained 0.0262 per cent of manganese, while the vehicle recovered from the paint contained only 0.0065 per cent. The rates of oxidation of the clarified vehicle and of the vehicle recovered from the paint were substantially the same as that of the original vehicle (Chart VIII).

Conclusions

1—The addition of lampblack or carbon black to raw linseed oil very markedly inhibits the oxidation of the oil.

2—The effect of the carbon pigments in inhibiting the oxidation of linseed oil is not due to the presence of oily or oil-soluble impurities in the pigments.

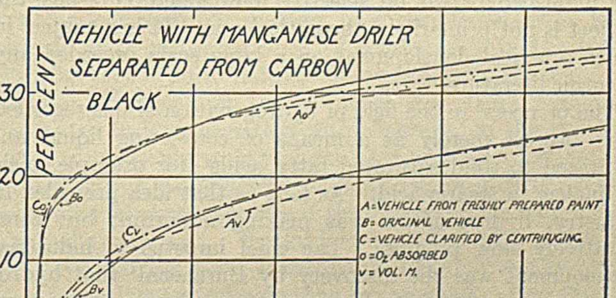

CHART VIII

3—The effect of the carbon pigments in delaying the oxidation of raw linseed oil is due to the continuous adsorption of the intermediate oxidation product which acts as the true catalyst in the drying reaction.

4—The carbon pigments only slightly retard the oxidation of freshly prepared paints containing cobalt drier. The inhibiting effect becomes more pronounced as the paints are allowed to stand. This is due to the gradual adsorption of the cobalt drier by the pigment.

5—When added to linseed oil containing lead drier, carbon black and lampblack almost completely inhibit the oxidation of the oil during the first few hours of exposure. This effect is due to the fact that the pigments adsorb not only a portion of the lead drier but also the small amount of autocatalytic oxidation product that is formed at the beginning of the oxidation.

6—Carbon pigments have little effect upon the rate of oxidation of linseed oil containing manganese drier.

Heterogeneous Catalysis[1]

III—Hydrogenation of Cottonseed Oil with Platinum

By A. S. Richardson and A. O. Snoddy

The Procter & Gamble Co., Ivorydale, Ohio

THE glycerides of cottonseed oil are derived from linoleic acid, oleic acid, and solid saturated acids, chiefly palmitic. Hydrogenation of such an oil may conceivably involve any combination of the following three changes: (1) linoleic to oleic acid; (2) oleic to stearic acid; (3) linoleic to stearic acid. The problem of the distribution of the total hydrogenation of cottonseed oil among these three changes belongs to a general field of investigation which has appropriately been described by various investigators as the problem of "selective hydrogenation."

The previous literature on the selective hydrogenation of fatty oils has been reviewed in the earlier papers of this series.[2] The present paper deals with the selective action of platinum black in the hydrogenation of cottonseed oil, but before proceeding to a discussion of the experimental data involved it will be in order to correct a rather widespread misunderstanding of the fundamental purpose of hydrogenation.

The predominating importance of selective hydrogenation in industry is pointed out. The hydrogenation of cottonseed oil with platinum catalyst has been investigated at temperatures varying from 40° to 240° C. The preferential conversion of linoleic acid to the oleic acid stage and also the formation of solid unsaturated acid is favored by increasing temperature over practically the whole of the range investigated. Hydrogenation of cottonseed oil with platinum catalyst does not appear to be so selective as with nickel catalyst.

Practical Importance of Selective Hydrogenation

Contrary to the impression which the casual reader may gain from a survey of the published papers on selective hydrogenation of oils, the subject is not primarily a theoretical one. It is a subject in which practical development on a large scale preceded any scientific literature.

The pioneers[3] in the field of hydrogenation of oils regarded their process merely as a means of converting liquid unsaturated to solid saturated fatty acids—for example, oleic or linoleic to stearic acid. As long as that idea prevailed in industry, hydrogenation was making important but comparatively slow progress. The chief impetus to industrial development was the discovery by Burchenal[4] that hydrogenation could be controlled so as to produce a product especially suited for edible purposes, in which the principal chemical change is the selective conversion of the highly unsaturated linoleic acid to the less unsaturated oleic acid, with the formation of relatively little stearic acid.

The mere fact that the average cottonseed oil is about 75 per cent derived from liquid fatty acids has never been a serious handicap to its use in edible fat. The average edible fat should and does contain a substantial excess of liquid constituents. However, the fact that about 65 per cent of this liquid fatty acid consists of linoleic acid renders cottonseed oil extremely susceptible to oxidation and resulting rancidity. Hence the possibility of converting linoleic to the relatively stable oleic acid by selective hydrogenation was even more attractive to the far-sighted manufacturer than the formation of solid saturated from unsaturated acid.

Burchenal's discovery was followed, in turn, by industrial development and by a series of investigations which show that hydrogenation inherently tends to be selective, but not completely so. Many conditions in practice may interfere with or defeat the purpose of selective hydrogenation. If this were not so, it is almost inconceivable that selective features of hydrogenation should have so long been unnoticed.

The most important factor to be controlled is the end point of hydrogenation. For instance, at a more or less well-defined critical point hydrogenation of vegetable oil containing linolein ceases to involve primarily the conversion of linolein to olein and results in substantial increase of stearin content. Carried beyond that point, hydrogenation becomes effectively less selective. Operating conditions may also render the process of hydrogenation effectively nonselective. For instance, unhydrogenated oil may be swept through the system into the finished product. This is particularly likely to occur in a continuous process, but may also occur in a batch process in which pockets of unhydrogenated oil persist throughout the reaction period as a result of incomplete agitation.

Temperature, perhaps, is the most important factor which has been shown to affect the inherent selective tendency of hydrogenation of oils in the presence of nickel catalyst. Moore, Richter, and Van Arsdel[5] found that the selective conversion of linolein to olein was favored by increasing temperature in the hydrogenation of cottonseed oil. Richardson, Knuth, and Milligan[2] have made the same observations on several oils in the temperature range 150° to 200° C., but have obtained conflicting results above 200° C.

Scope of Present Work

The present work was undertaken at the suggestion of H. J. Morrison for the immediate purpose of extending the

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[1] Presented as a part of the Symposium on Cotton and Its Products and Vegetable Oils before the joint session of the Divisions of Agricultural and Food Chemistry, Biological, Cellulose, and Industrial and Engineering Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

[2] Richardson, Knuth, and Milligan, This Journal, **16**, 519 (1924); **17**, 80 (1925).

[3] Leprince and Sieveke, German Patent 141,029 (August 14, 1902); Normann, British Patent 1515 (January 21, 1903).

[4] U. S. Patent 1,135,351 (application filed November 10, 1910, patent granted April 13, 1915).

[5] This Journal, **9**, 451 (1917).

Table I—Hydrogenation of Cottonseed Oil with Platinum Black

Temp. ° C.	Iodine Value				Solid acids Per cent	Composition of Mixed Acids, Per cent			
	Oil	Mixed acids	Solid acids	Unsaturated acids		Saturated acids	Oleic	"Iso-oleic"	Linoleic
	104.6[a]	109.4	2.7	148.4	27.1	26.3	25.6	0.8	47.3
40	75.8	79.3	5.4	125.1	38.9	36.6	36.6	2.3	24.5
70	74.9	78.3	5.8	124.9	39.9	37.3	36.0	2.6	24.1
100	74.2	77.6	13.4	118.7	40.7	34.6	38.7	6.1	20.6
120	75.5	79.0	12.2	119.7	39.3	34.0	39.2	5.3	21.5
140	73.3	76.7	14.4	116.4	40.6	34.1	40.3	6.5	19.1
160	73.0	76.4	15.7	114.9	40.6	33.5	41.2	7.1	18.2
180	74.9	78.3	18.6	116.5	41.4	32.8	39.0	8.6	19.6
200	79.4	83.1	18.6	122.2	40.3	32.0	35.6	8.3	24.1
220	76.8	80.3	20.5	117.1	40.6	31.4	39.0	9.2	20.4
240	77.4	81.0	23.7	119.6	43.8	32.3	34.2	11.5	22.0

[a] Original oil.

knowledge of the effect of temperature on selective hydrogenation to cover the case of cottonseed oil hydrogenated with platinum catalyst. The use of this catalyst readily allows a range of hydrogenation temperature considerably greater than is practical with the use of nickel. The results have a greater interest than their bearing on the effect of temperature on selective hydrogenation, as will be pointed out.

Experimental

Platinum dioxide ($PtO_2.H_2O$) was prepared according to the method of Adams.[6] A mixture of 200 grams of refined cottonseed oil and 0.1 gram of platinum dioxide was heated to reaction temperature in a Pyrex flask through which a slow stream of electrolytic hydrogen was being passed. As soon as reaction temperature was reached the mixture was mechanically agitated.

Hydrogenation was effected at temperatures varying from 40° to 240° C., the iodine value of the finished products varying from 73 to 79.4. Temperature was held to within ±2° C. of the reaction temperature recorded.

All hydrogenated products were examined by the Twitchell[7] method for the separation of solid from liquid fatty acids. From (1) the weight of the solid fatty acid fraction, (2) the iodine value of the solid fraction, and (3) the iodine value of the mixed fatty acids, the composition of the mixed fatty acids of each hydrogenated product was calculated according to the method previously outlined by Richardson, Milligan, and Knuth.[8] The results are shown in Table I. It should be understood that the term "iso-oleic" acid refers to the unsaturated fatty acids present in the solid fraction and is not meant to convey any impression whatsoever regarding the number of isomeric forms which may be present in this material.

Discussion of Results

If hydrogenation were completely selective in the sense of preferential conversion of linoleic to oleic acid, none of the hydrogenated products within the range of iodine value given in Table I would show any appreciable change in solid saturated fatty acids and the net result of hydrogenation would be a decrease in linoleic content with a corresponding increase in oleic acids (no distinction being made between solid and liquid oleic, since either might be produced by selective hydrogenation of linoleic acid). As a matter of fact, this condition does not even approximately hold for any of the products obtained.

If all products shown had been hydrogenated to the same iodine value, the degree to which hydrogenation was selective in each case could be determined by comparing directly the increase in solid saturated acid, this increase being greatest for the least selective conditions of hydrogenation. Since iodine values of the finished products are not quite uniform, a better basis of comparison is given in Table II, which shows the net change of linoleic, oleic, and stearic acid content and shows also the ratio of increase in oleic to increase in stearic. As hydrogenation becomes increasingly selective this ratio becomes larger. It is assumed, of course, that all increase in saturated acids is due to stearic.

Table II—Distribution of Change after Hydrogenation

Temp. ° C.	*a* Decrease in % linoleic	*b* Increase in % oleic[a]	*c* Increase in % stearic	Ratio *b:c*
40	22.8	12.5	10.3	1.2
70	23.2	12.2	11.0	1.1
100	26.7	18.4	8.3	2.2
120	25.8	18.1	7.7	2.4
140	28.2	20.4	7.8	2.6
160	29.1	21.9	7.2	3.0
180	27.7	21.2	6.5	3.3
200	23.2	17.5	5.7	3.1
220	26.9	21.8	5.1	4.3
240	25.3	19.3	6.0	3.4

[a] Including solid isomers.

The most striking conclusion from the results obtained is that hydrogenation with platinum is by no means so selective as with nickel catalyst. In fact, the highest ratio of increase in oleic to increase in stearic found in Table II is less than the lowest ratio calculated for any sample of cottonseed oil hydrogenated to within the same range of iodine values with nickel catalyst by Richardson, Milligan, and Knuth.[2] At first glance, one might question the appropriateness of speaking at all of the selective action of platinum catalyst at the lower temperatures studied, but careful inspection will show that in all cases the amount of stearic formed is substantially less than would be expected if hydrogenation of linoleic to oleic and of oleic to stearic proceeded continuously at rates proportional to the concentration of the reacting acids. Hence even hydrogenation with platinum black is selective to a considerable degree.

The results obtained indicate that increasing temperature favors selective hydrogenation. Such irregularities as will be noted are probably matters of experimental error and certainly of minor importance as compared with the total drift from the lowest to the highest temperatures studied.

While hydrogenation with nickel has been preferred in industry to hydrogenation with platinum on the basis of cost, it is highly probable that the base metal catalyst would in the long run be preferred on the basis of quality of hydrogenated oil obtained, even if the two catalysts were available at the same cost. Partial hydrogenation with platinum to a given melting point is calculated to produce a product more susceptible to oxidation than hydrogenation with nickel. It is important to note that this difference would be particularly great if the comparison were between a product hydrogenated with platinum at low temperature and one hydrogenated with nickel at high temperature, whereas the chief supposed advantage of platinum catalyst is the possibility of operating efficiently at very low temperatures.

The effect of temperature on the formation of solid unsaturated acids is even more striking than the effect of temperature on the degree to which hydrogenation is selective. The amount of "iso-oleic" acid obtained by hydrogenation at 40° C. was barely beyond experimental error, but the amount steadily increased, with increasing temperature of hydrogenation, to 11.5 per cent at 240° C.

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[6] *J. Am. Chem. Soc.*, **44**, 1397 (1922); **45**, 1071, 2171 (1923).

[7] This Journal, **13**, 806 (1921).

[8] *Ibid.*, **16**, 520 (1924).

The Fluosilicates as Insecticides[1,2]

By S. Marcovitch

Agricultural Experiment Station, Knoxville, Tenn.

THE first extensive experiments with the fluosilicates as insecticides were carried out at Knoxville, Tenn., in the spring of 1924. Comparatively favorable results were obtained which were reported in Bulletin 131 of this station. The sodium salt was the only one available in commercial quantities, but it was not particularly adapted for dusting. Last summer one concern placed a "light" and "extra light" sodium fluosilicate on the market, and there has also appeared a commercial calcium fluosilicate. These chemicals were tried out in the field and much additional information was obtained. The results are not entirely conclusive, however, because the hot, dry summer kept the bean beetles from multiplying.

Sodium Fluosilicate—"Extra Light"

The "extra light" consists of 70 to 75 per cent sodium fluosilicate. According to the distributors, the remainder is silica. It was found, however, to be alumina which was used as a colloid to make a bulkier precipitate. This material occupies about 60 cubic inches to the pound and represents a decided improvement as far as bulk is concerned. The individual particles vary in size from 5 to 30 microns. A good grade of calcium arsenate occupies 80 cubic inches to the pound and the particles appear to be 2 to 4 microns in size. For many insects there appears to be sufficient fluorine in the "extra light" when used undiluted to secure a kill. For insects that feed sparingly, such as the boll weevil, the large amount of filler detracts seriously from the value of the material. It cannot be mixed with hydrated lime without seriously impairing its toxicity. When used undiluted the "extra light" is safer on foliage than the commercial sodium fluosilicate. On tobacco severe injury sometimes results.

Calcium Fluosilicate

The calcium fluosilicate was marketed as "calcium fluosilicate compound." This material is a by-product in the volatilization method of treating phosphate rock for phosphoric acid. It is insoluble and, therefore, safe on foliage, such as tobacco. It is light and fluffy, the particles being about 5 microns in size, and marketed in two forms, one occupying approximately 70 cubic inches to the pound and the other approximately 120 cubic inches to the pound. When used at the rate of 5 pounds per acre, the "compound" is not so toxic as the sodium fluosilicate. However, at the rate of 30 pounds to the acre, the control against the Mexican bean beetle was good.

The manufacturers have discovered a method of increasing the fluorine content of the "compound" which should materially enhance its value as an insecticide.

Test with the Fluosilicates against Certain Insects

The "calcium fluosilicate compound" appears to be very effective against flea beetles, such as the new mint flea beetle in Michigan. In Arkansas, Baerg[3] found that the blister beetles, heretofore not successfully controlled by arsenicals, are very susceptible to the fluosilicates. These beetles are especially injurious to soy beans where they are found in swarms. No appreciable injury was caused by the commercial sodium fluosilicate to soy bean foliage or alfalfa when diluted with an equal quantity of hydrated lime.

The control of the striped cucumber beetle has previously been far from perfect. It is a very difficult insect to poison with arsenicals because they act as repellents. Since the beetle has the habit of cleaning its feet by drawing them through its mouth, it would be expected to yield to the fluosilicates, and such was found to be the case. On June 12, several rows of cucumbers were dusted lightly with commercial sodium fluosilicate about seven o'clock in the morning. Eight hours later it was difficult to find a live specimen, while dead beetles were numerous on the ground about the plants. As some foliage injury is produced when the commercial sodium fluosilicate is used undiluted, it would be advisable to mix it with 2 or 3 parts of hydrated lime. The "extra light" sodium fluosilicate also gave good control and no burning when used undiluted. Cage tests showed that the beetles succumbed to heavy applications of the calcium fluosilicate compound.

When the fluosilicates were mixed with bran in the proportion of 1 to 20, they were found effective in cage tests against grasshoppers and cutworms. There is some evidence that arsenic is somewhat repellent when used in cutworm baits, but this does not appear to be the case with the fluorine compounds.

Roaches were readily controlled with commercial sodium fluosilicate by sprinkling some of the powder in the corners of the pantry or on kitchen floors. In a few cases dead mice were found where the powder had been used. Sodium fluosilicate is also very useful against chicken lice when dusted in the feathers.

One great advantage of the fluosilicates over the arsenicals is their effectiveness against a variety of insects which cannot be controlled by arsenic. Furthermore, the fluosilicates appear fully as toxic as the arsenicals in quantitative tests against certain insects, whereas against man arsenic is far more poisonous. Sollman[4] states that the fatal dose for the trioxide varies from 0.1 to 0.3 gram. Arsenic is also a nerve and capillary poison so that minute quantities are capable of destructive action. The fatal dose for sodium fluosilicate is not given, but for sodium fluoride is said to be 0.5 gram per kilogram of body weight. This means that arsenic trioxide is from 100 to 300 times as poisonous to higher animals as sodium fluoride.

Compatibility with Fungicides or Insecticides

Calcium fluosilicate does not appear to react to any great extent with lime-sulfur or Bordeaux mixture. Sodium fluosilicate, however, precipitates sulfur out of the lime-sulfur and the two are, therefore, not compatible, especially for use on apples. A 3:3:50 Bordeaux with sodium fluosilicate at the rate of 2 pounds to 50 gallons of water was not injurious to potato foliage and was toxic to the larvae of the potato beetle.

According to Kerr and Smith,[5] sodium fluosilicate with either calcium arsenate or Paris green tends to liberate free, water-soluble arsenic (As_2O_5) with consequent injury to foliage. In one experiment 87.87 to 93.80 per cent of the total amount of As_2O_5 in the calcium arsenate was leached

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[1] Received February 18, 1926.

[2] A somewhat more detailed account of the fluosilicates is to appear in *Bulletin* 134 of the Tennessee Experiment Station.

[3] Ark. Agr. Expt. Sta., *Bull.* 201 (1925).

[4] Manual of Pharmacology, 1924.

[5] The Official Record, U. S. Dept. Agriculture, December 2, 1925, p. 5.

out of a combination of distilled water and a mixture of equal parts of calcium arsenate and sodium fluosilicate. With lead arsenate only 1.5 per cent of the total amount of As_2O_5 was leached out, while Paris green gave 9.4 per cent. Sodium fluosilicate in a mixture of calcium arsenate or Paris green is, therefore, not safe to foliage. Calcium arsenate left in dust guns may also be responsible for foliage injury when the same gun is used for dusting with sodium fluosilicate.

Germicidal Value

In a paper presented before the American Phytopathological Society on December 31, 1925, H. W. Anderson discussed "The Control of Bacterial Spot of Peach with Sodium Silicofluoride." Bacterial spot (*Bacterium pruni*), considered the most serious disease of the peach in Illinois, is not controlled by the ordinary fungicides. Dr. Anderson found that sodium silicofluoride in dilutions of 1 to 4000 to 1 to 4500 would always render both sterile when inoculated with *Bacterium pruni*. Sodium silicofluoride was found only moderately fungicidal, inhibiting the germination of bitter rot spores (*Glomerella cingulata*) in dilutions of 1 to 800 when added directly to the spores suspension. Field tests showed practically no infection of bacterial spot, whereas those trees not sprayed with sodium silicofluoride showed 20 to 80 per cent of the leaves infected.

The Determination of Fluorine[1]

By F. G. Hawley

International Smelting Co., Inspiration, Ariz.

A short résumé is given of some of the difficulties usually encountered when determining fluorine by the methods commonly used. A new method is described in which fluorine is determined indirectly. It is first precipitated as lead chlorofluoride, and after filtering from the solution this is decomposed and the amount of chlorine present determined, and from it the amount of fluorine is calculated. The method is especially recommended for low- to medium-grade ores, on which it gives excellent results. On high-grade material the results are not quite so accurate.

Experimental data are given showing the degree of accuracy that may be attained under different conditions with pure material, and also that possible in presence of various other elements.

The difficulties attending the quantitative determination of fluorine in ores or minerals containing considerable amounts of other elements are quite generally recognized. By using long and laborious methods and taking special precautions fairly accurate results may frequently be obtained, but in general the methods in use are far from satisfactory.

The two methods most frequently used are the Berzelius-Rose method, in which the fluorine is precipitated and weighed as calcium fluoride, and the volumetric method of Offerman, wherein the fluorine is volatilized as silicon tetrafluoride, which is received in water and the hydrofluosilicic acid formed is titrated with alkali.

The Berzelius-Rose method is probably used more commonly than that of Offerman and in the hands of an expert will generally yield results that are fairly accurate, but most chemists usually get low results. An objection to this method is the necessity of removing all silica, which requires two filtrations. Phosphates, if present, must also be removed. The precipitated calcium fluoride is gelatinous and difficult to filter. The presence of calcium carbonate partly remedies this, but then a good separation of the fluoride from the carbonate is rather difficult. The Offerman method is simple in operation but requires considerable special and cumbersome apparatus. For some minerals it is unreliable because of difficulty in completely decomposing the fluorine compounds with sulfuric acid. Excellent critical reviews of these methods, as well as some others, have been given by Hillebrand,[2] Adolph,[3] and Wagner and Ross.[4]

A method published by Starck,[5] in which the fluorine is precipitated as the double salt, lead chlorofluoride, and weighed as such, has several advantages, the principal ones being the granular nature of the precipitate, which permits easy filtering, and the fact that under the conditions of the assay lead chlorofluoride is somewhat more insoluble than calcium fluoride. A serious objection is that several other acid radicals, such as sulfates, phosphates, arsenates, etc., would, if present, also form insoluble lead salts and be weighed with the lead chlorofluoride. The procedure as published is only applicable to soluble fluorides and therefore is of very limited application.

A method has been devised which is free from the foregoing objections, and seems equally well adapted to simple fluorides, as fluorspar, and to more complex minerals, such as topaz or the micas. It can be used successfully in presence of fairly large amounts of most of the other elements. The accuracy obtainable, especially on low-grade and impure material, is somewhat greater than that usually obtained by the Berzelius-Rose method. Small amounts of sulfates and phosphates have little influence on the results, but when a large percentage is present the determination is less accurate. If either is present in notable amounts it can be removed by a preliminary leach with 10 per cent acetic acid.[6]

Several variations of the method are given in order to make it better adapted to varied conditions. In each, the fluorine is determined indirectly, being first precipitated as lead chlorofluoride, the chlorine in this determined, and from it the amount of fluorine calculated.

Method

Fuse 0.5 gram of sample with 7 or 8 grams of Na_2CO_3 + K_2CO_3 in a platinum crucible or dish. If the sample does not contain about four times as much silica as fluorine it should be added, but avoid much excess. If sulfur is present, add enough sodium peroxide to oxidize it, also avoiding much ex-

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[1] Received February 2, 1926.

[2] "The Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* **700**.

[3] *J. Am. Chem. Soc.*, **37**, 2500 (1915).

[4] This Journal, **9**, 1116 (1917).

[5] *Z. anorg. Chem.*, **70**, 173 (1911).

[6] Scott, This Journal, **16**, 703 (1924).

cess. When well fused pour on a smooth, clean copper or iron plate. Place the dish and melt in a casserole with water, cover, and heat until disintegrated. Remove the platinum dish, rinse, and let the solution settle, then decant the clear liquid through a filter into a 400-cc. beaker. Break up any lumps and wash two or three times by decanting as before, add about one gram of sodium carbonate, a very little water, and again boil and filter. This second boiling with a strong solution of sodium carbonate usually recovers an appreciable amount of fluorine from the residue. On high-grade ores a refusion with sodium carbonate is a slightly better procedure. Cover the beaker containing the filtrate, which should have a volume of 150 to 250 cc., depending on the silica and fluorine present, and add 16 drops of concentrated hydrochloric acid. High-grade samples may require 22 to 24 drops, but much more than this might later precipitate some lead chloride.

Warm to about 40° C., add methyl orange indicator, and while stirring add, drop by drop, enough nitric acid to finish neutralizing, and then 3 drops excess; then add 10 drops of glacial acetic acid and 25 cc. of a filtered 10 per cent solution of lead acetate containing 1 per cent of acetic acid. The precipitate of lead chlorofluoride, which is dense and granular, usually forms at once, but precipitation may not be complete for 30 to 40 minutes. Stirring and cooling helps, but it should not be cooled below 15° C. lest lead chloride crystallize out. Other lead salts, as the sulfate and phosphate, may also precipitate. Filter and wash three times with cold water that is saturated with lead chlorofluoride and then twice with cold water. The results are only slightly lower if all washing is done with water.

Rinse as much of the precipitate as possible back into the beaker, place it under the funnel, and pour through the filter 20 or 30 cc. of hot 25 per cent nitric acid to dissolve the lead chlorofluoride, then wash with water. A little heat and stirring may be necessary for solution, but care should be taken not to heat enough to expel any chlorine. If there is much lead chlorofluoride it may not all dissolve, but this is not necessary unless lead sulfate is also present. Much of this would interfere later, so the lead chlorofluoride should all be dissolved and the lead sulfate filtered off. Some lead sulfate will dissolve, but it does no harm. Much care should be taken after washing the lead chlorofluoride that no chlorine is introduced from fumes, beaker, funnel, or the nitric acid used.

To the solution add enough silver nitrate to precipitate all chlorine, stir hard, filter, and wash.

The next step is to determine the amount of chlorine present. This can be accomplished in several ways, depending on the appliances available and the preference of the chemist. A reliable and convenient method, which most chemists would probably prefer, is to add an excess of standard solution of silver nitrate, stir to coagulate the silver chloride, and filter; determine the remaining silver nitrate by the well-known Volhard volumetric method, in which the silver nitrate is titrated with a standard solution of ammonium or potassium thiocyanate, using ferric nitrate or sulfate as an indicator. Deducting the silver nitrate found from the amount added gives the amount that has combined with the chlorine and is also equivalent to the fluorine. If decinormal solutions are used each cubic centimeter of silver nitrate precipitated by the chlorine of lead chlorofluoride is equivalent to 0.0019 gram fluorine.

Another method, which is quite reliable and fairly convenient for any one having a rotating electrolytic machine, is to dissolve the lead chlorofluoride in dilute nitric acid as before, precipitate the chlorine with silver nitrate, which need not be a standard solution, filter off the silver chloride, wash well, and dissolve in a minimum amount of potassium cyanide and precipitate the silver by electrolysis. This is best done in a volume of about 150 cc. and electrolyzing for about an hour at 0.2 ampere. The weight of silver times 0.176 equals the weight of fluorine. The silver can also be determined by a fire assay, making a small correction for slag and cupellation losses.

Accuracy of Method

To prove the accuracy of the method and to test the reliability under various conditions, a good many tests were made, some of which are given. Except where stated otherwise, the determinations were made as directed in the regular method, being finished by the electrolysis of the silver cyanide solution, and weighing the deposited silver.

The volumetric determination of chlorine was not a part of the original procedure, having been suggested after most of the experimental work was completed. However, enough work was afterwards done with this method to prove that it is fully as accurate as the electrolytic procedure. Six samples were run in duplicate by both methods; the results were practically the same, the maximum difference being 0.0010 gram and the average difference 0.0002 gram.

In making these tests the first requirement was a soluble salt of fluorine having a definite composition, to be used as a standard. Potassium fluoride was first tried, but was unsuitable because of the difficulty in preparing a normal salt; it is also somewhat hygroscopic. Sodium fluoride has neither of these defects and proved to be a very good salt for the purpose. It was made from C. P. sodium carbonate by adding an excess of C. P. hydrofluoric acid in a platinum dish, evaporating dry, and then heating just enough to decompose the acid fluoride and leave the normal salt. The purity of this was checked by changing known amounts of it to normal sulfate and weighing. It was tested for chlorine but only a trace was found.

Chlorine Required to Precipitate PbClF

The first test made was to determine the amount of chlorine required when precipitating lead chlorofluoride. An excess is certainly necessary but too much will cause lead chloride to precipitate. It seemed probable that the ratio of chlorine to fluorine in lead chlorofluoride might not remain exactly constant if precipitated in presence of varying quantities of chlorine. It is obvious that the amount of chlorine in the solution cannot be kept at any definite concentration because varying amounts will be removed from solution by precipitating as lead chlorofluoride. The quantity, of course, depends on the fluorine present. However, the amount so removed will generally not be large enough to affect the concentration appreciably.

In this experiment hydrochloric acid of 1.19 specific gravity was used. Nitric acid, sodium carbonate, etc., were used as in a regular determination. The results are given in Table I.

Table I

Fluorine present, 0.0454 gram

HCl used Drops	Fluorine found Gram
10	0.0452
15	0.0452
20	0.0456
25	0.0464
30	0.0474

The experiment was repeated with quite similar results. From this it may be seen that when fluorine is precipitated in presence of a considerable amount of chlorine a slight excess of this will be found in the lead precipitate. However, if only moderate quantities of chlorine are present a small variation will not affect the result enough to impair seriously the accuracy of the assay. For most work about 16 drops seem to be a satisfactory amount, but for high-grade material 20 to 24 drops may be better.

It was found that in order to form a precipitate of lead chloride as much as 60 to 70 drops of hydrochloric acid had to be used, but when considerable sodium nitrate is also present, as it must be when a carbonate fusion is made, somewhat less would cause precipitation. A precipitate of lead chloride can hardly be mistaken for lead chlorofluoride, for the crystals of the former are considerably larger and more brilliant and will readily dissolve on warming.

Time for Complete Precipitation of PbClF

Tests were next undertaken to determine the length of time needed for the lead chlorofluoride to stand in order to insure complete precipitation. The temperature of each solution was approximately 25° C. The solutions were stirred occasionally.

Table II

Fluorine present, 0.0227 gram

No.	Time of standing Minutes	Fluorine found Gram
1	5	0.0218
2	15	0.0225
3	30	0.0228
4	60	0.0230
5	120	0.0229

These results indicate that standing an hour before filtering is sufficient. Possibly for very small amounts a longer time might be better.

Effect of Varying Amount of Fluorine

Table III shows the recovery when working with varying amounts of fluorine. Sodium fluoride was weighed into beakers containing 5 grams of sodium carbonate dissolved in 200 cc. of water. Hydrochloric and nitric acids were then added and the determination was finished as usual.

Table III

	FLUORINE			FLUORINE	
No.	Present Gram	Found Gram	No.	Present Gram	Found Gram
1	0.0009	0.0006	6	0.0454	0.0462
2	0.0023	0.0020	7	0.0454	0.0463
3	0.0045	0.0044	8	0.1362	0.1350
4	0.0045	0.0048	9	0.1362	0.1374
5	0.0113	0.0119	10	0.1816	0.1786

When but little fluorine is present the results are a little low, while with larger amounts they are slightly high. On high-grade samples the results are apt to be erratic.

Wagner and Ross,[4] who made some rather extensive tests on various methods for determining fluorine, report similar results when using Starck's method, in which the lead chlorofluoride is weighed. They consider that the high results were caused by adsorption of silica. Probably a different explanation would have to be sought in this case for even if the silica were adsorbed it should not affect the amount of chlorine present in the precipitate.

The determination of fluorine in minerals that require a fusion, such as fluorspar, cannot be made quite so accurately as it can on soluble fluorides, because of the difficulty of getting the fluorine completely in solution. Hillebrand[2] refers to this difficulty and to the necessity of making a refusion of the residue to recover the remaining fluorine. This increases the accuracy, but the results are still not quite so good as those from soluble fluorides.

Table IV gives the results of tests made to determine the recovery of fluorine from varying amounts of fluorspar. The material used was prepared from a very pure crystal of the natural mineral. On the last seven tests, which contained the larger amounts of fluorine, refusions were made on the residues.

It will be seen that when only a small amount of fluorine is present the loss is not appreciable but when more is present it may amount to considerable, especially if the residue is not retreated.

Table IV

	FLUORINE			
No.	Present Gram	Found Gram	Fluorine from refusion Gram	Total fluorine recovered Gram
1	0.0010	0.0011	....	....
2	0.0020	0.0018	....	....
3	0.0050	0.0046	....	....
4	0.0100	0.0098	....	....
5	0.0250	0.0253	....	....
6	0.0250	0.0239	....	....
7	0.0500	0.0485	....	....
8	0.0500	0.0486	0.0006	0.0492
9	0.1000	0.0988	0.0004	0.0992
10	0.1000	0.0974	0.0010	0.0984
11	0.1500	0.1401	0.0056	0.1457
12	0.1500	0.1451	0.0030	0.1481
13	0.2000	0.1840	0.0136	0.1976
14	0.2000	0.1802	0.0162	0.1964

The refusion adds considerably to the time and labor required, besides increasing very materially the amount of sodium salts in the solution, which is undesirable.

Experiments were undertaken to determine if the fluorine remaining in the residue from the first fusion could be extracted as well by boiling with a small amount of a strong solution of sodium carbonate. The results, given in Table V, indicate that for low- to medium-grade samples boiling with sodium carbonate is quite reliable. For high-grade material a refusion is preferable as somewhat more fluorine is extracted.

Table V

		FLUORINE RECOVERED		
No.	Fluorine in CaF_2 Gram	1st fusion Gram	Refusion Gram	Na_2CO_3 boil Gram
1	0.0488	0.0471	0.0012	....
2	0.0488	0.0472	....	0.0010
3	0.1465	0.1382	0.0062	....
4	0.1465	0.1379	....	0.0050
5	0.1465	0.1385	....	0.0048

Effect of Varying Volume of Solution

The next experiment was to determine the effect of variation in the volume of the solution when precipitating the lead chlorofluoride, results of which are given in Table VI.

Table VI

No.	Fluorine in CaF_2 Gram	Volume of solution Cc.	HCl Drops	Lead acetate Cc.	Fluorine recovered Gram
1	0.0244	150	15	25	0.0246
2	0.0244	300	20	30	0.0242
3	0.0244	400	25	35	0.0234

Effect of Varying Amount of Silica

Table VII shows the effect of a variation in the amount of silica present during fusion. If insufficient is present, too much fluorine remains in the residue. Very little trouble was encountered from gelatinous silica in the acetic acid solution.

Table VII

				FLUORINE FOUND		
No.	Fluorine in CaF_2 Gram	SiO_2 added Gram	Na_2CO_3 used Gram	1st fusion Gram	2nd fusion Gram	Total Gram
1	0.2000	0.7	10	0.1800	0.0168	0.1968
2	0.2000	0.5	8	0.1750	0.0229	0.1979
3	0.2000	0.4	8	0.1617	0.0359	0.1976

Effect of Adding Various Substances

In Table VIII may be found the results of adding various substances, and under a number of different conditions.

Table VIII

				FLUORINE	
No.	SUBSTANCE ADDED	Gram	Source of fluorine	Present Gram	Found Gram
1	FeS_2 not oxidized	0.1	CaF_2	0.0244	0.0204
2	FeS_2 oxidized by air	0.1	CaF_2	0.0244	0.0143
3	FeS_2 oxidized by HgO	0.1	CaF_2	0.0244	0.0120
4	FeS_2 oxidized by KNO_3	0.1	CaF_2	0.0244	0.0198
5	FeS_2 oxidized by Na_2O_2	0.1	CaF_2	0.0244	0.0224
6	FeS_2 oxidized by Na_2O_2	0.1	CaF_2	0.0488	0.0469
7	K_2SO_4 (= 0.0435 gram SO_3)	0.2	NaF	0.0227	0.0223
8	K_2SO_4 (= 0.1087 gram SO_3)	0.5	NaF	0.0227	0.0221
9	$Na_2HPO_4.12H_2O$ (= 0.02 gram P_2O_5)	0.101	NaF	0.0227	0.0229
10	$Na_2HPO_4.12H_2O$ (= 0.05 gram P_2O_5)	0.252	NaF	0.0227	0.0236
11	$Na_2HPO_4.12H_2O$ (= 0.10 gram P_2O_5)	0.504	NaF	0.0227	0.0272
12	$PbCO_3$	0.3	CaF_2	0.0244	0.0248
13	$PbCO_3$	0.3	CaF_2	0.0244	0.0237
14	ZnO	0.1	CaF_2	0.0244	0.0234

The most striking feature of this series is the effect of sulfides, which cause a loss of fluorine. This appears to occur during the oxidization of the sulfur and would probably occur in any method in which a fusion is used. When sulfur is added in the form of a sulfate the loss is very much less and is probably from a different cause. No entirely satisfactory method was found to eliminate this trouble. The least loss appears to occur when just enough sodium peroxide is added to the flux to oxidize the sulfide.

Phosphorus pentoxide when present is precipitated in the acetic solution by the lead acetate. This will dissolve in the nitric acid added to dissolve the lead chlorofluoride, and it might reasonably be expected not to interfere with the determination. The fact that it does so to some extent is probably due to the fact that when lead phosphate precipitates in presence of chlorine it carries with it some lead chloride (the same as the mineral pyromorphite), which causes results to be somewhat too high.

Apparently the presence of lead and zinc has little effect on the result.

Chemistry of Wood[1]

VIII—Further Studies of Sapwood and Heartwood

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

U. S. Forest Products Laboratory, Madison, Wis.

The present paper represents a continuation of a previous study of the chemistry of sapwood and heartwood[2] to determine whether any additional generalizations can be made in grouping hardwoods and softwoods on the basis of chemical differences between sapwood and heartwood. The methods of analysis are identical with those used in former experiments of this series.[3] The determinations were made in duplicate, and the average of each pair of determinations is shown in the accompanying table.

Discussion of Results

The results confirm the conclusions stated in the sixth paper[2] of this series, to the effect that softwoods form a single group having high relative amounts of extractives in the heartwood. Also, with only one exception, the softwoods here reported exhibit another characteristic in common with those reported in paper VI, in that the high extractives in the heartwood are accompanied by low percentages of lignin and cellulose. In the exceptional case of white spruce the lignin and cellulose content is approximately the same in sapwood and heartwood. The hardwoods, also in accord with the findings of the earlier paper,[2] are distributed between two groups having high relative amounts of extractives in the sapwood and heartwood, respectively.

The acetic acid obtained by acid hydrolysis is uniformly higher in the sapwood than in the heartwood of both hardwoods and softwoods.

By the results here reported more species have been fitted into the scheme of classification advanced in the sixth paper of the series. Whether additional groups of softwoods exist is a question that can be answered only after a larger number of species have been analyzed. Combining results for the hardwoods listed in the sixth and the present paper, it is seen that Group A (with high extractives in the sapwood)

Analyses of Sapwood and Heartwood of Some American Woods
(Results in percentage of oven-dry (105° C.) samples)

				Solubility in										In Cellulose				
Species	Sample	Moisture	Ash	Cold water	Hot water	Ether	1% NaOH	Acetic acid	Methoxyl	Pentosan	Methyl pentosan	Cellulose	Lignin	Pentosan	Methyl pentosan	Alpha	Beta	Gamma
Hemlock:																		
Sapwood	219	6.39	0.37	1.16	2.28	0.34	10.93	1.83	4.95	8.79	3.59	54.76	31.82	5.32	2.04	45.39	33.85	20.76
Heartwood	220	6.90	0.51	4.12	5.36	0.70	15.01	1.73	5.36	9.06	2.76	52.83	30.30	4.37	4.31	48.17	22.66	29.17
Redwood:																		
Sapwood	231	6.69	0.27	4.28	6.50	1.95	15.54	0.99	5.28	10.04	2.80	46.35	33.98	6.62	1.07	52.20	35.05	12.75
Heartwood	232	7.53	0.14	10.53	14.39	2.07	25.85	0.48	5.11	8.86	2.08	41.54	31.82	6.54	1.46	56.18	31.02	12.80
White spruce:																		
Sapwood	500	6.59	0.28	1.54	1.99	....	10.83	1.74	4.11	12.84[a]		59.30	26.71	8.54[a]		...	...	...
Heartwood	501	5.37	0.26	2.38	3.31	....	11.83	1.64	4.37	13.63[a]		59.45	26.93	9.47[a]		...	...	...
Red alder:																		
Sapwood	201	5.02	0.32	4.28	5.35	1.03	20.16	3.53	5.29	20.81	1.13	56.36	25.97	20.98	0.72	42.02	35.53	22.45
Heartwood	202	6.82	0.45	3.97	5.21	1.39	20.01	3.50	5.33	21.03	1.20	57.41	26.68	20.80	0.82	49.19	29.82	20.99
Sapwood	203	5.77	0.24	3.49	4.75	0.90	20.25	3.69	5.27	20.76	1.47	57.28	26.64	19.30	1.13	40.93	37.44	21.65
Heartwood	204	3.70	0.23	3.31	4.67	0.77	21.61	3.40	5.26	20.51	1.91	57.75	26.94	20.23	1.79	38.67	38.50	22.83
Red mulberry:																		
Sapwood	223	5.82	1.03	9.12	12.56	1.75	29.08	4.07	4.24	21.16	1.86	47.80	22.76	22.81	1.21	75.51	15.80	8.69
Heartwood	224	5.82	0.48	7.08	10.20	1.71	27.58	3.63	4.47	20.28	1.68	48.56	24.00	23.03	2.04	57.72	25.77	16.51
Sugar maple:																		
Sapwood	225	5.80	0.31	3.05	4.15	0.58	19.21	3.79	5.78	20.50	2.06	56.29	25.37	20.18	1.48	63.82	3.49	22.69
Heartwood	226	5.71	0.66	2.19	3.15	0.58	19.18	2.23	5.88	20.42	1.56	56.47	27.37	20.57	1.38	66.83	12.62	20.55
Catalpa:																		
Sapwood	227	3.95	0.53	6.55	9.37	0.93	28.11	4.59	4.83	22.75[a]		55.79	21.06	22.83[a]		72.25	18.35	9.40
Heartwood	228	3.90	0.34	6.46	9.24	0.71	28.56	4.37	4.38	22.54[a]		55.99	20.90	22.86[a]		71.41	17.86	10.73
Red oak:																		
Sapwood	229	4.14	0.14	3.57	6.13	1.24	22.04	5.08	6.05	21.88	1.87	53.98	24.47	22.46	1.69	70.18	13.22	16.60
Heartwood	230	3.78	0.18	5.74	8.29	1.23	24.10	3.67	5.98	20.95	1.69	53.58	23.12	22.68	2.00	72.13	12.10	15.77
Locust:																		
Sapwood	221	5.08	0.55	3.08	3.91	0.74	17.64	3.16	4.20	21.64	1.99	60.31	23.22	21.70	0.00	65.96	24.46	9.58
Heartwood	222	6.55	0.14	8.29	11.04	1.70	25.72	2.86	4.54	20.77	1.70	52.04	23.11	24.78	0.00	44.97	38.93	16.60
Eucalyptus:																		
Sapwood	215	4.98	0.41	2.01	3.10	0.38	15.72	3.14	6.45	20.47	1.13	55.29	26.60	19.16	0.82	43.77	41.77	14.46
Heartwood	216	7.07	0.18	8.07	10.43	1.09	23.85	2.25	5.82	18.81	1.10	51.08	27.53	18.88	1.31	59.08	26.97	13.95
Sapwood	217	4.64	0.42	2.22	3.33	0.45	17.54	2.61	6.43	21.31	1.33	56.67	28.21	18.51	1.33	36.39	45.68	17.93
Heartwood	218	6.58	0.26	6.69	10.23	0.72	25.12	1.84	6.06	19.86	1.33	52.31	30.00	19.08	1.22	47.21	36.84	15.95

[a] Combined pentosans and methyl pentosans reported as pentosans.

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[1] Presented before the Division of Cellulose Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923. Received January 28, 1926.

[2] This Journal, **15**, 1055 (1923).

[3] *Ibid.*, **14**, 1050 (1922).

includes white ash, pignut hickory, red alder, red mulberry, sugar maple, and catalpa; Group B (with high extractives in the heartwood) includes yellow poplar, yellow birch, white oak, red oak, locust, and eucalyptus.

Conclusions

1—In softwoods the water, ether, and alkali extracts are higher in the heartwood than in the sapwood, and the cellulose and lignin are correspondingly lower in the heartwood (except in white spruce, in which cellulose-lignin content is approximately the same in the two bands of growth).

2—On the basis of water, ether, and alkali extractives, hardwoods are divided into two groups: (*a*) those with high extractives in the sapwood, and (*b*) those with high extractives in the heartwood. The former have low cellulose in the sapwood, the latter low cellulose in the heartwood.

3—Acetic acid by hydrolysis is higher in the sapwood than in the heartwood of all the woods.

Industry Finds a New Tool—X-Rays

By D. H. Killeffer, Associate Editor

The discovery of the X-ray has opened the door to vast stores of industrially important facts. Already it is revolutionizing the metallurgical industry and as our knowledge of X-ray technic increases new wonders are being revealed in other fields.

INDUSTRY usually looks, to its own hurt, with disdainful indifference upon the newest advances of what it considers "high brow" pure science until its operations are revolutionized by the application of some newly discovered principle or method. Each year, each month, almost each day, sees some advance of pure science put into the overalls of industry. The scientific oddity of yesterday becomes the foundation of tomorrow's practice. Science and scientists repeatedly prove the truth of that and industry teems with illuminating illustrations. Yet it is one thing to prove and to illustrate, and quite another to realize in practice a point of view so obviously axiomatic. So it has been with X-rays.

How distant seem the experiments of Roentgen leading to the discovery of a new kind of radiation, which for want of a better name he called X-rays, from the hardening of steel, the sealing of an envelope, the multitudes of catalytic reactions, and the vastly important problems of corrosion. Yet in the scientific toy of a very few years ago—few of us fail to recall with what awe and wonder we first beheld the bones in our own hands in the fluoroscopic screen of a side show—has been found the key to vast stores of industrially important facts about diverse kinds of matter. Already our theories of the hardening of steel and the ductility of metals have undergone a complete revolution and our preconceived ideas of colloids, crystalloids, and amorphous matter are being materially modified as the result of the use of this new tool. Only a beginning has been made and no one's imagination is yet equal to the task of foreseeing the possible end. Already industry has taken profitable cognizance of this apparently purely theoretical advance and has made it its own.

Properties of X-Rays

X-rays were discovered by their ability to penetrate matter opaque to visible light. They could be made to affect a photographic plate through the human body and to reveal in bold outline its parts of different opacity to them. Bones, fractures, and foreign materials of any kind within the human body could be discerned as if the surrounding tissues were rendered invisible. One might even imagine that the tellers of fairy tales foresaw such a thing when they conferred upon their characters the ability to render themselves invisible. This phenomenon of selective absorption of X-rays has become of the greatest practical importance, particularly in the field of metallurgy where minute flaws in castings may have serious effects on their usefulness. Rays of greater and greater penetrative power have finally made it quite an ordinary thing for an investigator to outline accurately voids one or two millimeters in dimensions in blocks of steel a decimeter thick without altering the steel in the least. It is thus possible to detect minute flaws in the interior of castings whose value would have to be destroyed to render any other method of test applicable.

Study of Castings

Industry moves forward as fast as it is supplied with the minutiae of its operation and no faster. For instance, the widening use of very high pressure superheated steam for power and of high-temperature and high-pressure cracking processes in refining petroleum has brought into prominence defects in cast-steel valves and pipe fittings not hitherto important. The casting of pipe fittings from steel has been considered a comparatively simple thing for the reason that strains in use have seldom been sufficiently great to give them a real test. However, under the severity of the newer types of service even very slight flaws soon showed themselves and often led to disastrous results. To correct this, careful studies of all parts of such castings by X-ray methods were made and casting practice improved to correct the defects found. The result has been a vast improvement in the quality and service of the finished fittings. Such methods had previously been applied with great success to the casting of cannon, their carriages, and other gross objects cast of steel.

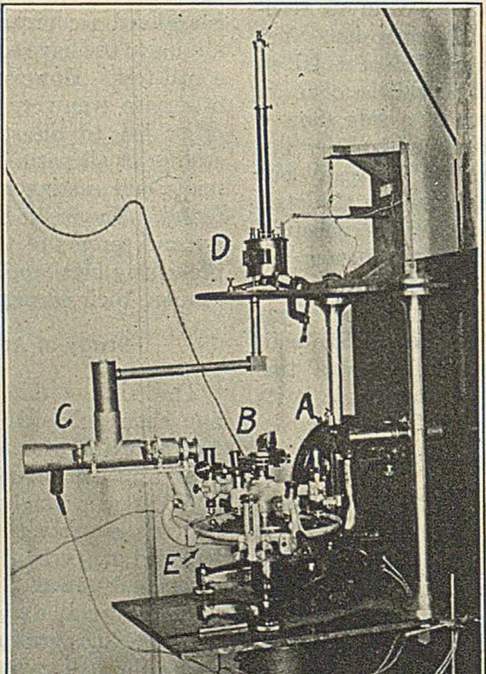
Study of Atomic and Molecular Structure

This kind of thing has proved very valuable to industry, but when compared with the possibilities in the study of so vast a field as atomic and molecular structure its importance is greatly overshadowed. In 1912, Von Laue in Germany and Bragg in England began the publication of a series of papers dealing with the ability of X-rays to be deflected, reflected or, perhaps better, refracted when passed through crystal substances. Basing their experiments on the analogy to the diffraction spectra produced by passing visible light through fine gratings, these investigators passed X-ray beams through crystals in various orientations and found that the deflected beams showed distinct maxima and minima as the crystal was rotated and that the angles of deflection were quite definitely properties of the internal structure of the crystal. Other investigators were attracted to the field thus opened, and fact has been piled upon fact until in the hands of a skilled worker this technic will now reveal far more about the infinitesimal structure of matter than was ever conceived possible before—quite as much, indeed, as had been imagined. So accurately can the spacings of atoms in a crystal be determined in this way that we may almost say that they are rendered visible and tangible.

Two general types of technic have been developed. The Laue method depends upon the diffraction of a pinhole beam of X-rays of various wave lengths by a single crystal variously oriented, and the powder method utilizes a monochromatic beam—i. e., a beam of rays as nearly as possible of a single wave length—from a slit and crystal powder in which there is opportunity for particles in every possible orientation. The deflected beam may be recorded on a photographic film for subsequent accurate measurement or it may be passed into a goniometric ionization chamber by which the angular deflection is easily determined. Many modifications of these methods are in use varying in detail and slightly in principle.

The use of diffraction patterns and the data deduced from them is far more interesting for the moment. Metals ordinarily crystallize in the cubic system, which is the simplest of all and hence, so far, the most carefully studied. From an X-ray diffraction pattern it is easily possible to determine the exact positions in space of each of the atoms making up metallic crystals. Each metal has its own characteristic spacings and thus it is possible easily to determine what metals are present in a mixture. If two metals are present as such, the diffraction pattern will show two series of characteristic lines, but if they should be in a completely homogeneous solid solution only one series of lines would show. In the simplest cases these lines are intermediate between the positions of those of the metals composing the solution. From the relative displacement of these lines it is easy to reach a close approximation to the constitution of the mixture. If the two metals form an intermetallic compound, an entirely new set of lines characteristic of that compound will be found. By no other method is it possible to determine conclusively whether compounds between the metals exist or not.

This technic is leading to very important facts as to the nature of alloys and the reasons for their changes in properties with changes in composition. For instance, it has been found that ductile metals, generally, crystallize in the form of what are called face-centered cubes; that is, each unit cube is made up of atoms arranged at the corners of the cube and in the centers of its faces. This unit structure is repeated throughout the crystal. Nonductile metals, generally, are to be found in the form of body-centered cubes; that is, the unit cube consists of atoms arranged at the corners and the center of a cube. It is the change between these two forms, and others somewhat different that are present in some metals, that appears to cause the remarkable properties of some alloys. Each atom appears to possess a very definite space characteristic of its own and if a small amount of a larger atom is introduced into the space lattice of a smaller one, rigidity results, whereas ductility is apparently increased if a smaller atom is introduced into the lattice of a larger one. Where intermetallic compounds exist the properties of the alloy are fundamentally altered but their presence is easily detected.



Goniometric Ionization Chamber for X-Ray Measurements

A beam of X-rays from the slit *A* is directed on the crystal *B* and is diffracted into the ionization chamber *C*. Its ionizing effect is measured by the galvanometer *D* and the angular diffraction is read off from the scale *E*.

Industrial Chemical Applications at M. I. T.

The metallurgical applications of X-ray technic are attracting the attention of many investigators, but for our present purposes more strictly chemical applications are probably more interesting. They are certainly newer, as many of the investigations to be mentioned below are still unfinished. For information about them the writer is indebted to the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology, the pioneer in industrial chemical applications of this newest of research tools. Work upon them is being vigorously prosecuted in this institution, where complete resources for this type of thing are available. Commercial materials, in particular, are being subjected to X-ray investigation and the bearing of their infinitesimal structures on their practical properties determined.

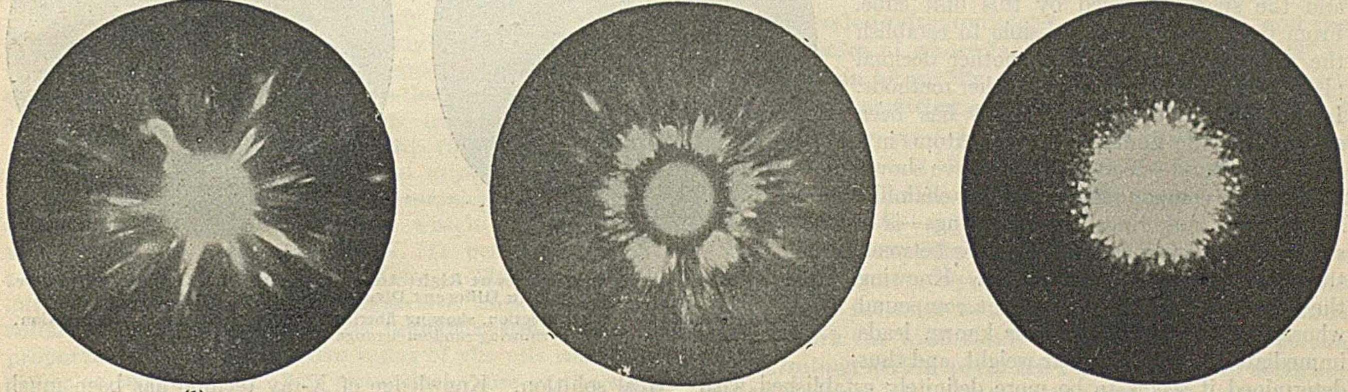
The existence of strains in metals and of preferred orientations of crystals that might lead to lines and planes of cleavage are far more readily detected by examination of the infinitesimal structure than by any other means yet devised. A steel casting whose structure appears to be perfectly uniform under the microscope may show decided strain lines when subjected to X-ray examination. In this way it is expected to reach methods of casting and annealing of a perfection hitherto impossible, and perhaps on this account it will be possible so to improve metal parts as to make considerable savings in the amount of metal necessary to give a particular strength and perform a particular task.

That the internal structure of metals is intimately related to their strength characteristics is obvious, and thus the more accurate determination of this by means of X-rays in respect to new alloys and the perfection of methods of handling them to get desired results is of extreme importance. Studies of such alloys as duralumin and others are being carefully made with the idea of preventing such disasters as that to the Shenandoah a few months ago.

The abrasion resistance of metals has hitherto not been related to any other property, and it is hoped that the new technic will reveal practical relations of this property to infinitesimal structure.

Evidence has already been deduced that the resistance of metals to corrosion is definitely a function of its composition, and further investigation is leading farther toward the goal of highly corrosion-resistant metal. In the case of copper tubing, for instance, used for liquid ammonia in a refrigerating plant, of two pieces of tubing showing the same composition within the limits of error of chemical analysis, one stood up for a satisfactory period with no apparent corrosion, while the other failed very quickly. X-ray analysis showed that the one that failed contained copper oxide apparently included in the crystal lattice, while the satisfactory piece had its oxide in segregations. In a similar manner it is possible to detect the lines characteristic of iron oxide in extremely low concentration in the metal.

On the other hand, if one has a mixture such as sodium chloride and potassium bromide which it is quite impossible to analyze by other methods, it is quite easy to say whether the bromine is combined with the sodium or with the potassium or with both, for the dimensions characteristic of the atoms involved are easily measured. Of course, no one would ordinarily care which way such a mixture was made up, but there are similar analytical dilemmas that are important and may be resolved in such a manner. For instance, there are the complex silicates known under the generic name of "asbestos." The use of asbestos as a support for the platinum catalyst in the contact mass in a sulfuric plant makes it essential that the particular material used stand up under the conditions there met. At present there is no way known of determining this except that of trial and error. Now it is easily possible to decide just what crystal sorts are present in any specimen of asbestos by means of the X-ray and, once having determined the preferred substances which a good asbestos should contain, it will not be difficult to state beforehand on the basis of X-ray evidence whether or not a particular sample is good.


(1) (2) (3)

Cast Steel

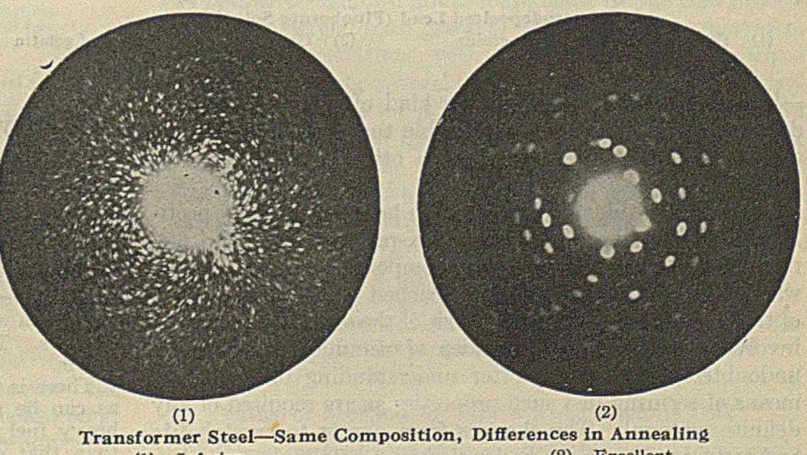
(1) As cast. Large crystals, preferred orientation and strain. (2) Normal commercial annealing practice. (3) Ideal structure, small equiaxial crystals with no orientation or strain.

Studies of the characteristics of catalysts are leading to a much better understanding of the form in which these are effective and to methods of getting them into such effective states.

Just as the strain in metals and their heat treatment or lack of it may be easily determined by X-ray crystallographic methods, so may the changes in structural properties of other materials under varying conditions be accurately measured. For instance, it has been long known that the repeated burning of plaster of Paris after setting results in a gradual progressive reduction in its setting strength. Studies are now in progress looking to the discovery of just why this occurs and already results seem to justify hope that the mystery may be solved, by a knowledge of the infinitesimal structure of the material. In a similar way it has been found that an optimum particle size exists for the plasticity of lime cements and mortars, which if taken into account may lead to extremely valuable results in the use of such materials.

The determination of ultimate particle size in any material may be readily accomplished by X-ray methods and leads to hitherto unexpected practical results. Plaster of Paris and lime cements have been mentioned. In a similar way it has been possible to determine with great accuracy the extent of polymerization of a number of materials ordinarily considered amorphous. The polymerization of certain resins can be measured in this way. It is hoped, too, that these methods may throw some light upon the phenomenon of adhesion, about which we now know practically nothing. The possibility that glue and certain other colloidal substances may reveal that their property of adhesion is due not to their lack of structure, but rather to their possible ability to accept the structure of the materials to which they are applied, is being carefully investigated by X-ray technic and with considerable hope of success. Already it has been possible to outline a definite structure for cellulose which probably will have important bearings on a number of diverse important affairs.

So far this discussion of chemical applications of X-rays has considered work completed or in progress at the Massachusetts Institute of Technology. It is not to be presumed from this that no other laboratories are similarly engaged. Both abroad and in America numbers of able investigators are carrying on fundamental researches following the new technic, but in general these are by nature more purely scientific than essentially industrial in their motives.

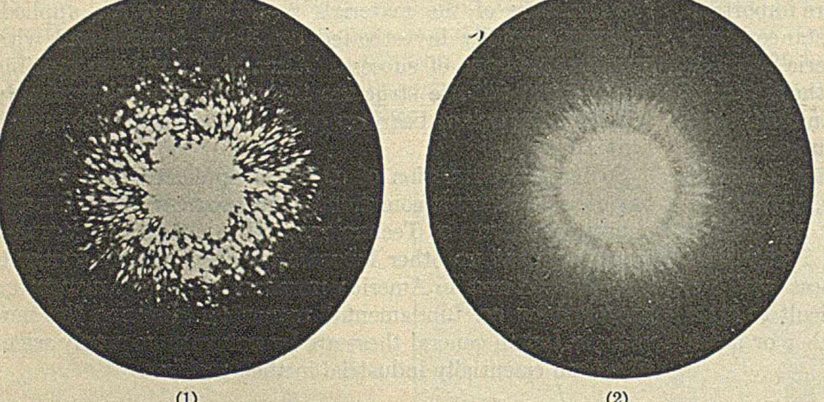

(1) (2)

Transformer Steel—Same Composition, Differences in Annealing

(1) Inferior (2) Excellent

Other Applications

The X-ray has given us a means for measurement of a number of physical constants with extreme accuracy and with much greater facility than other methods allowed. When tungsten is to be drawn into filaments for electric lamps of such extreme fineness that their diameters fall well within the limit of error of ordinary measuring methods, the density of the metal becomes of extreme importance in permitting measured lengths of filament to be weighed and its diameter calculated. Application of the methods of X-ray crystallography made it possible to determine the number of atoms in a unit cube of the metal, and the space occupied by this unit cube. From these data it was possible to establish the density of tungsten to another decimal place beyond that possible by other methods. In an entirely unrelated field it has been shown that the number of carbon atoms in a chain compound—X-ray methods have shown that chain compounds are actual chainlike spirals and not rings or near rings—is a straight-line function of the distance between the crystal planes of the substance. Knowing the number of carbon atoms in a compound whose empirical composition is known leads immediately to its molecular weight, and thus determined it seems to be more definitely established with less chance of error than by ordinary cryoscopic methods, particularly where solvents are likely to exert polymerizing or dissociating effects. Such complicated materials as fats, greases, and waxes and their derivatives which can be obtained in crystalline form—the crystalline form is essential—lend themselves readily to this kind of molecular weight determination. It is not improbable that a modification of this method may be applicable to other families of compounds.

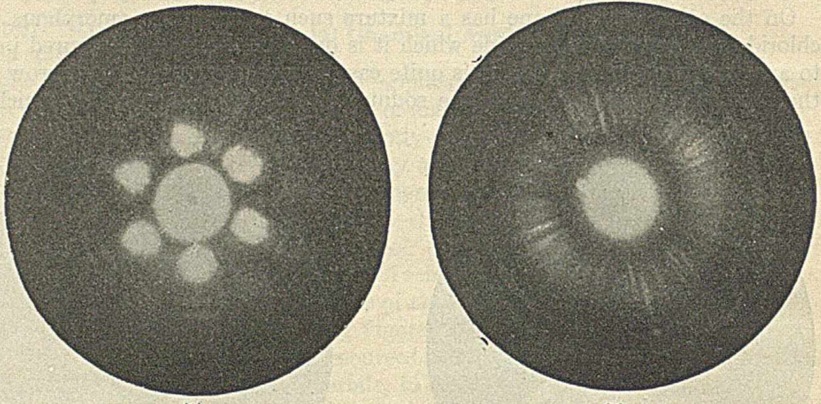

(1) (2)

Electrodeposited Lead (Fluoborate Solution)

(1) Poor deposit—large loose grains (2) Good deposit with trace of gelatin

The ceramic industry may hope to have many of its problems solved by the application of X-ray methods. No one now knows what the preferred compounds are in ceramic ware and usually good mixes are reached only by the method of trial and error. Crystal analysis of the various compounds involved in the different grades of ceramic products will undoubtedly lead to a better understanding of ways and means of securing just such properties as are required of any definite material. The changes from quartz to crystobalite and to tridymite cannot be studied in any other way, and as the changes here involved are exceedingly important in refractories such studies may be expected to lead to much improvement in this field.

We may expect application of X-ray methods to reveal facts of vast importance in fields yet untouched as a wider understanding of the subject is reached. At the present time work in this field is confined to a very few investigators, of whom the majority are devoting themselves to metallurgical problems as these offer the greatest hope of quick and practical solution. Knowledge of X-ray technic has been much more widespread among physicists than among chemists and chemical engineers, who have been rather awed, perhaps, by methods many consider too high-brow and too foreign to their field for practical application. From the few instances cited here it should be evident that an intimate knowledge of physical quantities as measured by X-rays and of the methods by which these are reached are neither so far from practical matters nor so difficult to grasp as has been generally supposed. We may all await with much interest and confidence the revelation of new wonders to which they may be expected to lead.


(1) (2)

Rolled Copper Bar, Two Pictures at Right Angles Showing Nonuniform Structure in Different Directions

(1) Perpendicular to rolling direction, showing fibering. (2) Parallel to rolling direction, showing random arrangement.

Acknowledgment

Many workers in the X-ray field have been kind enough to assist the author of this article with information about their work. The illustrations accompanying it have been provided by George L. Clark, of the Massachusetts Institute of Technology, to whom the author's particular thanks are due.

Quality of Motor Gasoline Remains Uniform

The quality of motor gasoline sold in the United States in the past few years has undergone very little change, the Bureau of Mines finds as the result of special semiannual surveys made in the larger cities, in each of which about 150 representative samples were examined.

Whether gasoline in the future will have approximately the same characteristics that it has had since 1920 will depend largely on whether it will be desirable that it have those characteristics. This question is bound up in automotive developments.

There is a distinct advantage in using a motor fuel as heavy as can be utilized by the engine, as the energy content of a heavy fuel in terms of B. t. u. per gallon is, in general, larger than that of a lighter fuel. Motor fuels are sold almost exclusively in this country on a volume basis. Another factor is that the demand for gasoline is enormous, and everything which can serve as motor fuel will, sooner or later, have to be so used. When crude oil and gasoline are as plentiful as they have been recently, there is no incentive to the most economical utilization; yet refining equipment used by progressive refiners is constantly being improved, and is measurably superior to what it was even five years ago.

Determination of the Concentration of Liquid Soaps by the Immersion Refractometer[1]

By L. F. Hoyt and Alma Verwiebe

Research Dept., Larkin Co., Inc., Buffalo, N. Y.

The refractive index of aqueous potash soap solutions made from a variety of thoroughly saponified vegetable oils, or their fatty acids, is directly proportional to the total solids content. The Zeiss immersion refractometer can be used to measure the refractive index of such soap solutions, and consequently their total solids content, with a high degree of accuracy up to the limit of the instrument, which corresponds to approximately 20 to 22 per cent solids. The Zeiss immersion refractometer can be easily read to 0.1 degree, which corresponds to about 0.025 per cent soap solids. (1 per cent potash-coconut oil soap solids = 4.0° Zeiss.) The slope of the curves obtained by plotting refractive indices *vs.* total solids of the different aqueous potash soaps is directly proportional to the refractive index of the oils measured either at 20° or 40° C. The numerical value of the slope ranges from 1.425×10^{-3}, for coconut oil, to 1.561×10^{-3}, for linseed oil.

The total solids content of a potash liquid soap whose Zeiss immersion refractometer reading at 20.0° C. and the refractive index of whose fat or oil stock at 20° or 40° C. are known can be readily and accurately calculated with the aid of the equation of Curve II or III of Figure 2 and the formula $y = ax + k$, in which y is the observed Zeiss refractive index, a is the slope calculated from the equation of Curve II or III, and k is 1.33299, the refractive index of water at 20.0° C.

The method described is particularly adapted to the routine or control analysis, during manufacture, of liquid soaps whose fat base is known and available. In such control work the total solids content of liquid soaps can be determined within a very few minutes with an accuracy of 0.05 per cent or approximately 1/400 of the total solids present in a 20 per cent liquid soap.

……

Liquid soaps commonly consist of a solution of a cold-made potash soap of a vegetable oil, frequently coconut oil, in soft or distilled water. They vary in solids content from about 10 per cent to 30 per cent or more and almost invariably contain the glycerol which is normal to a cold-process soap. Some grades of liquid soap, particularly those of higher soap content intended for use as shampoo soaps, often contain an appreciable percentage of alcohol.

The analysis for total solids in such soaps is ordinarily made by drying a weighed sample with or without the addition of alcohol at 105° C. for several hours. Exact determination of the total solids is both slow and uncertain, since long-continued drying results in a gradual loss of glycerol. Table I shows the relationship between the total solids and glycerol of an aqueous potash-coconut oil liquid soap, samples of which were dried at 105° C. for varying lengths of time.

Table I—Potash-Coconut Oil Liquid Soap

Time of drying Hours	Volatile at 105° C. Per cent	Glycerol in dried sample Per cent	Indicated per cent of anhydrous, glycerol-free soap
0	...	2.10	...
2	78.89	2.07	19.04
3	79.70	2.07	18.23
5	79.74	2.08	18.18
7	79.75	2.07	18.18
8	79.88	2.05	18.07
20	...	1.76	...
48	...	1.46	...

The results of Table I indicate that a 2-hour drying of a liquid soap sample (without addition of alcohol) is too brief to remove all of the moisture and that such samples can be heated up to about 8 hours at 105° C. before loss of glycerol begins to be appreciable.

The true soap content of a liquid soap can be accurately determined by the American Chemical Society's method for total anhydrous soap,[2] but this method is time-consuming. The method used in some laboratories—i. e., of decomposing a soap with acid, weighing the fatty acids, and calculating the anhydrous glycerol-free soap—while giving satisfactory results with some soaps, yields inaccurate results on a soap made wholly or largely from coconut oil, for the reason that an indeterminate amount of the soluble and volatile fatty acids of coconut oil is lost in decomposing and drying.

A rapid and accurate method for determining the soap solids content of liquid soaps of known fat composition was accordingly sought, for control purposes in manufacture.

Method

It was found that the Zeiss immersion refractometer could be used for this purpose. The range of this instrument—i. e., of the older type, with one prism only—is from 1.32736 to 1.36640 and it is applicable to the determination of the soap solids content of wholly aqueous liquid soaps up to a concentration of 20 to 22 per cent.

Note—It should be emphasized that all the determinations herein described were made on aqueous solutions of various potash soaps of commercial oils. The immersion refractometer method is not directly applicable to the analysis of liquid soaps containing alcohol.

A potash-coconut oil liquid soap, made by the cold process from a commercial soap grade of coconut oil, was diluted to different concentrations with distilled water. The total solids content of the several dilutions was determined by drying 2-gram samples for 8 hours at 105° C. The refractive index was determined by the Zeiss immersion refractometer at exactly 20° C. The values of total solids plotted against refractive index give the curve shown in Figure 1.

All the points are thus seen to be on a straight line, whose equation is $y = ax + k$, in which,

y = refractive index at 20° C.
x = per cent soap solids
k = 1.33299 (14.5° Z.), the refractive index of distilled water at 20.0° C. on Zeiss instrument
$a = 1.426 \times 10^{-3}$

Value of Method for Soaps from Various Oils

To determine the value of this method for liquid soaps made from other oils, liquid soaps were made up at approximately 20 per cent concentration and adjusted to a free-alkali content of 0.05 per cent KOH from the thoroughly saponified cold-made potash soaps of cottonseed, corn, olive, and linseed oils and their respective fatty acids, and of coconut oil fatty acids. The total solids content of each of these soaps

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[1] Presented before the joint meeting of the Eastern New York, Cornell, Syracuse, Rochester, and Western New York Sections of the American Chemical Society, Niagara Falls, N. Y., January 29 and 30, 1926.

[2] This Journal, 14, 1160 (1922).

was determined by 8-hour drying at 105° C., and five readings taken on each of two separate portions of the ten samples with the Zeiss immersion refractometer at 20.0° C. The soap solids content of these several soaps was computed from their refractive indices and the coconut oil curve of Figure 1.

The calculated total solids were found to differ from the actual value by an amount which is a function of the refractive index of the original oil or fatty acid.

As would be expected, this difference is greater in the soaps made from fatty acids since the glycerol content of the soaps made from the oils themselves lowers the refractive index of the soap solids, although the higher the refractive index of the oil the greater the observed differences.

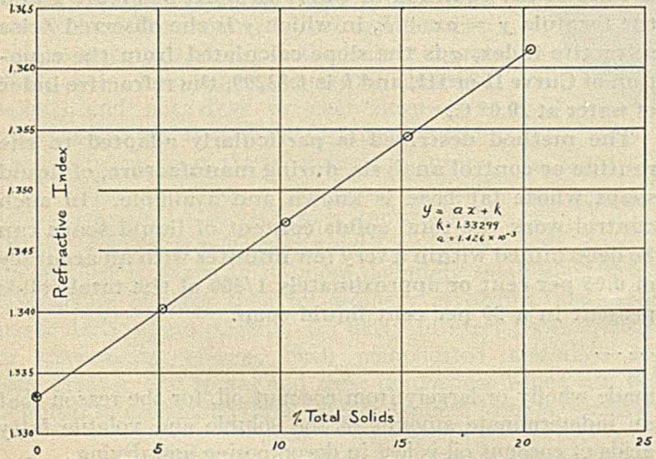

Figure 1—Potash–Coconut Oil Liquid Soap

Portions of each of the ten liquid soaps except the coconut oil soap were diluted with an exactly equal weight of distilled water, thus giving samples of one-half of the soap content of the originals. The refractive index of these dilute soaps was determined at 20.0° C. The values so obtained in every case were found by plotting to fall exactly on the respective straight lines drawn between $n_D^{20} = 1.33299$ (0 per cent solids, n_D^{20} of distilled water) and the n_D^{20} points of the original concentrations, thus proving that in all of these liquid soaps refractive index is directly proportional to concentration. The slope of each curve was calculated and plotted against the refractive index of the oils and fatty acids determined at 40° and 20° C., with results shown in Figure 2. The equations of these curves all have the general formula:

$$y = bx + c$$

in which y = slope of a potash liquid soap refractive index–concentration curve
x = refractive index of corresponding oil or mixed fatty acids

b and c are constants as follows:
Curve I, for fatty acids at 40° C.: $b = 0.00538$, $c = -0.006411$
Curve II, for oils at 40° C.: $b = 0.00562$, $c = -0.006726$
Curve III, for oils at 20° C.: $b = 0.00569$, $c = -0.006754$

Figure 2 shows that the slope of the curve of concentration versus refractive index of the potash liquid soaps of various oils is proportional to the refractive index of these oils whether measured at 40° or 20° C. In the case of corresponding fatty acids (Curve I) results are not so consistent. It was not possible directly to measure the refractive index of these fatty acids at 20° C. for comparative purposes.

To determine further the validity of the curves of Figure 2, the following test was made. The refractive index of an edible tallow was determined on the Abbé refractometer at 40° C. The tallow was then saponified with potash and a liquid soap made therefrom by dissolving the soap in distilled water. The refractive index of the aqueous liquid soap was determined with the Zeiss immersion refractometer at 20.0° C. The slope of a tallow potash liquid soap was calculated from the equation of Curve II and the concentration of the soap solution calculated. The following data were obtained:

Refractive index of tallow at 40° C.	1.4592
Refractive index of tallow-potash liquid soap at 20° C.	1.36214
Slope of tallow-potash liquid soap curve	0.001473

Then, since $y = ax + k$, and k is 1.33299, x, the concentration of the liquid soap, is 19.78 per cent total solids. A determination of the total solids of this liquid soap was then made by direct drying at 105° C., the results being 19.85 per cent for 4-hour drying and 19.81 per cent for 8-hour drying.

Effects of Excess Free Alkali and Excess Free Fat

The effects of both excess free alkali and excess unsaponified free fat on the accuracy of the results by this method have been investigated, with results shown in Table II.

Table II

Sample	COCONUT OIL SOAP	Refractive index	PER CENT TOTAL SOLIDS From curve	Direct drying
1	0.05 per cent free alkali, KOH	1.36173	20.11	20.04
2	0.27 per cent free alkali, KOH	1.36193	20.30	19.84
3	0.71 per cent free fat	1.36246	20.62	20.80

It is obvious that neither free fat nor free alkali would occur in a finished liquid soap made by the careful saponification of coconut oil of known saponification value with alkali of known strength.

FREE ALKALI—To a well-saponified potash–coconut oil liquid soap containing 0.05 per cent free alkali as KOH and 20.11 per cent total solids by the refractometer was added a sufficient quantity of a 20.1 per cent solution of pure potassium hydroxide in distilled water—i. e., a solution of the same moisture content as the liquid soap itself—to increase the free-alkali content of the mixture to 0.27 per cent as KOH while the water content remained unchanged. Determination of the total solids content by the immersion refractometer and the coconut oil curve showed a definitely higher amount than was actually present (Sample 2, Table II).

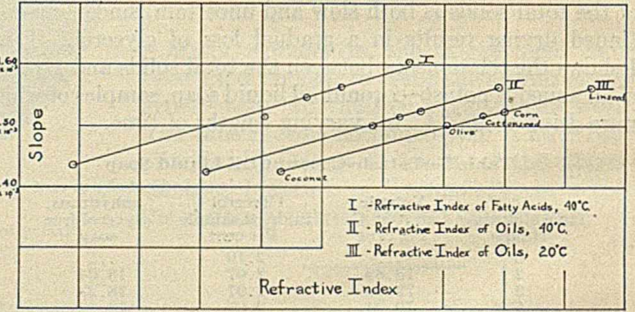

Figure 2—Slope of Soap Concentration Curves *vs.* Refractive Index of Oils and Fatty Acids

FREE FAT—A special potash–coconut oil liquid soap was made up using an insufficient amount of potash for complete saponification, so that the finished liquid soap (Sample 3, Table II) contained 0.71 per cent unsaponified coconut oil (equivalent to about 5 per cent of the coconut oil used). Determination of the total solids content by the refractometer gave a result definitely lower than obtained by direct drying, but it should be noted that this finished liquid soap revealed the fact that it was incompletely saponified by remaining persistently turbid.

Note—It does not follow that a turbid liquid soap necessarily contains free fat, since persistent turbidity would also be caused by dissolving the soap base in hard, or incompletely softened, water.

There is no legitimate excuse, of course, for any liquid soap containing as much free alkali as 0.27 per cent KOH or as much free fat as 0.7 per cent being on the market.

The Oxygen Bomb Method for Sulfur Determinations[1]

By M. J. Bradley, R. M. Corbin, and T. W. Floyd

UNIVERSITY OF ILLINOIS, URBANA, ILL.

THE quantitative determination of sulfur in petroleum and coal distillation products is difficult and tedious, and considerable care is necessary in order to obtain accurate results. The analytical procedures published may be roughly grouped into three classes: (*a*) dry fusion methods, (*b*) oxidation with liquid reagents, and (*c*) combustion methods. Any one method cannot be used successfully for all the various fractions of these hydrocarbons. However, in the combustion group for light oils the lamp method,[2] and for the heavier fractions the oxygen bomb method,[3] have been recommended. When checking the lamp method on a known organic sulfur compound, dissolved in light oil, the results were found to be low, even when such added refinements as washing the lamp with amyl acetate and finally burning the wick were employed. In the usual oxygen bomb method the light fractions oxidize with explosive violence and the heavy tars and residues are difficult to get completely burned. The following research was undertaken in order to overcome some of these difficulties and to modify the methods, if possible, so that the light and heavy fractions might be safely analyzed by the oxygen bomb method.

Theoretical

The oxidation of sulfur dioxide to trioxide, on account of its technical importance, has been studied by several investigators, and from the results of Bodenstein and Pohl[4] the writers have calculated the degree of dissociation of SO_3 to $SO_2 + {}^1/_2 O_2$ at various temperatures and 1 atmosphere pressure. The graph of these results shows that dissociation commences around 450° C. and is complete at 1000° C.

From the equation

$$SO_2 + {}^1/_2\, O_2 \rightleftarrows SO_3$$

the following expression for the dissociation constant,

$$\left(\frac{P_{SO_2}\sqrt{P_{1/2\,O_2}}}{P_{SO_3}} = K_P\right)$$

may be obtained. Since this dissociation takes place with an increase in volume, pressure will tend to inhibit it. Also a large excess of oxygen over that required for the reaction will tend to decrease the dissociation of sulfur trioxide at a given temperature. For example, at 525° C. and 1 atmosphere pressure, sulfur trioxide was found by calculation to be 11.6 per cent dissociated. By increasing the partial pressure of oxygen to 20 atmospheres the degree of dissociation was decreased to around 4 per cent. However, the equilibrium is not affected by change in pressure due to the addition of inert gases, such as obtained as combustion products in calorimetric determinations. The equilibrium is affected, however, by the increase in temperature accompanying such a combustion and, as shown by the foregoing calculations, no sulfur trioxide would exist above 1000° C. In calorimetric determinations on coal and oil the maximum temperature reached is well above 1000° C., so that no sulfur trioxide would exist until after the combustion was completed and the bomb cooling down. It is possible to cool the bomb so rapidly that even at the optimum temperature there would not be sufficient time for all the sulfur dioxide to be oxidized to trioxide unless some activating catalysts were present. These assumptions were verified in the following experimental results.

Experimental

The determinations were made in an Illium oxygen bomb,[5] fitted with a double valve attachment which made it possible to release the gases from the bomb very slowly, after combustion, so that they could be bubbled through a wash train of solution. The procedure was similar to that recommended for calorimetric determinations, except in some instances a few cubic centimeters of 10 per cent sodium carbonate solution were placed in the bottom of the bomb to neutralize the acids formed in the combustion.

The analysis of small amounts of sulfur dioxide and trioxide in the presence of each other entails considerable difficulty. The procedure finally adopted was to cool the bomb slowly after the combustion was completed and then release the gases slowly through a 10 per cent sodium carbonate solution in the wash train. The last traces of gas were obtained by applying suction to the wash train and at the same time admitting a spray of distilled water into the bomb. The absorption solution plus the bomb and train washings were diluted to 500 cc. in a volumetric flask and aliquot portions used for analysis. In some cases a smaller volumetric flask was employed. Sulfur dioxide was determined by titrating the alkaline solution with 0.002 *N* iodine solution, using starch paste as an indicator. Sulfur trioxide was determined by making the alkaline solution acid with hydrochloric acid, boiling to expel any sulfur dioxide, and finally precipitating the SO_4 as barium sulfate with a few cubic centimeters of hot barium chloride solution. The resulting precipitate was digested for a couple of hours, filtered, washed, ignited, and weighed as barium sulfate. Total sulfur was determined on the undiluted solution by treating with a few drops of bromine water to oxidize any sulfite to sulfate, taking to boiling to expel the excess bromine, and finally precipitating the barium sulfate as described.

Pure Sulfur

Several combustions were made with pure sulfur, using 0.25-gram samples and 20 atmospheres initial oxygen pressure. No constant results were obtained, the amount of sulfur dioxide varying from 14.5 to 43 per cent. If the bomb was placed in hot water and allowed to stand more than one-half hour before releasing the pressure the percentage of sulfur dioxide was considerably lowered. Practically all the sulfur dioxide remaining was liberated when the pressure was released from the bomb. Increasing the initial oxygen pressure up to 40 atmospheres did not materially increase the amount of sulfur trioxide formed. The amount of sulfur in the $SO_3 + SO_2$ equaled the sulfur used, indicating complete combustion.

In order to provide a gaseous atmosphere in the bomb, which might increase the rate at which sulfur dioxide oxi-

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[1] Received December 19, 1925.

[2] *Bur. Mines, Tech. Paper* 8.

[3] *Ibid.*, **298**, p. 51.

[4] *Z. Elektrochem.*, **11**, 373 (1905).

[5] Bradley, Rosecrans, and Corbin, THIS JOURNAL, **18**, 307 (1926).

dizes to trioxide, 0.04 gram of ammonium nitrate was added to the 0.25 gram sulfur and combustions were run at 20 atmospheres oxygen pressure. This would provide a nitrogen content approximately 5 per cent of the weight of sulfur, and under these conditions the resulting SO_2 content varied from 12 to 20 per cent.

Several determinations were made using 0.25 gram sulfur plus 0.04 gram ammonium nitrate plus 0.5 gram compressed benzoic acid at 20 atmospheres initial oxygen pressure. No sulfur dioxide could be detected in the resulting products of combustion. In determinations on sulfur and benzoic acid without the addition of ammonium nitrate, mixtures of sulfur trioxide and dioxide resulted. Therefore, it seemed necessary to have nitrogen oxides and water vapor both formed in the combustions in order to get complete oxidation of sulfur dioxide to trioxide in these determinations.

In some determinations the ammonium nitrate was omitted and 5 atmospheres of commercial nitrogen were added with the 20 atmospheres of oxygen to the bomb. Complete oxidation of the sulfur resulted; however, when determinations were being made upon heavy oils the ammonium nitrate was preferable as complete combustion was more often obtained when ammonium nitrate was added. It was found that 0.011 gram of nitrogen was oxidized if calculated as nitric acid, when 0.5 gram of compressed benzoic acid was burned in the bomb with 20 atmospheres of oxygen and 5 atmospheres of nitrogen. Increasing the initial oxygen pressure by 5-atmosphere intervals up to 50 atmospheres did not materially increase the amount of nitrogen oxidized.

Bituminous Coal

Several sulfur determinations were made on an Illinois coal of the following analysis:

	Per cent
Volatile matter	44.60
Fixed carbon	43.95
Ash	11.45
Sulfur	4.88
Total carbon	74.8
B. t. u.	12,435
Unit B. t. u.	14,370

The addition of ammonium nitrate to the charge did not increase the amount of sulfur determined, and with this coal no sulfur dioxide could be detected in the gases when released, regardless of the rate at which the bomb cooled down after combustion. Apparently, the nitrogen content of coal furnishes more than sufficient nitrogen oxides and the hydrogen compounds enough vapor to oxidize rapidly the sulfur dioxide to trioxide as the bomb cools down. When 1 gram of coal was oxidized under these conditions the maximum temperature developed was far in excess of that required completely to dissociate the sulfur trioxide. Allowing a heat loss of 50 per cent by the time the maximum temperature was attained, the maximum temperature was approximately 1800° C. These results are reported in another paper.[5]

Crude Petroleum

An Illinois crude petroleum of the following partial analysis:

Specific gravity	0.850 at 15.5° C.
Unsaturated	26 per cent
Sulfur	0.30 per cent
B. t. u.	18,883

was used in determinations with and without the addition of ammonium nitrate. When ammonium nitrate was added the sulfur found was approximately 0.10 per cent greater than when it was not added. Moreover, better combustions were obtained when ammonium nitrate was added to the charge.

A great many sulfur determinations were made on a heavy Mexican crude petroleum with a sulfur content of 4.94 per cent. In the dry fusion methods from 25 to 50 per cent of the sulfur was lost. The sodium peroxide method in all instances gave slightly higher results than the oxygen bomb without the addition of ammonium nitrate. However, when ammonium nitrate was added to the charge in sufficient quantities to give a nitrogen content of 5 per cent of the sulfur present, the amount of sulfur determined was from 0.20 to 0.30 per cent higher than without ammonium nitrate and no sulfur dioxide was detected in the escaping gaseous products of combustion. Under these conditions the peroxide and oxygen bomb methods checked very closely on this high sulfur oil.

It was also found that by the addition of ammonium nitrate or potassium chlorate to a charge of asphalt, low-temperature tar, or coal tar, complete combustion was more generally obtained.

Light Oils

Crude benzene (light oil) in weights varying from 0.68 to 1.55 grams were sealed in thin-walled glass bulbs and these placed in an Illium crucible in such a way that the hot fuse wire caused the bulb to break and liberate the sample. The sulfur content checked at 0.41 per cent when either a few drops of fuming nitric acid were placed in the bomb or some ammonium nitrate was added in the crucible. However, without these it was impossible to get check results, as much sulfur was liberated in the gases as sulfur dioxide, although theoretically there was more than sufficient nitrogen in the air in the bomb at the start to furnish the oxides deemed necessary to catalyze the oxidation to sulfur trioxide.

Samples of commercial kerosene in weights up to 1.25 grams were oxidized by methods similar to the benzene experiments, but the results were so variable that larger samples were desirable. Accordingly, a thick-walled Pyrex bulb was filled with 2.25 grams of the sample and after being provided with a small ring of naphthalene (approximately 0.1 gram) around the capillary tube, it was placed in the crucible in the bomb so that the fuse wire ignited the naphthalene, breaking the bulb. The sample oxidized with explosive violence, smashing the 0 to 200-atmosphere Bourdon gage which was attached.

This part of the work is being continued and other methods of controlled oxidation for light oils give promise of making the oxygen bomb available for sulfur determinations on these lower boiling fractions.

Summary of Results

1—Pure sulfur when burned in an oxygen bomb forms SO_2 and SO_3 in varying amounts. Increasing the initial oxygen pressure in the bomb up to 50 atmospheres does not materially affect the equilibrium. The bulk of the SO_2 escapes when the pressure is released from the bomb.

2—The addition of compounds which form water vapor and nitrogen oxides during combustion to the sulfur charge provides an activating atmosphere in the bomb, under which the sulfur is completely oxidized to sulfur trioxide.

3—The addition of ammonium nitrate to a charge of heavy tars, pitches, and asphalts accelerates combustion and also promotes the sulfur trioxide formation.

4—Sulfur determinations upon coals, crude petroleums, crude benzene, and kerosene were satisfactorily carried out by the oxygen bomb method.

Production of manufactured nonmetallic mineral products in Canada in 1925 reached a value of $115,587,316, an increase of nearly $4,500,000 over 1924 and the highest since 1920.

Chemical Reactions in the Gas Producer[1]

By John A. Goff

DEPARTMENT OF MECHANICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA, ILL.

It is of interest to know just how much information relative to the chemical reactions taking place in the gas producer can be obtained from the direct application of the laws of chemical equilibrium to the problem. With certain assumptions as to the manner of operation of the producer and the character of the fuel used, the following data can be obtained for any given ratio of steam to air in the incoming blast: (*a*) the temperature at which the producer will operate continuously, (*b*) the composition of the resulting producer gas, and (*c*) the thermal efficiency of the producer. The ratio of steam to air in the blast which will give maximum thermal efficiency can also be determined.

Incidental to the main purpose of the analysis, it is shown that although five chemical reactions are possible in the formation of producer gas, only three of these are independent from the standpoint of chemical equilibrium, and as far as the final results are concerned, only three need be considered. Choosing three convenient to our purpose, it is then possible to determine the amount of fuel burned according to each of these three reactions for any given ratio of steam to air in the blast.

THE direct application of the laws of chemical equilibrium to the problem of the gas producer yields information of interest and of a certain amount of importance. Neuman[2] and Husson[3] have discussed the equilibria involved from a theoretical standpoint, but the methods employed by them are essentially different from those of the present article which, it is believed, possess certain advantages of simplicity and clearness.

Assumptions

It may first be assumed that the producer gas will contain no free oxygen. The experiments of Haslam, Entwistle, and Gladding[4] show that when a mixture of air and water vapor enters a gas producer the free oxygen in this mixture is completely consumed in the first 3 or 4 inches of the fuel bed above the ashes, and that carbon dioxide alone is formed according to the reaction

$$C + O_2 = CO_2 \qquad (A)$$

Furthermore, it may be assumed that, together with Reaction A, only four more are possible—namely,

$$\begin{aligned} C + H_2O &= H_2 + CO & (B)\\ C + 2H_2O &= 2H_2 + CO_2 & (C)\\ C + CO_2 &= 2CO & (D)\\ CO + H_2O &= CO_2 + H_2 & (E) \end{aligned}$$

In using these five reaction equations it is assumed that the fuel fired to the gas producer is pure carbon free from hydrocarbons such as methane, or at least that not any of these hydrocarbons exist as such in the final gas mixture.

Again, it is assumed that the final gas mixture is in chemical equilibrium with the carbon in a certain zone in which the temperature can be regarded as uniform. Specifically, let it be supposed that surrounding the fuel bed of carbon at the temperature T (° F. abs.) there is a certain mixture of gases also at the temperature T. According to the previous assumptions this gas mixture will contain only CO, CO_2, H_2, H_2O, and N_2, the free oxygen in the air introduced having disappeared completely. Hence the following schedule can be written:

$$\begin{aligned} CO &= x \text{ mols} & H_2O &= u \text{ mols}\\ CO_2 &= y & N_2 &= v\\ H_2 &= z \end{aligned}$$

There are certain relations between these quantities, which state that the total number of molecules of N_2, H_2, and O_2 are constant. Supposing that the mixture of air and water vapor entering the producer contains 4.8 mols of air plus σ mols of water vapor, the desired relations are

$$\begin{aligned} v &= 3.8\\ u + z &= \sigma\\ {}^1/_2x + y + {}^1/_2u &= 1 + {}^1/_2\sigma \end{aligned}$$

and the above schedule becomes

$$\begin{aligned} CO &= x\\ CO_2 &= y\\ H_2 &= x + 2y - 2\\ H_2O &= \sigma - (x + 2y - 2)\\ N_2 &= 3.8 \end{aligned}$$

The amount of water vapor, σ, introduced with the air can be fixed quite arbitrarily, but if too much is introduced the temperature of the gas producer will steadily decrease, while if too little, it will rise. If it be stipulated that just enough water vapor, σ, be introduced with the air to maintain a constant temperature T, then σ can be expressed linearly in terms of x and y, the coefficients being functions of the temperature. This is possible because, no matter what final gas mixture is assumed, it can be thought of as the result of three reactions. That is, suppose that 1 mol of carbon is oxidized by Reaction A, the result is

$$\begin{aligned} CO &= 0 & H_2O &= \sigma\\ CO_2 &= 1 & N_2 &= 3.8\\ H_2 &= 0 \end{aligned}$$

Then let x mols of carbon be reduced by Reaction B, changing the gas composition to

$$\begin{aligned} CO &= x & H_2O &= \sigma - x\\ CO_2 &= 1 & N_2 &= 3.8\\ H_2 &= x \end{aligned}$$

and finally let $(y - 1)$ mols of carbon be reduced by Reaction C, thus making

$$\begin{aligned} CO &= x\\ CO_2 &= y\\ H_2 &= x + 2y - 2\\ H_2O &= \sigma - (x + 2y - 2)\\ N_2 &= 3.8 \end{aligned}$$

which is the general composition.

The heats of reaction of the Reactions A, B, and C can be found from data given by Goodenough and Felbeck,[5] as follows:

$$\begin{aligned} C + O_2 &= CO_2 + 174{,}290 \text{ B. t. u.} & (A)\\ C + H_2O &= H_2 + CO - 49{,}460 \text{ B. t. u.} & (B)\\ C + 2H_2O &= 2H_2 + CO_2 - 31{,}370 \text{ B. t. u.} & (C) \end{aligned}$$

To be sure these quantities depend on the temperature, but that variation is small and can be neglected. The total heat evolved in forming the gas mixture to be studied is then

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[1] Received October 22, 1925.

[2] *Stahl u. Eisen*, **33**, 394 (1913).

[3] *Rev. ind. minèrale*, **2**, 373 (1922).

[4] THIS JOURNAL, **17**, 586 (1925).

[5] University of Illinois Expt. Sta., *Bull.* **139**.

$$Q_e = 174{,}290 - 49{,}460\,x - 31{,}370\,(y - 1)$$

Now this heat is assumed to be used up in three ways: (*a*) to heat σ mols of water at temperature $t = 62°$ F. to the boiling point corresponding to atmospheric pressure, vaporize it, and raise the temperature of the vapor formed to the temperature T; from data given by Goodenough,[5,6] this amount of heat is found to be given by the expression

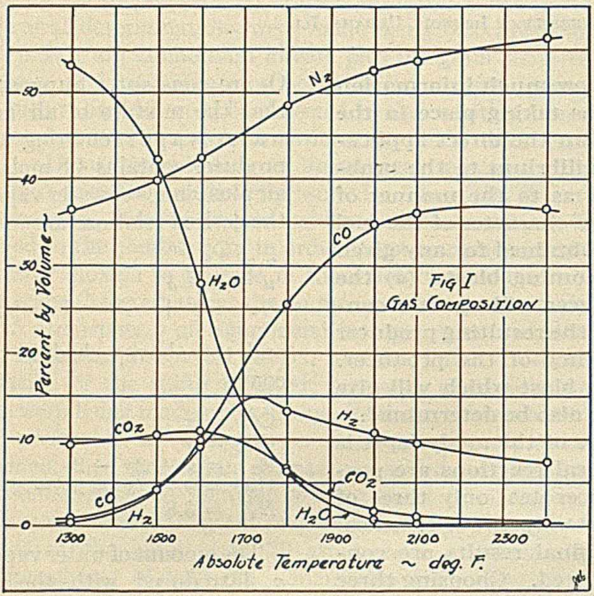
Fig I
Gas Composition

$$Q_a = \sigma(13{,}830 + 9.152\,T)$$

(*b*) to heat 4.8 mols of air from $t = 62°$ F. to the temperature T, the heat required being given by the expression

$$Q_b = 4.8 \times 7.221 \times (T - 522)$$
$$Q_b = 34.66\,T - 18{,}090$$

and (*c*) to supply radiation and conduction losses Q_r. This quantity of heat would perhaps be proportional to the temperature under which the gas producer is operated, but for the present discussion will be taken to be zero although to do otherwise would not complicate the problem. A heat balance will be established if

$$Q_e = Q_a + Q_b + Q_r$$

or, with $Q_r = 0$, if

$$174{,}290 - 49{,}460\,x - 31{,}370\,(y - 1) = 13{,}830\,\sigma + 9.152\sigma\,T + 34.66\,T - 18{,}090$$

an equation which expresses σ linearly as follows:

$$\sigma = L - mx - ny$$
$$L = \frac{223{,}750 - 34.66\,T}{13{,}830 + 9.152\,T}$$
$$m = \frac{49{,}460}{13{,}830 + 9.152\,T}$$
$$n = \frac{31{,}370}{13{,}830 + 9.152\,T}$$

Derivation of Equilibrium Equations

We wish now to make use of the assumption that the final gas mixture shall be in chemical equilibrium. For this purpose suppose that the mixture should suffer a change due to one or all of the Reactions B, C, D, E. In particular, let

dx_b mols of carbon be gasified by Reaction B
dx_c mols of carbon be gasified by Reaction C
dx_d mols of carbon be gasified by Reaction D
dx_e mols of CO enter into Reaction E

Then the number of mols of H_2 formed will be

$$dn_{H_2} = dx_b + 2dx_c + dx_e$$

and similarly

$$dn_{CO_2} = dx_c - dx_d + dx_e$$
$$dn_{H_2O} = -\,dx_b - 2dx_c - dx_e$$
$$dn_C = -\,dx_b - dx_c - dx_d$$
$$dn_{CO} = dx_b + 2dx_d - dx_e$$

Now it can be shown that a criterion for chemical equilibrium in a mixture of gases is the vanishing of the sum $\Sigma f_i dn_i$. In this sum the *dn*'s have the meaning already assigned to them, and the *f*'s are certain functions of the temperature and the partial pressures. If this sum be formed and the terms rearranged, the following expression results:

$$\begin{aligned}\Sigma f_i dn_i &= dx_b(f_{H_2} + f_{CO} - f_{H_2O} - f_C)\\ &+ dx_c(2f_{H_2} + f_{CO_2} - 2f_{H_2O} - f_C)\\ &+ dx_d(2f_{CO} - f_{CO_2} - f_C)\\ &+ dx_e(f_{H_2} - f_{CO} + f_{CO_2} - f_{H_2O})\end{aligned}$$
$$\text{or } \Sigma f_i dn_i = C_1 dx_b + C_2 dx_c + C_3 dx_d + C_4 dx_e$$

But in order to have stable equilibrium the above expression must vanish for all possible values of the *dx*'s and hence each coefficient must vanish separately. However, these coefficients are connected by such relations as

$$C_2 - C_1 = C_4$$
$$C_2 - C_3 = 2C_4$$
$$C_1 - C_3 = C_4$$

so that, instead of four independent equilibrium conditions, there are but two, for making any two of the coefficients vanish insures the vanishing of the other two. The equilibrium equations most convenient for our purposes are the following:

$$2f_{CO} - f_{CO_2} - f_C = 0 \qquad (1)$$
$$f_{H_2} + f_{CO_2} - f_{CO} - f_{H_2O} = 0 \qquad (2)$$

The function *f* is defined by the equation

$$f = i - Ts$$

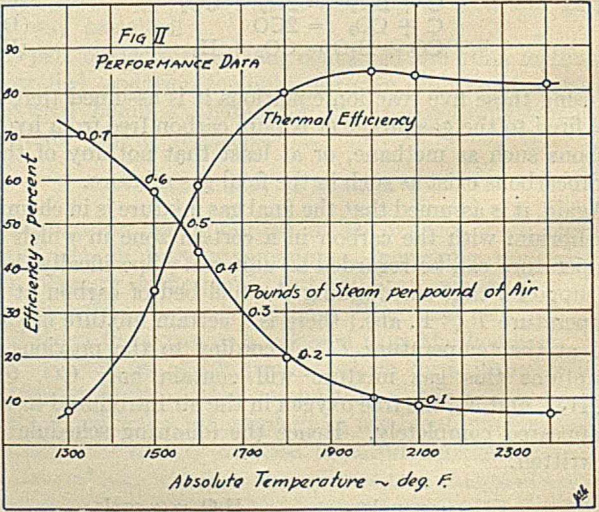
Fig II
Performance Data

where *i* is the thermal potential $(u + pv)$ of the gas in B. t. u. per mol, T is the absolute temperature in degrees Fahrenheit, and *s* the entropy per mol which is expressible in terms of the specific heat, γ, of the gas at constant pressure and the partial pressure, p, of the gas as follows:

$$s = \int \frac{\gamma}{T}\,dT + s_0 - R\log_e p$$

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[6] "Properties of Steam and Ammonia."

s_0 and R being constants. When the expressions for the various f's are substituted in (1) and (2) these lead to the ordinary forms of the equilibrium equations—namely,

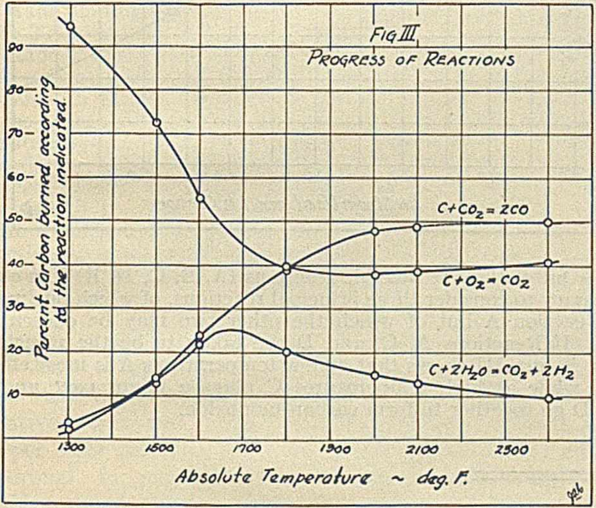
$$\frac{p_{CO}^2}{p_{CO_2}} = A_c \qquad (1)$$

$$\frac{p_{H_2} \cdot p_{CO_2}}{p_{CO} \cdot p_{H_2O}} = A_w \qquad (2)$$

wherein A_c and A_w are functions of the temperature T, which can be computed from data given by Goodenough and Felbeck[5,7] the values of which are tabulated in Table I.

Table I—Values of Log A_c and Log A_w Computed from Previous Data[5,7]

Temp. ° F. abs.	1300	1500	1600	1800	2000	2100	2400
Log A_c	$\bar{4}.7295$	$\bar{2}.3056$	$\bar{2}.9433$	0.0023	0.8414	1.1997	2.0849
Log A_w	$\bar{1}.0108$	$\bar{1}.4007$	$\bar{1}.5552$	$\bar{1}.8074$	0.0018	0.0828	0.2778



Each of the partial pressures is expressible in terms of x and y, since the composition of the gas mixture is now

$$\begin{aligned} CO &= x \\ CO_2 &= y \\ H_2 &= x + 2y - 2 \\ H_2O &= L - mx - ny - (x + 2y - 2) \\ N_2 &= 3.8 \\ \hline \text{Total} &= L - mx - ny + x + y + 3.8 \end{aligned}$$

The usual procedure of suppressing the partial pressure of the carbon has been followed which amounts to assuming that the solid carbon exerts the total pressure, P. Assuming further that the total pressure P is one atmosphere ($P = 1$), the equilibrium equations can be written

$$\frac{x^2}{y\,(L - mx - ny + 3.8 + x + y)} = A_c \qquad (1)$$

$$\frac{y\,(x + 2y - 2)}{x\,(L - mx - ny - x - 2y + 2)} = A_w \qquad (2)$$

and these equations are to be solved simultaneously for values of x and y. The method used is to choose a particular temperature $T = T_0$ and compute the constants L, m, n, A_c, and A_w; then by trial to find a value of $y = y_0$ which yields the same value of x_0 from either of Equations 1 and 2. Having found x_0 and y_0, the gas composition in mols can be written down and then reduced to a percentage composition. Also σ can be computed.

Other related data are presented in Tables II to V and Figures I and II.

Table II—Values of the Coefficients L, m, and n as Computed from Equations Already Deduced

Temp. ° F. Abs.	1300	1500	1600	1800	2000	2100	2400
L	6.9447	6.2321	5.9103	5.3254	4.8060	4.5676	3.9272
m	1.9223	1.7946	1.7370	1.6323	1.5390	1.4965	1.3815
n	1.2192	1.1382	1.1017	1.0353	0.9763	0.9492	0.8764

Table III—Values of x_0 and y_0 Which Satisfy the Equilibrium Equations

Temp. ° F. Abs.	1300	1500	1600	1800	2000	2100	2400
x_0	0.0758	0.3744	0.8772	2.0022	2.5180	2.5569	2.4795
y_0	0.9840	1.0027	0.9686	0.5162	0.1260	0.0582	0.0075

Table IV—Gas Compositions in Per cent by Volume

Temp. ° F. Abs.	1300	1500	1600	1800	2000	2100	2400
CO	0.72	3.91	9.78	25.50	34.70	36.00	36.55
CO_2	9.37	10.45	10.84	6.58	1.73	0.82	0.09
H_2	0.42	3.96	9.08	13.20	10.60	9.47	7.29
H_2O	53.19	42.05	27.95	6.23	0.52	0.18	0.00+
N_2	36.30	39.63	42.35	48.49	52.45	53.53	56.07
	100	100	100	100	100	100	100

Table V—Miscellaneous Calculations

Temp., ° F. Abs.	1300	1500	1600	1800	2000	2100	2400
Water Vapor Introduced into Gas Producer with Air							
Mols steam per 4.8 mols air (σ)	5.599	4.419	3.320	1.523	0.808	0.686	0.495
Lbs. steam per lb. air (0.13σ)	0.728	0.575	0.432	0.198	0.105	0.089	0.064
Lbs. steam per lb. carbon consumed	7.820	4.670	2.700	0.908	0.459	0.395	0.298
Gas Heating Value at t = 62° F.							
B. t. u. per mol.	1312	8820	21,256	44,640	53,160	53,545	51,968
B. t. u. per cu. ft.	3.45	23.2	55.8	117.0	139.5	140.5	136.5
Efficiency of Gas Producer[a]							
Per cent	7.43	35.48	59.24	79.75	83.66	83.54	81.32

[a] $\dfrac{\text{Heating value in B. t. u. per mol}}{\text{Heating value of carbon in producing 1 mol producer gas}}$

Determination of Amount of Fuel Burned

It was shown that any given possible gas composition consistent with our original assumptions can be looked upon as the result of Reactions A, B, and C taken together, 1 mol of carbon entering A, x mols entering B, and $(y - 1)$ mols entering C. However, with one exception all the values of y found make $(y - 1)$ negative, indicating that Reaction C would have to proceed from right to left. That is, if the three reactions

$$C + O_2 = CO_2 \qquad (A)$$
$$C + H_2O = CO + H_2 \qquad (B)$$
$$C + 2H_2O = CO_2 + 2H_2 \qquad (C)$$

are assumed to be the *only* reactions involved, which is entirely possible, then the last one listed must proceed from right to left with the formation of water vapor, instead of from left to right with the formation of carbon dioxide.

A somewhat better combination consists of the three reactions taken in the following manner: 1 mol of carbon enters Reaction A; $\frac{x + 2y - 2}{2}$ mols of carbon enter Reaction C; and $x/2$ mols Reaction D $-$ $C + CO_2 = 2CO$. The resulting gas composition is the same as before, so that this combination is just as good as the preceding and has the advantage that none of the quantities 1, $\frac{x + 2y - 2}{2}$, and $x/2$ is negative for any temperature considered. The ratio $\frac{1}{x + y}$ will, in this case, represent the fraction of the total carbon which is burned according to Reaction A, $\frac{x + 2y - 2}{2(x + y)}$ that according to Reaction C, and $\frac{x}{2(x + y)}$ that according to D. These results are tabulated in Table VI and exhibited graphically in Figure III.

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[7] See also Lewis and Randall, *J. Am. Chem. Soc.*, **37**, 464 (1915).

Table VI—Distribution of Total Carbon among Three Principal Reactions

	Temp., ° F. Abs.	1300	1500	1600	1800	2000	2100	2400
	REACTION							
A	$C + O_2 = CO_2$	94.3	72.6	54.2	39.7	37.8	38.3	40.3
C	$C + 2H_2O = CO_2 + 2H_2$	2.1	13.6	22.1	20.5	14.6	12.9	9.9
D	$C + CO_2 = 2CO$	3.6	13.8	23.7	39.8	47.6	48.8	49.8
		100	100	100	100	100	100	100

Conclusions

In discussing the results of the present analysis, it is well to restate the assumptions under which it is made:

1—The producer gas contains no free oxygen, it having entirely disappeared according to Reaction A, which is complete at all temperatures considered.

2—The fuel fired to the producer, which is operated continuously, is pure carbon.

3—The producer gas is in chemical equilibrium with the hot carbon at the temperature *T* and under atmospheric pressure.

4—Just enough steam is introduced with the air to maintain a constant temperature.

5—Radiation and conduction losses have been disregarded.

Under these assumptions, we can conclude that:

1—The nitrogen content of the producer gas increases with the temperature because less and less steam is being introduced with the air blast.

2—Above 2100° F. the carbon dioxide and water practically disappear, a statement which has been made by F. Haber.[8]

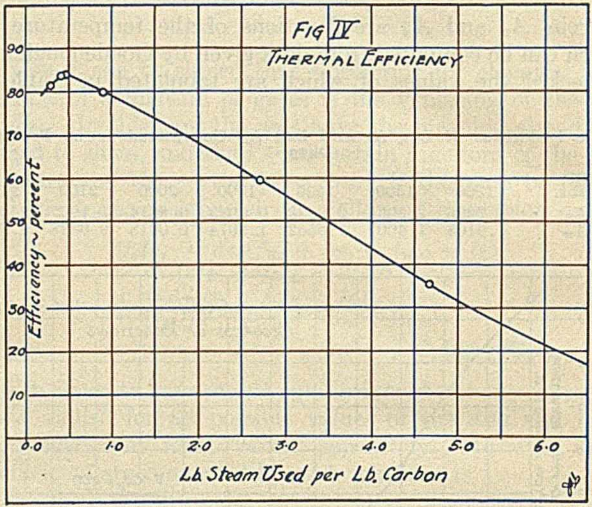
3—If operated at a temperature of 1750° F. a maximum hydrogen content is obtained, but at higher temperatures the hydrogen content drops while the carbon monoxide content rises and remains practically constant.

4—At very low temperatures (1300° F.), the water or steam goes through the producer practically as such and enters but slightly into reduction reactions.

5—The efficiency of the producer increases with the temperature at which it is operated up to 2000° F. and then decreases because the amount of heat carried away by the hot gases leaving the producer increases with the temperature.

6—The amount of steam in the air blast required to maintain a given temperature is less the higher the temperature.

7—For maximum efficiency, under the assumptions made, approximately 0.4 pound of steam per pound of carbon should be used (Figure IV).



8—Out of the five possible reactions (A, B, C, D, E) it is only necessary to consider three principal reactions, of which one must be Reaction A but of which the other two may be chosen at will. If Reactions A, C, and D are taken to be the principal ones, Figure III shows that at low temperatures A is most effective, while at high temperatures C plays a minor part, and A and D go together to form carbon monoxide.

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[8] "Thermodynamics of Technical Gas Reactions," p. 313.

Piperonal in Vanilla Extract[1]

By C. B. Gnadinger

McLaughlin-Gormley-King Co., Minneapolis, Minn.

The use of piperonal (heliotropine) in vanilla extract is largely due to the belief that this substance is a natural constituent of vanilla beans. Krebs[2] called attention to the heliotrope odor of Tahiti beans, while Busse[3] and Göller[4] suspected that both vanillons and Tahiti beans contained piperonal. These opinions, which were based on the odor of the beans, have been given prominence in literature, but it has not been proved that piperonal occurs in any variety of vanilla beans. Wahlbaum[5] concluded that Tahiti vanilla does not contain piperonal.

Little attention has been paid to the use of piperonal as an adulterant of vanilla extract, and it seemed worth while to determine if extracts of known purity made from the different varieties of beans respond to qualitative tests for this compound. The results obtained made it desirable to investigate the composition of vanillons. Vanillons are said to be obtained from the vines of *V. pompona*, *V. guianensis*, and undetermined species.[3] They cannot legally be used in vanilla extract.

Experimental

Extracts of standard strength were prepared from Mexican, Bourbon, South American, Java, and Tahiti beans and from vanillons; the beans were obtained from different sources. These extracts were subjected to the phloroglucinol test and the gallic acid test for piperonal.

The phloroglucinol test was applied in this manner:

Fifty cubic centimeters of extract were de-alcoholized by evaporating spontaneously before a fan to about 40 cc. and transferred to a separatory funnel with water. The solution was extracted once with 50 cc. of ether, and the ether solution was separated, washed three times with 15-cc. portions of 2 per cent sodium hydroxide solution, and once with 15 cc. of water. The ether was then evaporated spontaneously, just to dryness, in a porcelain dish. A few minute crystals of phloroglucinol were added, followed by a few drops of concentrated hydrochloric acid. A deep red color, similar to that produced by vanillin, is formed if piperonal is present.

The Mexican, Bourbon, South American, and Java extracts gave negative results; the Tahiti extracts gave doubtful reactions; and the extracts of vanillons yielded strong positive reactions. Bourbon extract containing 0.005 gram of added piperonal per 100 cc. yielded a strong red color. The first four varieties of beans named apparently do not

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[1] Received January 20, 1926.

[2] *Pharm. Zentralhalle*, **36**, 487 (1895).

[3] *Arb. kais. Gesundh.*, **15**, 107 (1898).

[4] *Pharm. Zentralhalle*, **45**, 192 (1904).

[5] Schimmel & Co., Semiannual Report, October, 1909, p. 142.

contain piperonal. The results obtained with the Tahiti and vanillon extracts were not conclusive, because these beans contain anise aldehyde, which gives an orange to red color with the phloroglucinol reagent.

The gallic acid test was first described by Labat.[6] It consists in heating an alcoholic solution of the material to be examined with sulfuric acid and alcoholic gallic acid solution. A characteristic emerald to blue color is formed if piperonal is present. Although Labat did not apply the test to vanilla, he found that the color reaction could be obtained with a variety of compounds that contain the methylene ether $\left(H_2C\begin{smallmatrix}\diagup O-\\ \diagdown O-\end{smallmatrix}\right)$ group. The writer found that cinnamic and anisic aldehydes, benzaldeyde, vanillin, and coumarin do not yield positive reactions. The test is far more selective than the phloroglucinol test.

One hundred cubic centimeters of the extract were de-alcoholized and extracted with ether and the ether extract was washed as in the phloroglucinol test. The ether solution was then shaken with 30 cc. of 15 per cent sodium bisulfite solution and allowed to stand 2 hours with frequent shaking. The bisulfite solution was separated and sodium carbonate was added until distinctly alkaline to litmus. The alkaline solution was extracted with 25 cc. ether and the ether solution of aldehydes was evaporated spontaneously. The residue was dissolved in 1 cc. of alcohol, and 0.1 cc. of this alcohol solution was heated for 2 minutes, in a steam bath, with 0.1 cc. of 20 per cent alcoholic gallic acid solution and 2 cc. concentrated sulfuric acid.

An emerald to blue color develops if piperonal is present. The reaction is much more sensitive when the gallic acid solution is added to the sulfuric acid before the alcoholic solution to be tested is added.

Seven samples of Mexican, Bourbon, South American, and Java extracts gave negative gallic acid reactions for piperonal; three samples of Tahiti extract gave strongly positive tests; and three vanillon extracts yielded even deeper color reactions than the Tahiti extracts. By adding piperonal to pure Bourbon extract it was found that 0.001 gram of piperonal per 100 cc. of extract gave a strong emerald color. Bourbon extract containing 5 per cent of Tahiti extract also showed a strong positive reaction.

Since vanillon extracts gave the strongest color reactions, an attempt was made to isolate piperonal from these beans.

Four kilograms of finely chopped vanillons were exhausted by percolation with ether. The ether extract was concentrated to 2 liters, and thoroughly washed with saturated sodium bisulfite solution. The bisulfite solution was separated, filtered, made alkaline to litmus with sodium carbonate, and extracted with ether. The ether solution was distilled with steam, and the distillate was extracted with ether. This ether extract was concentrated to 50 cc. and washed, first with dilute sulfuric acid, then with 2 per cent sodium hydroxide solution, and finally with water. It was then filtered, dried over calcium chloride, filtered, and evaporated. The weight of the mixed aldehydes obtained was 0.8 gram.

A minute amount of this liquid material developed the characteristic blue color with gallic acid. However, by far the larger part of the material consisted of anise aldehyde; as shown by the melting point of the semicarbazone, 204.6° C, and by the melting point of the acid obtained on oxidizing with permanganate, 183.2° C. Piperonal could not be isolated from the mixed aldehydes, although a small amount apparently was present.

Discussion

Mexican, Bourbon, South American, and Java vanilla beans do not contain piperonal. This was clearly shown by the two sensitive reactions. Vanillons and Tahiti beans apparently contain minute quantities of piperonal. At least they contain an aldehyde which responds to the same tests as piperonal and probably contains the methylene ether group, as piperonal does.

In the gallic acid test, the bisulfite treatment is necessary to separate the aldehydes from anisyl alcohol. This separation must be made because this alcohol forms a deep red color with sulfuric acid, obscuring the blue color produced by piperonal. If anisyl alcohol is known to be absent the gallic acid test may be carried out in the same manner as the phloroglucinol test, which is much shorter. After evaporating the final ether extract the residue should be dissolved in 1 cc. of alcohol and 0.1 cc. of this solution should be used for the test. The gallic acid test is extremely sensitive and it was found that 0.00001 gram of piperonal will give a light green color. Although a number of alkaloids and other compounds respond to this test, piperonal is the only aldehyde which, so far, is known to give the reaction.

When examining samples of unknown origin, anisyl alcohol should first be sought by the method previously described by the writer.[7] If this alcohol is found, the extract contains Tahiti or vanillon extract, and will consequently react positively to the gallic acid test for piperonal.

If anisyl alcohol is absent and the gallic acid test is positive, the addition of piperonal is indicated. Care is necessary in reaching a conclusion in such a case because an extract may contain only 1 or 2 per cent of Tahiti extract, when the anisyl alcohol test will be doubtful while the gallic acid test will be positive. This difficulty can be overcome by using several hundred cubic centimeters of the extract for the anisyl alcohol determination.

An extract which gives a positive reaction for either anisyl alcohol or piperonal cannot be pure Mexican, Bourbon, South American, or Java vanilla extract.

Summary

Although piperonal is frequently mentioned as a constituent of vanilla, it has not been isolated from any variety of beans.

Vanillons and Tahiti beans appear to contain a small amount of piperonal since their extracts respond to the qualitative tests for piperonal.

The method described can be used for detecting the addition of minute amounts of piperonal to extracts of Bourbon, Mexican, Java, and South American beans. These varieties of beans do not contain piperonal.

The similarity in chemical composition between Tahiti beans and vanillons is very striking. These beans differ markedly from the other varieties, to which they are inferior in flavor, and it is questionable whether the use of either should be permitted in vanilla extract, unless labeled to indicate the variety.

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[6] *Bull. soc. chim.*, **5**, 742; *Bull. soc. pharm. (Bordeaux)*, **57**, 259 (1919).

[7] THIS JOURNAL, **17**, 303 (1925).

Committee Named to Reduce Waste in Metals

A definite program of procedure for the coördination of efforts of various technical, scientific, trade, and other organizations for a more effective elimination of waste in the metal trades was adopted at a conference on May 13, under the auspices of the Department of Commerce. Formation of the National Committee on Metals Utilization was effected to supervise the elimination of waste products in coöperation with the Department of Commerce.

Secretary of Commerce Hoover presided at the opening of the conference, and spoke on the merits of the work to be undertaken. W. C. Wetherill, director of metals utilization of the same department, who has been spending several months in preliminary work in the field, outlined the achievements in simplification of trade practices and other related work.

R. M. Hudson, chief of the Division of Simplified Practice, spoke of the achievements to date in reduction of variety and dimensions in the elimination of waste.

Distillation Studies[1]

By E. H. Leslie and J. C. Geniesse

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

A careful study has been made of the performance of an effective specially designed laboratory fractionating column. The apparatus and its operation are described in detail. Thermal efficiencies of all parts of the apparatus were determined as a necessary part of the analysis of its performance. The results obtained by use of the laboratory column were compared with those possible only by use of the hypothetical column of infinite number of equilibrium units.

The characteristics of the system chloroform-toluene are outlined and data necessary for the rapid analysis of these solutions are presented.

The influence of vapor velocity on the effectiveness of the laboratory column was studied. Information so gained, taken together with that secured by critical study or review of work by others, leads to the conclusion that vapor velocity can be disregarded as a variable factor in column design and operation, provided the velocity is not so high as to cause excessive entrainment or priming.

The suggestion is made, based on data presented, that reflux ratio may also be without influence on the effectiveness of a fractionating column.

The effectiveness of the column packings was found to vary inversely with the diameter, as has previously been shown by Peters.

Charts are presented that show at a glance the relationship of reflux ratio, number of equilibrium units, and change in composition for solutions of chloroform and toluene.

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THE object of this investigation was to make a complete analysis of the performance of an effective laboratory distillation equipment and to determine how closely its performance approached that of the hypothetical ideal apparatus of infinite number of equilibrium units and minimum vaporization and reflux. Further objects were to secure data on the effect of vapor velocity in a packed column and on the relative effectiveness of packings of different diameters. Also the preparation of charts to make clear the relationships between reflux ratio and fractionation effected by one equilibrium unit was intended.

Scope of Experimental Work

The experimental work consisted in determining the actual heat, weight of vapor, and reflux ratio required for the separation of 1 gram of practically pure chloroform from chloroform-toluene solutions of four different concentrations. Solutions containing 15, 25, 35, and 50 per cent of chloroform by weight were distilled through the column packed with 5.6-mm. Lessing rings, and 25 and 50 per cent solutions were distilled through the column packed with 6.5-mm. rings. Solutions containing more than 50 per cent chloroform were not used, because it would have been almost impossible accurately to measure the small reflux required. Each solution was distilled at different rates so that the effect of rate could be studied.

The System Chloroform-Toluene

The system chloroform-toluene was selected because a solution of these components is easily analyzed by determination of its specific gravity, the equilibrium diagram is accurately known, and reasonably accurate latent heats and specific heats are known.

The latent heats of chloroform and toluene at their normal boiling points are 58.5 and 86.0 calories per gram, respectively. Kauffman gives the equation $C_t = 0.3834 - 0.001043t$ for the specific heat of liquid toluene. The specific heat for the vapor was taken as 0.320. Liquid chloroform has a specific heat of 0.238 and that of the vapor is 0.144. The latent heats at various temperatures for both liquids were calculated from these data (Table I). The latent heats, at the boiling point, of solutions of all compositions are shown in Figure 1.

Table I—Latent Heats of Chloroform and Toluene at Various Temperatures

Temperature ° C.	Latent Heat Chloroform Cal./gram	 Toluene Cal./gram
61	58.50	93.40
65	58.11	92.83
70	57.64	92.12
75	57.16	91.42
80	56.69	90.74
85	56.21	90.00
90	55.74	89.26
95	55.27	88.47
100	54.79	87.68
105	54.32	86.82
110	53.84	86.00

The compositions of liquid and vapor and the boiling points of solutions of chloroform and toluene as determined by Rosanoff[2] were used. Since the data were not complete it was thought advisable to determine the equation of the curve passing through the known points. The equation is

$$y = \frac{x}{0.320 + 0.517x + 0.163x^2}$$

in which x is the composition of the liquid and y the composition of the vapor, both in terms of chloroform and expressed by weight as decimal parts of unity. At no point

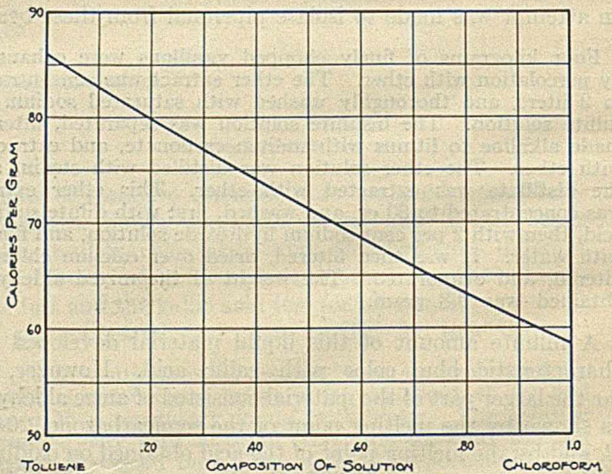

Figure 1—Latent Heats of Solutions of Chloroform and Toluene

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[1] Received February 2, 1926.

[2] *J. Am. Chem. Soc.*, **36**, 1803 (1914).

does the curve represented by this equation deviate more than 0.2 per cent from the smoothest curve that can be drawn through Rosanoff's data. Table II gives the values of x and y as determined by the equation.

Table II—Values of x and y of the Vapor-Liquid Composition Curve for the System Chloroform-Toluene

x	y	x	y	x	y
0.000	0.000	0.350	0.672	0.700	0.918
0.050	0.143	0.400	0.724	0.750	0.937
0.100	0.268	0.450	0.768	0.800	0.955
0.150	0.372	0.500	0.808	0.850	0.970
0.200	0.465	0.550	0.842	0.900	0.981
0.250	0.542	0.600	0.871	0.950	0.991
0.300	0.612	0.650	0.896	1.000	1.000

Purification of Chloroform and Toluene

U. S. P. chloroform and toluene were used. Both liquids were fractionated twice, using a reflux ratio of approximately 8. The first and last portions were necessarily discarded. The purified chloroform had a distillation range of 0.2° C. and the toluene 0.1° C.

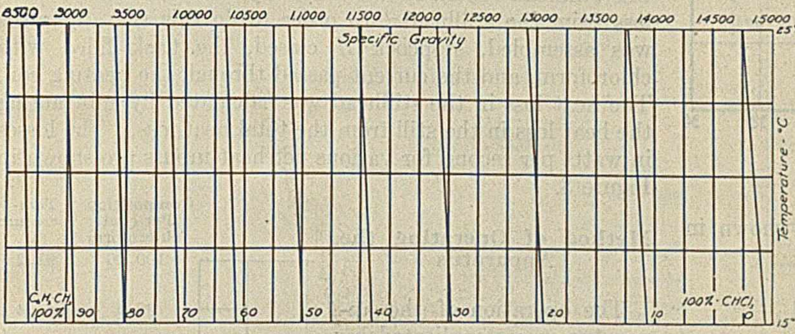


Figure 2—Specific Gravities of Solutions of Chloroform and Toluene between 15° and 25° C.

Analytical Procedure

The analyses of the solutions were made by determining specific gravities with a Westphal type balance. An accuracy of ±0.0003 was obtained with this instrument. Too much time was required to bring the liquid to the same temperature each time before determining its specific gravity. Therefore, a chart giving the change of density with temperature for solutions of different compositions was constructed (Figure 2). Errors involved in this analytical procedure were not over ±0.1 per cent.

Apparatus

The apparatus (Figure 3) comprises a still, *A*, an insulated and jacketed column, *B*, a stillhead, *C*, where the temperature of the vapor is taken before it is divided into product and reflux, a reflux condenser, *D*, an orifice meter, *E*, for measurement of the reflux liquid, and a condenser, *F*.

The still is a 2-liter Pyrex flask with a bulb blown on the bottom. Heat is supplied by passing an electric current through a submerged resistance coil placed in the bulb so that all but a few cubic centimeters of the liquid can be vaporized.

The column consists of a 4-foot Pyrex glass tube 0.9 inch in internal diameter and jacketed by another glass tube. The tubes are lagged with 0.5 inch of asbestos paper. A galvanized iron jacket, *J*, is placed outside of the lagging, leaving an annular space 1 inch wide between the asbestos and the jacket tube. Air at the temperature of the still is blown into the lower end of the annular space. Thermometers are placed at regular intervals along the jacket so that the temperature of the annular space can be noted. The double glass tubing and lagging tend to minimize any heat exchange with the outside resulting from slight variations of the temperature of the air in the jacket.

The volume of the column is 30.5 cubic inches. 5.6- and 6.5-mm. Lessing rings are used for column packing. The total weight of the small packing is 453 grams and that of the large packing 333 grams. The total surface area of the small packing is 687 square inches and that of the large packing 527 square inches. The sheet metal used to make the rings is 0.25 mm. thick.

The stillhead is a short glass tube to which are sealed the delivery tube and stopcock, *G*, through which the product makes its exit, and a side arm, *C*, through which the reflux liquid enters. The stopcock *G* is an ordinary one with a V groove filed on the inside of the male member. A pointer is fastened to the handle of the stopcock and moves over a dial so that the cock can be opened accurately to any desired extent. The vapor to be condensed and used as reflux liquid ascends through stopcock *H* to condenser *D*. A thermometer indicates the temperature of the vapor in the stillhead.

The flowmeter *E* consists of two concentric glass tubes. The reflux liquid from the condenser *D* flows into the annular space and through an orifice near the bottom of the inner tube and thence into the stillhead. The volume of liquid flowing through the orifice meter depends upon the temperature, composition, and height of liquid above the orifice.

With the apparatus described it is possible accurately to control the amount of reflux liquid. If stopcock *H* is closed and *G* opened there is practically no reflux. If stopcock *G* is closed and *H* opened there is total reflux. Any amount between no reflux and total reflux is obtained by adjusting stopcocks *G* and *H*.

Calibration of Flowmeter

In order to calibrate the flowmeter its lower end was disconnected from the apparatus and placed over a graduate. Stopcock *G* was closed, and chloroform put in the still and heated. The height of the liquid in the meter was read for various rates of distillation, thus giving a series of values. These are plotted in Figure 4. The calibration was made with chloroform alone since that liquid is the only one refluxed under ordinary conditions.

During fractionation there is some heat loss from the flowmeter, thereby cooling the reflux liquid below its boiling point. This cooling of the reflux liquid results in the condensation of chloroform in the stillhead. It was necessary to determine the quantity of reflux formed in this manner so that it could be added to the amount indicated by the flowmeter. The grams per minute to be so added for various flowmeter readings are shown in Figure 5.

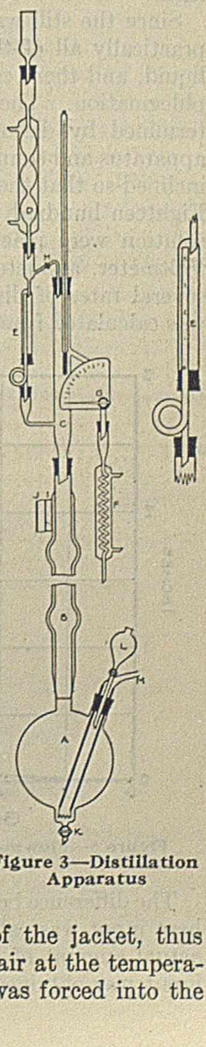


Figure 3—Distillation Apparatus

Control of Jacket Temperature

In order to control the temperature of the jacket, thus making the column essentially adiabatic, air at the temperature of the boiling solution in the flask was forced into the lower end of the annular space. Some of the air was allowed to escape through holes in the jacket so as to get the proper temperature gradient along the column. The correct temperature gradient was obtained by assuming that the column was working under equilibrium conditions and that the equilibrium units were of equal length. Both of these assumptions proved to be justified. Compositions and corresponding temperatures in a typical instance are shown in Figure 6.

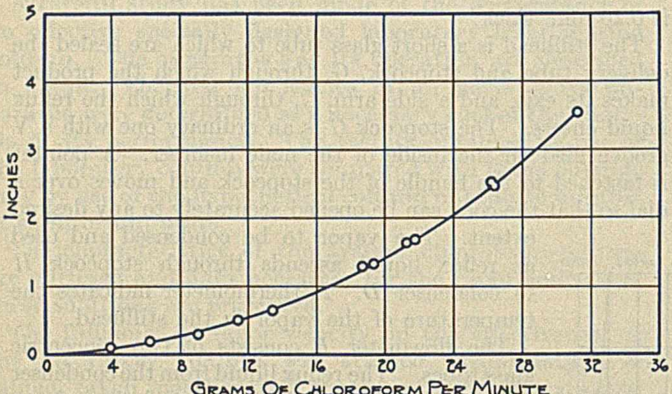


Figure 4—Flowmeter Calibration Curve

Thermal Efficiency of the Apparatus

In order to make corrections for heat losses it was necessary to determine the thermal efficiencies of all parts of the apparatus.

Since the still was kept over 80 per cent full at all times, practically all of the heat loss in the still was through the liquid, and there could have been little fractionation by dephlegmation. The thermal efficiency of the still was determined by disconnecting the flask from the rest of the apparatus and connecting it directly to an ordinary condenser inclined so that the product could be collected in a graduate. Eighteen hundred to two thousand cubic centimeters of the solution were placed in the flask and the current passed. Voltmeter, ammeter, and graduate readings were taken for several rates of distillation. The total or gross heat input was calculated from these data.

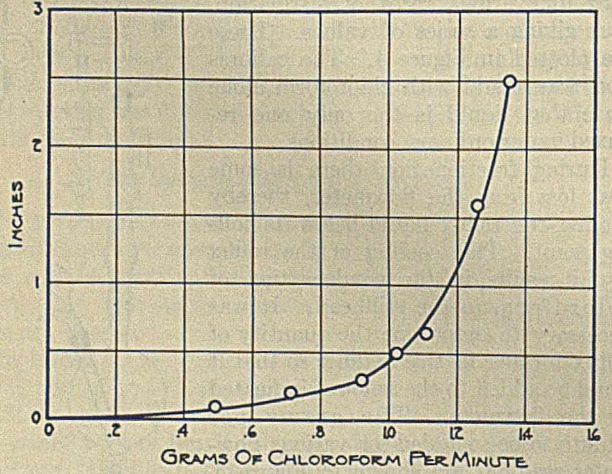
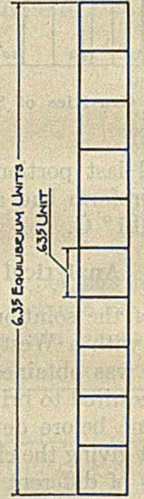


Figure 5—Flowmeter Correction for Cooling of Reflux Liquid

The difference between the heat loss in the still and the total heat input was called the net heat input because it was the actual amount of heat causing vaporization. The net heat input was obtained by multiplying the number of grams of condensate by the latent heat at the temperature of ebullition. Gross and net heat inputs were determined for solutions containing 15, 25, 35, 50, and 100 per cent chloroform. The results, expressed in watts per second, are shown in Figure 7.

To prove whether or not the column was adiabatic the stillhead was replaced by an ordinary condenser, the still and column being run as usual. It was found that the heat loss was the same as when the still was used alone. The column therefore functioned adiabatically.

As may be seen in Figure 3, the product and reflux were taken directly from the stillhead. Since the product was practically pure chloroform, the vapor in the stillhead was also all chloroform. Obviously, all of the heat loss in the stillhead resulted in the condensation of chloroform that then acted as reflux liquid. In order to ascertain the quantity of this stillhead reflux, it was necessary to determine the heat loss from the stillhead. In order to do this the apparatus was assembled, stopcock *H* closed, the flask filled with chloroform, and the current passed through the heating coil. The heat loss in the stillhead was calculated by subtracting the heat loss in the still from the total heat loss. The losses in watts per second for various net heat inputs are shown in Figure 8.



Composition Per cent chloroform	Temperature ° C.
100.00	61.2
99.5	61.4
98.2	61.8
95.8	62.8
91.6	64.5
85.9	66.9
78.2	70.1
70.8	73.4
62.2	77.6
54.8	81.4
50.0	83.8

Figure 6—Composition and Temperature Gradients along Column in a Particular Instance

Method of Operating the Apparatus

The operation of the apparatus was complicated by the fact that it was necessary to control and synchronize two independently variable conditions—namely, the weight of reflux per unit weight of product and the instantaneous composition of the liquid in the still.

The solution of chosen composition was placed in the flask, the electric heating circuit closed, and hot air blown into the jacket. Stopcock *G* was closed so that there was total reflux. The required change in composition was at first obtained in the lower part of the column while the upper part was not functioning because a minimum number of equilibrium units were required when the reflux was total. Under those conditions the whole column was at a lower temperature than the jacket. If stopcock *G* was opened to the required extent, and 25 cc. of product collected, the column walls and packing would change temperature rapidly as a result of changing phase composition within the column. During this period of adjustment chloroform would condense because the temperature of the column walls and packing would be gradually increased to the equilibrium temperature corresponding to the state at which final readings were to be taken. Obviously, experimental readings taken under such conditions would not be correct. To rectify this state of affairs an extra 200 cc. of chloroform was added to the solution in the still. When the column was thoroughly heated, stopcock *G* was opened to the required extent and the 200 cc. of chloroform collected, thus bringing the composition of the liquid in the still to that desired. If the next 25 cc. collected as product was substantially pure chloroform, but the second 25 cc. contained some toluene, it is obvious that the reflux ratio during the collection of the first 25 cc. was the lowest that allowed the production of pure chloroform. If the first 25 cc. contained some toluene there was not enough reflux. The experiment then had to be repeated with stopcock *G* more nearly closed. If both 25-cc. samples were practically pure chloroform the reflux ratio was too great. It was then necessary to repeat the experiment with the stopcock opened more.

During the determinations readings were taken of the current flow in the heating coil, voltage drop across the heating coil, temperature of the vapor as it left the stillhead, head of liquid in the flowmeter, barometric pressure, and the time required for the collection of 25 cc. of product. Table III shows the data taken during one determination.

Table III—Data Taken in Each Experiment

Composition of still liquid, 0.50 per cent chloroform

	Initial	Final
Current, amps.	4.43	4.43
Voltage	52.0	52.0
Temperature	60.8° C.	61.0° C.
Flowmeter	0.83 inch	0.82 inch
Barometric pressure	734 mm.	
Time	92 seconds	
Dial	2.0	

Typical Method of Calculating Results

Q_s, *the heat required per gram of product*, equals the net heat input per minute divided by the weight of product collected in one minute. The total watts supplied equals volts times amperes, or 52.0 × 4.43 = 231. By reference to Figure 7 it is seen that 231 gross watts correspond to 173 net watts for a solution whose composition is 50 per cent. The rate of product separation is 23.9 grams per minute. The heat required per gram of product is:

$$Q_s = \frac{173 \times 0.24 \times 60}{23.9} = 104 \text{ calories}$$

V_s, *the grams of vapor required for the separation of 1 gram of product (vaporization)*, equals the net heat input per minute divided by the latent heat per gram of the vapor and by the weight of product separated per minute. From Figure 1 the latent heat of the vapor (0.808 $CHCl_3$) in equilibrium with the liquid (0.500 $CHCl_3$) in the still is seen to be 62.8 calories per gram. Then

$$V_s = \frac{173 \times 0.24 \times 60}{62.8 \times 23.9} = 1.657 \text{ grams}$$

L_R, *the weight of reflux liquid per gram of product (reflux ratio)*, may be calculated in two ways. The first method is by the use of thermal equivalents. Since the column is adiabatic all toluene that vaporizes in the still must vaporize a thermally equivalent weight of chloroform during the process of countercurrent contacting in the column. Therefore, all heat put into the column may be expressed directly as grams of chloroform leaving the top of the column. All of the chloroform not collected as product is returned to the top of the column as reflux. Therefore

$$L = \frac{\dfrac{\text{heat input per minute}}{\text{latent heat of chloroform}} - \text{grams of product per minute}}{\text{grams of product per minute}}$$

$$L_R = \frac{\dfrac{173 \times 0.24 \times 60}{58.5} - 23.9}{23.9} = 0.78 \text{ gram}$$

The second method of calculating the weight of reflux liquid consists in totaling the following quantities:

(1) Weight of liquid corresponding to the flowmeter reading
(2) Weight of chloroform condensed in stillhead due to cooling of the reflux liquid in the flowmeter
(3) Weight of chloroform condensed in the stillhead as a result of heat loss in that part of the apparatus

Referring to Figure 4, 0.825 inch head of liquid in the flowmeter corresponds to 15.1 grams of reflux per minute. The heat loss in flowmeter is equivalent to 1.2 grams of reflux (Figure 5). Also, 1.9 grams of chloroform are condensed per minute in the stillhead. The last quantity is obtained from the curve in Figure 8. The sum of these three quantities, or the total reflux, divided by the rate of product formation equals the reflux ratio. Hence

$$L_R = \frac{18.2}{23.9} = 0.76 \text{ grams}$$

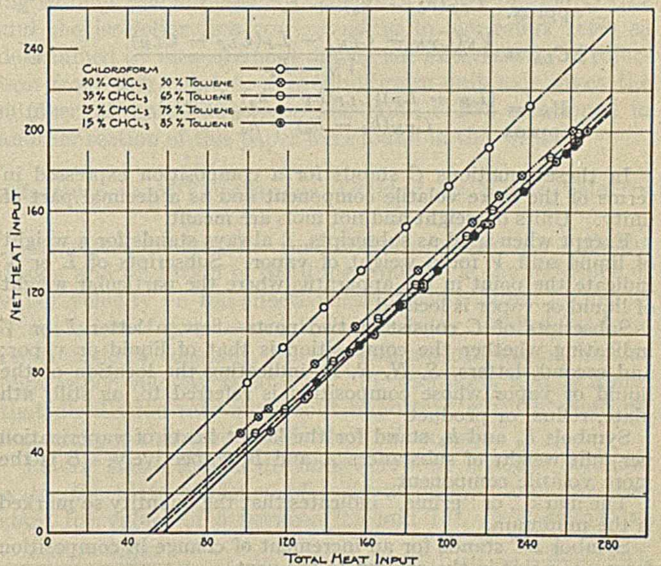


Figure 7—Thermal Efficiency of the Distillation Flask

The excellent agreement between the values of L_R calculated by these two methods illustrates how closely it is possible to work. It also shows that the column really functions adiabatically.

The number of equilibrium units (as from data in Table III) represented by the column under the above conditions may be found by ascertaining the intersection of the iso-reflux ratio line 0.77 and the abscissa C_{LN} = 0.500 in Figure 12, and by reading the corresponding ordinate. The value is approximately 9; that is, there are nine equilibrium units in the column, each unit having an average length of 5.3 inches.

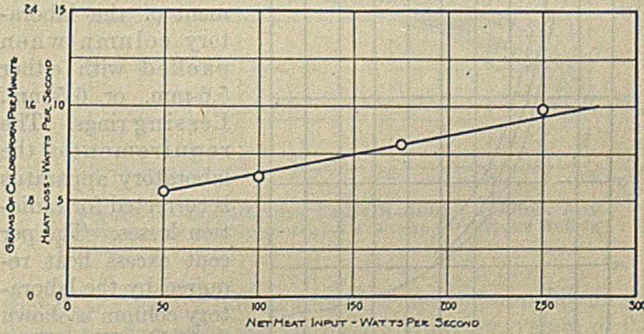


Figure 8—Heat Loss from Stillhead

Results of Experimental Work

As stated at the outset of this paper, one object of the work was to compare the performance of the column with that of the hypothetical column of infinite number of sections and minimum vaporization and reflux ratios. In order to do this use has been made of the following equations[3] for the

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[3] Leslie, "Motor Fuels," p. 87.

calculation of the quantities pertaining to the hypothetical column:

$$V'_s = \frac{L_P(C_{LP} - C_{LS})}{C_{VS} - C_{LS}} \tag{1}$$

$$Q'_s = V'_s \, [h_b C_{VS} + h_a(1 - C_{VS})] \tag{2}$$

$$\underset{\text{approx.}}{L_R =} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{LP}(h_b - h_a) + h_a} - L_P \tag{3}$$

$$\Delta C_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \tag{4}$$

$$\underset{\text{approx.}}{V_N =} \frac{(L_R + L_P)[C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \tag{5}$$

In these equations C stands for a composition expressed in terms of the more volatile component and as a decimal part of unity. Units of weight and not mols are meant.

Except when used as subscripts, L always stands for a weight of liquid and V for a weight of vapor. Subscripts of L or V indicate the point in the apparatus where the particular weight of liquid or vapor is located.

Subscripts of C consist of two parts—first, a letter L or V indicating whether the composition is that of liquid or vapor; and second, letters, S, N, R, P, indicating the location of the liquid or vapor whose composition is referred to, as still, nth plate, reflux, or product.

Symbols h_a and h_b stand for the latent heats of vaporization per unit weight of substances A and B, respectively. B is the more volatile component.

The mark ′, or "prime," indicates that the quantity so marked is the minimum.

Symbol ΔC stands for an increment of change in composition from one point in the column to the next.

Q_s represents the heat input to the still per unit weight of product.

Heat Required per Gram of Product

The minimum heat required for the separation of 1 gram of almost pure—that is, 99.98 per cent—chloroform in the hypothetical column of infinite number of equilibrium units was calculated by use of Equations 1 and 2. The quantity within the parenthesis of Equation 2 can be read directly from Figure 1.

Figure 9 serves to compare the calculated heat requirement of the hypothetical column with the actual heat requirement of the laboratory column when packed with either 5.6-mm. or 6.5-mm. Lessing rings. The requirement of the laboratory apparatus is corrected for radiation losses. The per cent excess heat required by the laboratory column is shown in Table IV. When the separation is easy little more heat is required by the laboratory column than by the ideal column, but as the separation becomes more difficult, or as the effectiveness of the column is reduced by increasing the size of the packing, the excess heat increases rapidly. This excess heat is the price that must be paid because the laboratory column comprises a finite number of equilibrium units, approximately eight in the column with 5.6-cm. ring packing, rather than the infinite number of the hypothetical column.

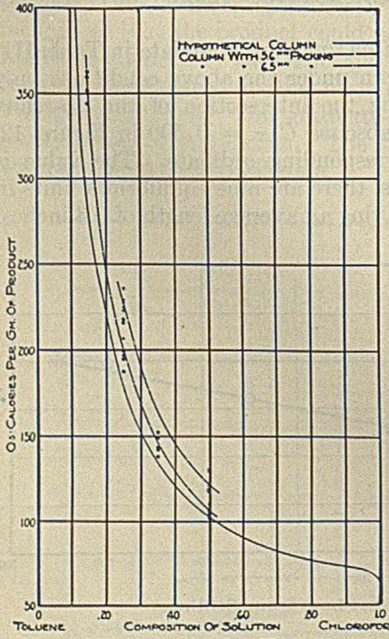

Figure 9—Comparative Heat Requirements of Laboratory Columns and Hypothetical Column

Table IV—Heat Required per Gram of Product

C_{LN}	Hypothetical column Cal./gram	Lab. column Av. cal./gram	Excess heat required by lab. column Per cent
	5.6-Mm. Ring Packing		
0.500	101.9	104.9	3
0.350	134.0	144.8	8
0.250	180.0	202.0	12
0.150	287.0	354.4	23
	6.5-Mm. Ring Packing		
0.500	101.9	122.0	20
0.250	180.0	224.7	25

Weight of Reflux per Gram of Product

The weight of reflux liquid required per gram of product by the column of infinite number of equilibrium units—that is, the minimum reflux—was calculated by use of Equation 3. The latent heats used in the numerator must be those corresponding to the temperature at which the vapor is formed in the still, and the value of h_b used in the denominator must be that corresponding to the boiling point of chloroform.

Figure 10 presents curves showing the minimum reflux and also the actual reflux required by the laboratory column when packed with 5.6- and 6.5-mm. rings and when producing 99.98 per cent chloroform. The per cents excess reflux shown in Table V are larger than the per cents excess heat shown in Table IV, mainly for the reason that they are based on the weight of reflux in the one case and on the approximate thermal equivalent of the weight of reflux plus unit weight of product in the other. Also, Equation 3 is approximate in that it does not take sensible heat quantities into account.

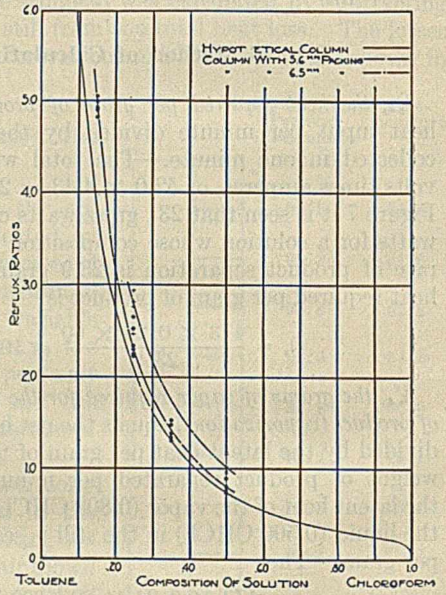

Figure 10—Comparative Reflux-Ratio Requirements of Laboratory Columns and Hypothetical Column

Table V—Weight of Reflux per Gram of Product

C_{LN}	Minimum reflux Grams/gram	Lab. column actual reflux Grams/gram	Excess reflux Per cent
	5.6-Mm. Ring Packing		
0.500	0.074	0.79	7
0.350	1.29	1.42	10
0.250	2.08	2.39	15
0.150	3.91	4.94	26
	6.5-Mm. Ring Packing		
0.500	0.74	1.05	42
0.250	2.08	2.78	34

Fractionation Characteristics of System $CHCl_3$-$C_6H_5CH_3$ and Determination of Equilibrium Units in Laboratory Column

The problem of calculating the number of equilibrium units required to effect the separation of 99.98 per cent chloroform from a solution of any given concentration, when operating with any given weight of reflux liquid per unit weight of chloroform, can be solved by the use of Equations 4 and 5.

If it is desired to generalize the problem so that the number of equilibrium units required when any reflux ratio is used and a solution of any concentration is distilled, this can be done by constructing a series of integral curves of $\frac{1}{\Delta C_{LN}} C_{LN}$ for a number of reflux ratios.[4] This has been done for the system chloroform-toluene. The results are presented as Figure 11. When operating with any chosen reflux ratios, the number of equilibrium units required to separate 99.98 per cent chloroform from a solution of composition C_{LN} is equal to the area bounded by the curve, the x-axis—i. e. $\frac{1}{\Delta C_{LN}} = 0$—and vertical lines through the abscissas C_{LN} and 1.0. If the vertical line through abscissa C_{LN} falls to the left of the asymptote (represented by dotted lines labeled with the value of the particular reflux ratio used) of the reflux curve, it means that the desired separation cannot be effected with that reflux ratio.

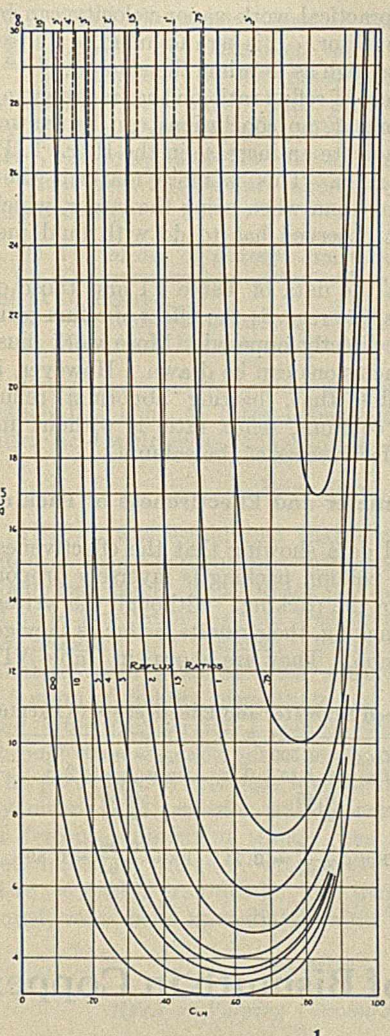

Figure 11—Integral Curves of $\frac{1}{\Delta C_{LN}} C_{LN}$

From the standpoint of easy use the integral curves of the curves of Figure 11 are to be preferred. These are shown as Figure 12. The number of equilibrium units required to effect the separation of a product of any possible composition from a solution of any concentration, when operating with any reflux ratio, can be read from this diagram.

Several interesting facts are disclosed by inspection of Figure 12. For example, when distilling a solution of some given composition, increase of reflux ratio at first has a large effect, but a point is soon reached from which any further increase is of little benefit in reducing the number of equilibrium units required. Likewise, it is evident that for a particular reflux ratio there is at first a great increase in the fractionating ability of a column as the number of equilibrium units is increased, but a number of units is soon reached beyond which the addition of even a very large number of units does little in the way of increasing the fractionating ability of the apparatus as a whole. For the accomplishment of any particular fractionation there is an optimum range of reflux ratio and number of equilibrium units, the exact choice resting on the relative cost of heat and overhead charges on investment.

In this investigation the writers were interested in determining the number of equilibrium units in the column when packed with 5.6-mm. and with 6.5-mm. Lessing rings. With Figure 12 at hand this is easily accomplished. A point is located representing the intersection of the vertical line passing through the abscissa corresponding to the particular C_{LN} and the iso-reflux line corresponding to the reflux ratio as determined by measurement during the experiment. Projection from this point to the equilibrium-unit axis gives the number of units directly. The H. E. T. P.'s mentioned in another section of this paper were found in this way.

Effectiveness of Column as Affected by Vapor Velocity

An important question that arises in connection with the design and operation of distilling columns is the influence of vapor velocity on the effectiveness of the column. That is, if a solution of given concentration is being distilled, and the reflux ratio is constant, will the column operate as well at high vapor velocity as at low? Furthermore, if it is found that distillation rate is without important effect at high reflux ratio, is this true also for low reflux ratio?

Peters[5] states that in distilling solutions of acetic acid and water the plate efficiency of a sieve-plate column was constant for values of ρ between 0.8 and 1.0. ρ is defined as $\frac{\text{heat in reflux}}{\text{total heat in vapor}}$, or, in our nomenclature, $\frac{L_R}{L_R + L_P}$. Although the point is not mentioned, Peters presumably meant that the reflux ratio was constant. However, values of 0.8 to 1.0 for ρ are equivalent to reflux ratios between 4.0 and ∞. For the particular solution distilled this is the range of high reflux ratio—that is, the range in which a change in reflux ratio would make little difference in the fractionation effected by a particular column. Consequently, it is entirely possible that the plate efficiency for values of ρ between 0.8 and 1.0 would be substantially constant and independent of reflux ratio as well as of vapor velocity, whereas, at lower values

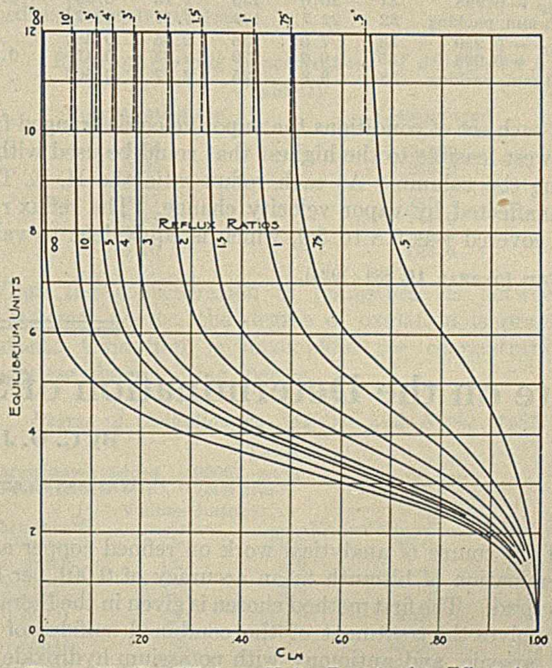

Figure 12—Equilibrium Units Required to Effect Any Separation of Chloroform and Toluene at Various Reflux Ratios

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[4] "Motor Fuels," p. 97.

[5] This Journal, 14, 477 (1922).

of ρ, the constancy of plate efficiency at various vapor velocities might hold only at constant reflux ratio. In passing, it should be noted that high reflux ratio for the distillation of one solution may be low reflux ratio for another. It all depends on how easily the components are separated.

Calingaert and Huggins[6] studied the exhaustion of ammonia-water solutions in a coke-packed column and drew the conclusion that "the efficiency of the still investigated was proportional to the reflux at constant vapor velocity, or inversely proportional to the vapor velocity at constant reflux." The present writers' findings are not in agreement with these conclusions. In fact, they are such as to indicate that the effectiveness of a packed column is not affected by vapor velocity within the range of conditions investigated. In Table VI data to illustrate this point are presented.

Table VI—Relation of Effectiveness of Packed Column to Vapor Velocity and Reflux Ratio

Conditions	Expt.	Grams product per minute	Calories per gram product	Reflux ratio $\frac{L_R}{L_P}$	Vapor velocity Ft./sec.	H. E. T. P. Feet
$C_{LN} = 0.500$	1	15.9	110	0.90	0.41	0.45
$C_{LP} = 0.998$	6	24.7	106	0.80	0.60	
5.6-mm. packing	7	27.1	106	0.81	0.67	
$C_{LN} = 0.350$	8	11.2	143	1.39	0.36	0.45
$C_{LP} = 0.998$	10	14.8	149	1.49	0.50	
5.6-mm. packing	12	18.1	152	1.54	0.62	
$C_{LN} = 0.250$	13	9.0	200	2.35	0.41	0.56
C_{LP}	15	10.5	200	2.35	0.47	
5.6-mm. packing	19	12.4	218	2.66	0.62	
$C_{LN} = 0.150$						0.59
$C_{LP} = 0.998$	20	6.0	346	4.82	0.48	
5.6-mm. packing	24	6.8	360	5.00	0.55	
$C_{LN} = 0.500$	25	14.7	121	1.03	0.40	0.61
$C_{LP} = 0.998$	31	20.0	130	1.18	0.59	
6.5-mm. packing	32	22.7	129	1.17	0.67	
$C_{LN} = 0.250$	33	7.0	236	2.95	0.38	0.63
$C_{LP} = 0.998$	35	9.2	229	2.83	0.47	
6.5-mm. packing	38	9.8	225	2.77	0.50	

For each set of conditions the vapor velocities ranged from the lowest feasible to the highest that could be used without priming the column. At each reflux ratio the H. E. T. P. was unaffected by vapor velocity change. The reflux ratio range covered was 0.8 to 5.0, which is equivalent to values of $H = \frac{\text{total heat}}{\text{heat in product}}$ of 1.8 to 6.0, or of $\rho = 0.44$ to 0.83.

Peters' work covered values of ρ from 0.8 to 1.0. Hence it appears that, for values of ρ between 0.44 to 1.0, and at any chosen but constant reflux ratio, the effectiveness of a packed column is not materially affected by a change in the velocity of the vapor. Since columns, particularly packed columns, will seldom be used with lower reflux ratios than 0.80, it follows that in practical work vapor velocity can be disregarded as a variable factor. It is here assumed, of course, that the velocity is not so high as to prime the column.

With regard to the effect of reflux ratio on the fractionating ability of column equipment, no conclusions can be drawn. The data in Table VI indicate an increase in the H. E. T. P. with increasing reflux ratio. This is more marked when using the smaller packing than when using the larger, which suggests that the effect observed has to do with fluid mechanics.

It will be noted that the data of Table VI and those of Calingaert and Huggins,[6] as regards the effect of reflux ratio on the H. E. T. P., are directly opposed. More work must be done before any conclusions can be drawn. However, it appears entirely possible that, barring abnormal reflux distribution in packed columns, reflux ratio is without important effect on the effectiveness of the column.

Relation between Diameter and Effectiveness of Packing

Peters[5] has presented data showing that the effectiveness of a particular form of column packing is inversely proportional to the diameter of the packing. Although the writers used only two sizes of packing, their results, as far as they go, confirm Peters' conclusion. They are shown in Table VII.

Table VII—Relation between Diameter and Effectiveness in Packing

Diameter of packing Mm.	H. E. T. P., Feet: $C_{LN} = 0.500$, $L_R = 0.8$ to 1.0	H. E. T. P., Feet: $C_{LN} = 0.250$, $L_R = 2.4$ to 2.8
5.6	0.45	0.56
6.5	0.61	0.63
Ratio $\frac{5.6}{6.5} = 0.86$	Ratio $\frac{0.45}{0.61} = 0.74$	Ratio $\frac{0.56}{0.63} = 0.89$

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[6] This Journal, 16, 584 (1924).

Note on the Determination of Small Amounts of Bismuth in Copper

By C. O. Jones and E. C. Frost

Western Electric Co., Inc., Chicago, Ill.

IN THE course of analytical work on refined copper a determination of bismuth to an accuracy of 0.001 per cent was desired. The first method chosen is given in the literature and involves the treatment of the combined sulfides of bismuth, arsenic, and antimony with potassium hydroxide and sodium sulfide solution for the purpose of removing the arsenic and antimony. This was tried on a prepared sample of 100 grams of chemically pure copper with the addition of 5 mg. of bismuth. The recovery, however, was only 3.3 mg. Additional work showed that a relatively large amount of bismuth was dissolved and lost when the combined sulfides were treated with potassium hydroxide and sodium sulfide solution.

The following colorimetric method, also found in the literature, was next tried:

> Dissolve a 200-gram sample of the copper in nitric acid, dilute with water, add a crystal of ferric sulfate, and make ammoniacal. Add a small amount of ammonium carbonate and sodium phosphate, boil, and allow the precipitate to settle. Filter, dissolve the precipitate in dilute sulfuric acid, and pass in hydrogen sulfide. The antimony and arsenic sulfides are separated from the bismuth sulfide by means of potassium hydroxide or yellow ammonium sulfide solution (sodium sulfide should not be used). Separate from the remaining copper by precipitating the bismuth as sulfide in ammoniacal potassium cyanide solution. Dissolve the bismuth sulfide in nitric acid, take to fumes with sulfuric acid, and remove any lead sulfate. Add potassium iodide and sulfurous acid and compare the color produced with the color of a standard bismuth solution similarly treated.

This method was tried on samples containing a known amount of bismuth, as follows:

Copper Grams	Bismuth: Added Per cent	Bismuth: Found Per cent
200	0.003	0.0028
200	0.003	0.0029
200	0.002	0.0018
200	0.000	Not determinable

This experimental work shows that the colorimetric method is better adapted for the determination of minute amounts of bismuth in copper.

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[1] Received March 11, 1926.

The Bismuthate Method for Manganese[1]

By Bart Park

MICHIGAN COLLEGE OF MINES, HOUGHTON, MICH.

IN THE bismuthate method for manganese originally proposed by Schneider[2] and modified by Reddrop and Ramage,[3] the manganese was oxidized in a solution containing nitric acid. This procedure has been adopted by Ibbotson and Briarley,[4] Blum,[5] Blair,[6] Brinton,[7] Demorist,[8] Kinder,[9] and later by Cunningham and Coltman.[10]

Nitric acid has certain inherent defects as a medium for this oxidation:

(1) The oxides of nitrogen must be removed.
(2) The permanganic acid is not so stable in nitric acid as might be desired.
(3) The temperature during oxidation must be kept low.
(4) Nitric acid has a tendency to react with ferrous iron.

The purpose of this study is to show that sulfuric acid, which has none of these defects, may be substituted for nitric acid with no loss in accuracy.

Procedure

After it was established that the oxidation proceeds in sulfuric acid, experiments were made to determine the conditions, if any, under which it is quantitative. A solution of pure manganous sulfate was prepared from the oxalate as proposed by Coltman.[11] Measured volumes of this solution were acidified with sulfuric acid, approximately 0.5 gram of sodium bismuthate was added to each portion, and after shaking for 1 minute the solution was filtered through asbestos and glass wool with the aid of suction. The permanganic acid was washed from the flask and filter by means of 3 per cent sulfuric acid. A weighed amount of ferrous ammonium sulfate was added and the excess determined by titration with dilute permanganate solution (1 cc. = 0.0002 gram Mn). The titrations, unless otherwise noted, were made immediately after the filtrations.

Results

Effect of Varying Concentration of Acid

Table I

Weight of manganese, 0.01 gram
Volume during oxidation, 75 cc.
Temperature, 25° C.
Weight of ferrous ammonium sulfate, 0.4 gram

Normality of H_2SO_4	$KMnO_4$ found Cc.
1.2	50.00
1.7	50.19
2.1	50.80
2.9	50.75
3.8	50.80
4.3	50.55
6.0	50.30

Table I shows that the maximum yield of permanganic acid is obtained in concentrations of sulfuric acid between two and four times normal.

Effect of Varying Temperature

Table II

Acidity, 3 *N*. Other conditions constant

Temperature ° C.	$KMnO_4$ found Cc.
15	51.79
25	51.77
35	51.74
40	51.80
45	51.85
50	51.80
60	51.60
70	51.50

It is evident from Table II that the degree of oxidation is independent of the temperature over a wide range and that the solution need only be cooled to below 50° C.

Effect of Standing after Filtration

Table III

Temperature, 20° to 25° C.

Time of standing	$KMnO_4$ found Cc.
1 minute	50.4
1 hour	50.3
2 hours	50.2
4 hours	50.0

Permanganic acid is quite stable in dilute sulfuric acid at ordinary temperatures.

Effect of Varying Concentrations of Manganese

Table IV

Concentration Mn Mg./cc.	$KMnO_4$ found Cc.
0.50	240.0
0.25	244.0
0.20	245.5
0.17	245.5
0.14	246.0
0.12	246.5
0.10	246.5

When the concentration of manganese is between 0.1 and 0.2 mg. per cc. the degree of oxidation is practically constant. Oxidation is incomplete for concentrations of manganese above 0.2 mg. per cc.

Degree of Oxidation in Sulfuric and Nitric Acids

Table V

Manganese added, 0.02067 gram
$Fe(NH_4SO_4)_2.6H_2O$, 0.7500 gram

Mn found Gram	Volume during oxidation Cc.	Normality		$KMnO_4$ found Cc.
		H_2SO_4	HNO_3	
0.02052	150	2.9	...	102.66
0.02053	250	2.9	...	102.75
0.02054	350	2.9	...	102.78
0.02051	100	1.8	3.2	102.63
0.02057	200	0.9	3.2	102.90
0.02052	100	...	3.2	102.69
0.02052	200	...	3.2	102.68
0.02054	100	...	4.8	102.78

Table V shows that the oxidation proceeds to the same degree in sulfuric acid of proper concentration as in nitric acid.

The weights of manganese found were calculated from the sodium oxalate value of the permanganate. The discrepancies between the weights added and the weights found disappear if manganous sulfate is used for the standardization.

Determination of Manganese in Iron Ores

The oxidation in sulfuric acid solution is particularly adapted to the determination of manganese in iron ores. The following method is both rapid and accurate:

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[1] Received November 27, 1925.

[2] *Dinglers polytech. J.*, **369**, 224 (1888).

[3] *J. Chem. Soc.* (*London*), **67**, 268 (1895).

[4] *Chem. News*, **84**, 247 (1901).

[5] *J. Am. Chem. Soc.*, **34**, 1379 (1912).

[6] *Ibid.*, **26**, 793 (1904).

[7] THIS JOURNAL, **3**, 237 (1911).

[8] *Ibid.*, **4**, 19 (1912).

[9] *Stahl u. Eisen*, **37**, 197 (1917).

[10] THIS JOURNAL, **16**, 58 (1924).

[11] *Ibid.*, **16**, 606 (1924).

Treat 0.5 to 3 grams of ore in an Erlenmeyer flask with sufficient hydrochloric acid to effect solution. Add 10 cc. of concentrated sulfuric acid and evaporate rapidly over a bare flame to copious fumes of sulfur trioxide. If the heating is continued until the interior of the flask is clear and the fumes appear only at the mouth, all the chlorides will be removed. If organic matter is present in the ore it may be completely removed by adding a little nitric acid prior to the fuming. This makes a preliminary oxidation with bismuthate unnecessary.

After the flask has cooled estimate the amount of acid present and add enough more to bring the volume up to 6 or 8 cc. Then add 90 to 100 cc. of water and heat to dissolve the sulfates, cool to below 50° C., and add a slight excess of sodium bismuthate; 0.5 gram is sufficient for ores containing up to 2 per cent of manganese. Agitate the solution for 1 minute and filter through glass wool and asbestos. Rinse out the flask with several small portions of 3 per cent sulfuric acid and wash the filter until all the permanganic acid has been removed. One hundred to 150 cc. are usually enough wash solution. Water may be used to wash out the permanganic acid, but in this case a larger volume is required.

Transfer the filtrate to a beaker, add a weighed excess of ferrous ammonium sulfate, and titrate with dilute standard permanganate solution.

Calculations for the Regeneration of Nitrating Acids[1]

By H. V. Hansen[2]

959—80th St., Brooklyn, N. Y.

Quick, accurate methods are given for calculating the amounts of two fortifying acids which will regenerate a given amount of used acid. The methods are easily adjusted to variations in the composition of the fortifying acid and altered specification for the nitrating acid. They are simple, and it is easy to give instructions for their use in routine work. A convenient check of the calculations practically eliminates erroneous results.

IN THE manufacture of nitrocellulose it is the practice to regenerate the used nitrating acids. The regeneration is usually accomplished by mixing a fixed amount of used acid with two fortifying acids in amounts dependent upon the composition of the used acid, which has been determined analytically. The purpose of this paper is to give methods for the calculation of the "butt-up"—the amounts of the fortifying acids which can regenerate a given amount of used acid.

Redpath,[3] Clement and Riviére,[4] Fowler,[5] and Young[6] have presented methods for the calculation of this problem. None of these methods or modifications thereof have found general use as they are laborious to adapt to variation of the composition of the fortifying acids. This disadvantage has been eliminated from the methods given herein.

General Considerations

The purpose of regeneration is to correct the effects of the nitration upon the nitrating acid, which are to decrease the amount of acid and the fraction of HNO_3 and to increase the fraction of H_2SO_4.

In usual works practice the regeneration is accomplished by applying a fortifying nitric acid and a fortifying sulfuric acid to the used acid as admixtures. The fortifying nitric acid produces a positive effect upon the fraction of HNO_3 in the used acid, a negative effect upon the fraction of H_2SO_4; the fortifying sulfuric acid produces opposite effects. It is easily comprehended that inside certain limits any combination of effects upon the fractions of HNO_3 and H_2SO_4 in the used acid can be produced by means of these fortifying acids, thus making it possible to adjust the composition of the used acid.

So far no consideration has been given to the effect of the fortifying acids upon the amount of used acid, and none will be given, as usual works practice has shown that in a properly designed nitrating system the amounts of the fortifying acids which readjust the composition of the used acid, for practical need, also readjust the amount of acid.

It is an analytical practice to evaluate the acids involved in the regeneration by their composition—e. g., the fortifying nitric acid as the acid which in 100 kg. contains 60 kg. HNO_3 and 35 kg. H_2SO_4. The commercial value of this acid is given thereby, but the value of the acid as an appliance to the regeneration of a used acid in a given nitrating system is only secondarily expressed. In this case the acid must be evaluated by the effects it produces upon the composition of the used acid when it is applied under such conditions that the used acid is regenerated. For the nitrating system used in the following as an example, the above-mentioned fortifying nitric acid is evaluated as the acid of which 100 kg., when applied under the conditions for regeneration, produce the effect of 0.0004 upon the fraction of HNO_3 and the effect of -0.00025 upon the fraction of H_2SO_4 in the used acid. The used acid must be evaluated as an acid acquiring effects upon the fractions of HNO_3 and H_2SO_4 for regeneration. The specified mixed acid is not involved in the regeneration, but is the product of the regeneration.

The evaluation of the acids for the regeneration will be used in the following mathematical discussion of the calculations involved in the regeneration. The quantities required in the discussion, together with their numerical values for the given quantities in the nitrating system used as an example, are given below.

Nomenclature

U, M, N, and S denote amounts of used, specified mixed, fortifying nitric, and fortifying sulfuric acid, respectively. n and s denote fractions of nitric and sulfuric acid, respectively, in the acids referred to by the subscripts. The symbols for the effects have been derived similarly.

U (100,000) = kg. charge of used acid
n_U = fraction of HNO_3 in used acid

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[1] Received July 14, 1925. Revised manuscript received February 18, 1926.

[2] Published with permission of the du Pont Viscoloid Company, with whom the author was previously employed.

[3] Worden, "Nitrocellulose Industry," **1911**, Vol. I, p. 138; "Technology of Cellulose Esters," Vol. I, Pt. 2, p. 1490.

[4] *Caoutchouc & gutta-percha*, **9**, 6244, 6329 (1912).

[5] *J. Soc. Chem. Ind.*, **38**, 34T (1919); **40**, 166T (1921).

[6] *Ibid.*, **39**, 315T (1920).

s_U = fraction of H_2SO_4 in used acid
N = kg. of fortifying nitric acid
n_N (0.60) = fraction of HNO_3 in fortifying nitric acid
s_N (0.35) = fraction of H_2SO_4 in fortifying nitric acid
S = kg. of fortifying sulfuric acid
n_S (0.00) = fraction of HNO_3 in fortifying sulfuric acid
s_S (1.05) = fraction of H_2SO_4 in fortifying sulfuric acid
n_M (0.20) = fraction of HNO_3 in specified mixed acid
s_M (0.60) = fraction of H_2SO_4 in specified mixed acid
$(e_N)_n$ = effect of N kg. of fortifying nitric acid upon fraction of HNO_3 in U kg. of used acid
$(e_N)_s$ = effect of N kg. of fortifying nitric acid upon fraction of H_2SO_4 in U kg. of used acid
$(e_S)_n$ = effect of S kg. of fortifying sulfuric acid upon fraction of HNO_3 in U kg. of used acid
$(e_S)_s$ = effect of S kg. of fortifying sulfuric acid upon fraction of H_2SO_4 in U kg. of used acid
e_n = effect of N plus S kg. of fortifying acids upon fraction of HNO_3 in U kg. of used acid
e_s = effect of N plus S kg. of fortifying acids upon the fraction of H_2SO_4 in U kg. of used acid
$(e_N)_t$ = effect of N kg. of fortifying nitric acid upon fraction of total acidity in U kg. of used acid
$(e_S)_t$ = effect of S kg. of fortifying sulfuric acid upon fraction of total acidity in U kg. of used acid

An acid will often be designated by means of the quantities that indicate its composition—e. g., the specified mixed acid is designated as acid n_M, s_M or acid 0.20, 0.60. The fraction of HNO_3 will always be mentioned first.

Mathematical Discussion

As the problem has been considered from a point of view which theoretically is the most logical but different from usual practice, the discussion may be best comprehended through the examples given below or similar examples worked out from the nitrating system with which the reader is familiar.

The first problem to be considered is the evaluation of the fortifying acids by the effects they produce upon the composition of the used acid when they are applied under such conditions that the used acid is regenerated.

If the used acid is regenerated, N kg. of fortifying nitric acid and S kg. of fortifying sulfuric acid have the effects upon U kg. of used acid, n_U, s_U, of increasing the amount by $(N + S)$ kg. and altering their composition to that of the specified mixed acid, n_M, s_M. However, only the effects $(n_M - n_U)$, $(s_M - s_U)$ upon the fractions of HNO_3 and H_2SO_4 in the U kg. of used acid are to be considered in the calculations, as no specification has been given for the amount of the regenerated acid.

The regeneration of U kg. of used acid—the conversion of U kg. of used acid into U kg. of specified mixed acid—has been obtained by the conversion of N kg. of fortifying nitric acid plus S kg. of fortifying sulfuric acid into N plus S kg. of the specified mixed acid, as illustrated to the right in Figure 1.

By HNO_3 and H_2SO_4 balances on U kg. of used acid plus N kg. of fortifying nitric acid and U kg. of acid $[n_U + (e_N)_n]$, $[s_U + (e_N)_s]$ plus N kg. of specified mixed acid, one obtains

$$Un_U + Nn_N = U(n_U + (e_N)_n) + Nn_M$$
$$Us_U + Ns_N = U(s_U + (e_N)_s) + Ns_M$$

or

$$(e_N)_n = \frac{n_N - n_M}{U} N \qquad (e_N)_s = \frac{s_N - s_M}{U} N \tag{1}$$

By HNO_3 and H_2SO_4 acid balances on U kg. of acid $[n_U + (e_N)_n]$, $[s_U + (e_N)_s]$ plus S kg. of fortifying sulfuric acid and U kg. of acid $[n_U + (e_N)_n + (e_S)]$, $[s_U + (e_N)_s + (e_S)_s]$ plus S kg. of specified mixed acid, it can be shown similarly that

$$(e_S)_n = \frac{n_S - n_M}{U} S \qquad (e_S)_s = \frac{s_S - s_M}{U} S \tag{2}$$

It will be noted that the effects of the fortifying acids are directly proportional to the amounts of the fortifying acids applied to the regeneration. Furthermore, they are independent of the composition of the used acid. Consequently, the effects derived for the fortifying acids would retain their value even if the composition of used acid were different—e. g., n'_U, s'_U. The amounts of the fortifying acids considered, N plus S kg., would then not regenerate the acid but as part of the butt-up for the used acid would have the effects of $[(e_N)_n + (e_S)_n]$, $[(e_N)_s + (e_S)_s]$. The fortifying acids are therefore evaluated for the calculations by these effects.

The effects of N kg. of fortifying nitric acid and S kg. of fortifying sulfuric applied to the regeneration of U kg. of any used acid are

$$e_n = (e_N)_n + (e_S)_n = \frac{n_N - n_M}{U} N + \frac{n_S - n_M}{U} S \tag{3}$$

$$e_s = (e_N)_s + (e_S)_s = \frac{s_N - s_M}{U} N + \frac{s_S - s_M}{U} S \tag{4}$$

Solving for N and S

$$N = \frac{(s_S - s_M) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} e_n - \frac{(n_S - n_M) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} e \tag{5}$$

$$S = \frac{(n_N - n_M) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} e_s - \frac{(s_N - s_M) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} e_n \tag{6}$$

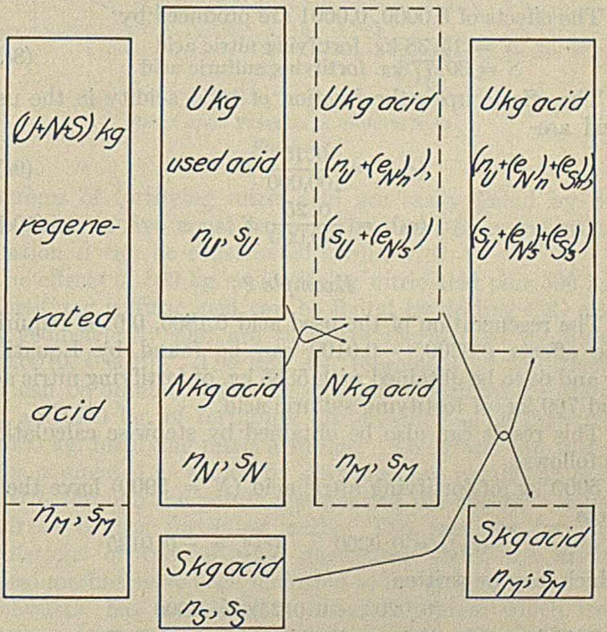
The butt-up can be determined by Equations 5 and 6, if

$$e_n = n_M - n_U \quad \text{and} \quad e_s = s_M - s_U$$

are substituted therein.

For practical calculations it will be appropriate to determine the amounts of the fortifying acids which have the effects

$$e_n = 0.0001 \text{ and } e_s = 0.0000$$



$(U + N + S)$ kg. of specified mixed acid obtained by the regeneration of

U kg. of used acid with N kg. of fortifying nitric acid and S kg. of fortifying sulfuric acid

Acids that may be considered formed during the regeneration

Figure 1

Equations 5 and 6 give

$$N = \frac{(s_S - s_M) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} 0.0001$$

$$S = \frac{(s_M - s_N) U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)} 0.0001 \tag{7}$$

The amounts of the fortifying acids which have the effects

$$e_n = 0.0000 \text{ and } e_s = 0.0001$$

are similarly

$$N = \frac{(n_M - n_S)\ U}{(s_S - s_M)(n_N - n_M) - (s_N - s_M)(n_S - n_M)}\ 0.0001$$

$$S = \frac{(n_N - n_M)\ U}{(s_S - s_M)\ (n_N - n_M) - (s_N - s_M)\ (n_S - n_M)}\ 0.0001 \qquad (8)$$

The effects of the fortifying acids upon the total acidity in the used acid will also be derived, as they will prove useful in the calculations.

From Equations 1 can be derived

$$(e_N)_t = (e_N)_n + (e_N)_s = \frac{(n_N + s_N) - (n_M + s_M)}{U}\ N \qquad (9)$$

and from Equations 2

$$(e_S)_t = (e_S)_n + (e_S)_s = \frac{(n_S + s_S) - (n_M + s_M)}{U}\ S \qquad (10)$$

Examples

The numerical values for the given quantities in the nitrating system used as an example have been indicated in the nomenclature.

Example 1

The equations derived in the foregoing discussion are

$$(e_N)_n = \frac{0.40}{100{,}000}\ N \quad (e_N)_s = \frac{-0.25}{100{,}000}\ N \qquad (1e)$$

$$(e_S)_n = \frac{-0.20}{100{,}000}\ S \quad (e_S)_s = \frac{0.45}{100{,}000}\ S \qquad (2e)$$

$$N = 346{,}200\ e_n + 153{,}800\ e_s \qquad (5e)$$

$$S = 192{,}300\ e_n + 307{,}700\ e_s \qquad (6e)$$

The effects 0.0001, 0.0000 are produced by

N = 34.62 kg. fortifying nitric acid
S = 19.23 kg. fortifying sulfuric acid (7e)

The effects of 0.0000, 0.0001 are produced by

N = 15.38 kg. fortifying nitric acid
S = 30.77 kg. fortifying sulfuric acid (8e)

The effects upon the fraction of total acidity in the used acid are

$$(e_N)_t = \frac{0.15}{100{,}000}\ N \qquad (9e)$$

$$(e_S)_t = \frac{0.25}{100{,}000}\ S \qquad (10e)$$

Example 2

The regeneration of the used acid 0.1800, 0.6100 requiring the effects 0.0200, −0.0100 can be found by Equations 5e and 6e to be obtained with 5386 kg. of fortifying nitric acid and 769 kg. of fortifying sulfuric acid.

This result can also be obtained by stepwise calculations as follows:

5000 kg. of fortifying nitric acid (N = 5000) have the effects

$$(e_N)_n = 0.0200 \qquad (e_N)_s = -0.0125$$

which may be written

$$(0.0200, -0.0125)_N = 5000$$

1000 kg. of fortifying sulfuric acid have the effects

$$(-0.0020, 0.0045)_S = 1000$$

5000, 1000 kg. of the fortifying acids have therefore the effects of

$$(0.0200, -0.0125) + (-0.0020, 0.0045) = (0.0180, -0.0080)$$

Acid 0.1800, 0.6100 is therefore converted by 5000, 1000 kg. of the fortifying acids into acid

$$[(0.1800, 0.6100) + (0.0180, -0.0080)] = \text{acid } (0.1980, 0.6020)$$

This acid requires for regeneration the effect of 0.0020 upon the fraction of HNO_3 that can be calculated from Equation 7e.

N = 34.62 × 20 = 692.4 fortifying nitric acid
S = 19.23 × 20 = 384.6 fortifying sulfuric acid

Acid 0.1800, 0.6100 is converted by

[(5000, 1000) + (692, 385)] = 5692, 1385 kg. of the fortifying acids

into acid

[0.1800, 0.6100 + (0.0180, −0.0080) + (0.0020, 0.0000)] = acid 0.2000, 0.6020

which for regeneration requires the effect of −0.0020 upon the fraction of H_2SO_4 that can be calculated from Equation 8e.

N = 15.38 × (−20) = −307.6 kg. fortifying nitric acid
S = 30.77 × (−20) = −615.4 kg. fortifying sulfuric acid

Acid 0.1800, 0.6100 will therefore be converted into acid 0.2000, 0.6000 by

[5692, 1385 + (−308, −615)] = 5384, 770 kg. of the fortifying acids

Example 3

The effects of 100 kg. of the fortifying acids are, respectively,

$$(e_N)_t = 0.00015 \qquad (9e)$$

$$(e_S)_t = 0.00025 \qquad (10e)$$

The effect upon the total acidity of 5384, 770 kg. of the fortifying acid is

$$\begin{array}{r} 53.84 \times 0.00015 = 0.00808 \\ 7.70 \times 0.00025 = 0.00192 \\ \hline 0.01000 \end{array}$$

or acid 0.1800, 0.6100 is converted by 5384, 770 kg. of the fortifying acids into an acid with the total acidity of (0.7900 + 0.0100) = 0.8000, the total acidity of the specified mixed acid.

If the fortifying acids have the total acidity of 0.94 and 1.04, respectively, instead of 0.95 and 1.05 as assumed in the calculations, the total acidity of the mixed acid would deviate from the specification as follows: The calculated butt-up of approximately 6200 kg. will contain 6200 × 0.01 = 62 kg. of HNO_3 and H_2SO_4 less than assumed and the fraction of total acidity of the 106,200 kg. of mixed acid will therefore be less than 62/100,000, or 0.0006 less than assumed in the calculations—i. e., 0.8000.

Arithmetical Method

The design of the calculations for the butt-up by means of the results obtained in the discussion will here be shown applied to the nitrating system indicated in the nomenclature. However, it can be applied to any nitrating system.

It will be assumed that the fractions of the total acidity of the fortifying acids vary 0.01 from the average value, and that the butt-up has been found to vary 1000 kg. from the average butt-up of 5000 kg. of fortifying nitric acid and 1000 kg. of fortifying sulfuric acid. The error introduced by the calculations in the fraction of total acidity in the mixed acid must not exceed the value of 0.0001. Furthermore, it is necessary that the specification for the nitrating acids be subject to slight variations.

In order that the calculations involved in the changing of the fortifying acids may be simple, the calculation of the butt-up will be carried out by means of the average butt-up (5000, 1000) and Equations 7 and 8. The average butt-up is evaluated for the fortifying acids in use; Equations 7 and 8 are evaluated for the average composition of the fortifying acids used in the system.

The figures then needed for the calculation of the butt-up have been calculated in the examples, but can be viewed most easily when they are arranged schematically as shown by the following tabulation:

Effects upon Fraction of: HNO_3	H_2SO_4	Kg. of Fortifying Acid Nitric	Sulfuric
0.0180	*−0.0080*	5000	1000
0.0001	0.0000	34.62	19.23
0.0000	0.0001	15.38	30.77
	Check factors:	*0.00015*	*0.00025*

Used acid 0.1800, 0.6100 (Example 2)

0.1800	0.6100		
0.0180	−0.0080	5000	1000
0.1980	0.6020		
0.0020		692	385
		5692	1385
	−0.0020	− 308	− 615
0.2000	0.6000	5384	770
		5400	750

Check: Acid 0.1800
0.6100
54 × 0.00015 = 0.0081
7.5 × 0.00025 = 0.00188
0.79998

When the fortifying acids are changed the figures printed in italic are the only ones that will change their value. For the fortifying acids 0.60, 0.34 and 0.00, 1.04 these figures will be calculated to be 0.0180, −0.0086, 0.00014, and 0.00024, respectively.

The calculations for acid 0.1800, 0.6100 are then

0.1800	0.6100		
0.0180	−0.0086	5000	1000
0.1980	0.6014		
0.0020		692	385
		5692	1385
	−0.0014	− 215	− 431
0.2000	0.6000	5477	954
		5500	950

Check: 0.6100
0.1800
0.0077
0.00228
0.79998

For the fortifying acids 0.61, 0.35 and 0.00, 1.06 the butt-up for acid 0.1800, 0.6100 is 5196, 642 rounded 5200, 650. The total acidity check gives 0.80001.

It will be noted that in the calculated examples the deviation of the total acidity is less than 0.0001. The maximum deviation of the total acidity will occur when 1000 kg. of the butt-up are calculated by means of Equations 7 and 8 and the fortifying acids have their maximum deviations from the average value. Under these conditions the total amount of acids—HNO_3 and H_2SO_4—in the regenerated acid deviates 10 kg. from the amounts assumed in the calculations. The total acidity of the regenerated acid will therefore deviate less than 10/100,000 = 0.0001 from the specification 0.8000. However, the check will always give the correct value for the total acidity.

If the variations in the composition of the fortifying acids had been larger, there could be calculated several schemes each covering appropriate parts of the ranges within which the fortifying acids vary.

If the composition of the used acid is such that the calculated butt-up deviates more than 1000 kg. from the average butt-up of 6000 kg., the calculations can be repeated using (5000, 1000 ±500, 100) kg. of the fortifying acids as the preliminary butt-up.

If the specification for the nitrating acid is changed within 0.001, the error introduced in the total acidity of the regenerated acid is less than 0.00006 for a butt-up of 6000 kg.

Since three significant figures are sufficient, it is permissible to use a slide rule for the multiplications.

Graphical Method

In this method the adjustment of the preliminary butt-up is read from a graph, thus eliminating all multiplications.

Equations 5*e* and 6*e* are represented in an e_n versus e_s diagram by two systems of parallel lines drawn for equal hundreds of *S* and *N* in Figure 2. The graph is constructed most easily, however, by the use of Equations 1*e* and 2*e*, which are the parametric equations of the two straight lines through 0.0

$$(e_N)_n = -1.6\ (e_N)_s \qquad (A)$$

$$(e_S)_n = -0.444\ldots\ (e_S)_s \qquad (B)$$

The line represented by Equation *A* or Equations 1*e* goes through A_1 (0.0020, −0.00125), as this point according to Equations 1*e* represents the effects of 500 kg. of fortifying nitric acid upon the fractions of nitric and sulfuric acid in 100,000 kg. of any (used or preliminary mixed) acid. OA_1 is therefore the line representing Equation *A* or Equations 1*e*. Any point on OA_1 represents the effects of fortifying nitric acid in amounts directly proportional to the distance between the point and *O*. Therefore, the effects of equal hundreds of kilograms of fortifying nitric acid are easily found by dividing OA_1 in five equal parts. The line OB_1 representing Equation *B* can be constructed similarly.

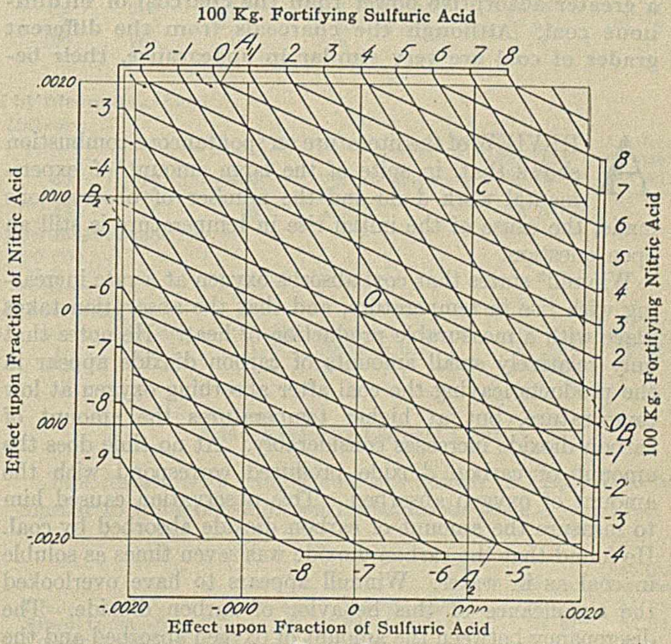


Figure 2

The effects of 500 kg. of fortifying nitric acid plus 500 kg. of fortifying sulfuric acid can be found by adding CA_1 and OB_1 geometrically and are therefore represented by point *C* (0.0010, 0.0010). The line A_1C represents all the effects that can be obtained by some amount of fortifying sulfuric acid and 500 kg. of fortifying nitric acid, and is therefore the 500 kg. fortifying nitric acid line. The graph can therefor be completed as shown by drawing lines parallel to OA_1 and OB_1 through the points representing the effects of equal hundreds of the fortifying acids. The readings for the calculations of the butt-ups mentioned under the arithmetical method have been indicated in the graph.

Schwartz[7] has mentioned a nitrating system which frequently mixed the acids with water. A graph similar to Figure 2 can easily be constructed for such a system.

The method of attack given in this paper has been employed by Redpath[3] in his graphical method and will prove equally useful in mathematical discussions of other problems concerning nitrating systems.

Acknowledgment

The writer wishes to express his appreciation to E. R. Hagan and Earl P. Raub for their assistance in preparing this paper.

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[7] *Z. ges. Schiess- Sprengstoffw.*, **8**, 288, 313 (1913).

Adsorption of Carbon Dioxide by Coal

By Eric Sinkinson and Homer G. Turner

Lehigh University, Bethlehem, Pa.

Coals of low and high grade, in a finely divided state, adsorb carbon dioxide. This gas is held very tenaciously, the last traces being removed with difficulty even under a vacuum of 0.003 mm. The adsorption is attended with a rise in temperature. Coals of high grade adsorb more carbon dioxide than do coals of low grade.

The natural charcoal content of high-grade coals has a greater adsorptive power than the charcoal of bituminous coal. Although the charcoals from the different grades of coal are very similar in appearance, their behavior towards carbon dioxide is strikingly different. The charcoals from the coals are relatively less active towards carbon dioxide than are artificially prepared charcoals. Indeed, the charcoals behave very much like the coals from which they are taken.

Carbon dioxide saturated with water is adsorbed to a greater extent than is dry carbon dioxide.

When a mixture of carbon dioxide and oxygen is employed, the degree of adsorption is directly proportional to the partial pressures of the gases in the mixture.

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A REVIEW of the literature on spontaneous combustion shows that, in spite of the large amount of experimental work done and the number of observations made, the cause of the initial rise in temperature is still an open question.

Winmill[2] states that coal absorbs oxygen at a rate increasing with rise in temperature, and that the absorption takes place with a measurable production of heat. He notes that only relatively small amounts of carbon dioxide appear in the products leaving the coal after absorbing oxygen at low temperature, but at higher temperatures the amount of carbon dioxide increases considerably. At no time does the amount of carbon dioxide produced correspond with the amount of oxygen absorbed. This observation caused him to measure the amount of carbon dioxide absorbed by coal. He found that the carbon dioxide was seven times as soluble in coal as in water. Winmill appears to have overlooked the significance of this behavior of carbon dioxide. The discrepancy between the amount of oxygen absorbed and the amount of carbon dioxide produced has also been noted by Chamberlin[3] and Katz.[4] Attention has been called to this behavior of carbon dioxide because of its bearing on the present investigation.

Parr and Kressman[5] point out that an initial stage of oxidation exists in bituminous coals, which does not result in the formation of carbon dioxide; and that coals vary widely in this property of absorbing oxygen without apparent production of carbon dioxide. This is regarded by them as an index of spontaneous combustion.

It is well known that porous substances such as charcoal have the property of adsorbing gases, the most easily liquefied gases being adsorbed to the greatest extent. Thus Travers[6] found the value $C\sqrt[3]{P}$ to be constant; where P is the pressure of carbon dioxide and C is the concentration of carbon dioxide within the charcoal. McBain[7] proved that when a gas is in contact with charcoal two processes take place, namely—a surface condensation, termed "adsorption," which occurs rapidly; and a slow diffusion into the interior of the charcoal, with the formation of a solid solution.

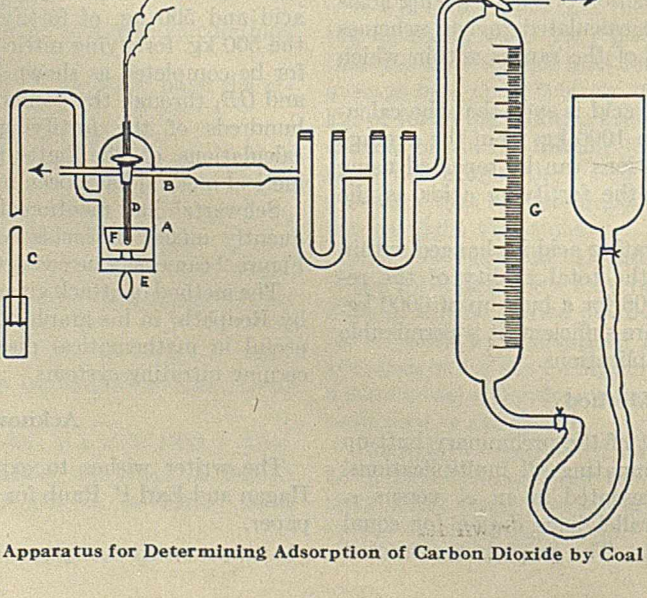
Apparatus

A 218-cc. flask, A, a side tube, B, fitted with a two-way stopcock in communication with a vacuum pump and 1000-cc. eudiometer, G, and a mercury manometer, C. A stopper, E, closes the bottom of the container and carries a cup-shaped vessel, F, to hold the coal under test. The sheath holding the thermocouple, D, is sealed in at the top of the apparatus, so that it is along the vertical axis of the container, and extends to the inside of the cup, F. The total volume of the flask and its connections is 235 cc. Provision is made for the insertion of drying tubes.

A 12-point copper-constantan thermocouple, in circuit with a temperature-recording potentiometer, measures the temperature. The thermocouple and recorder were calibrated with the cold junction in ice.

Procedure

Ten grams (except where otherwise noted) of the material under test are placed in the flask, which is closed and evacuated for 20 minutes by a mechanical pump. A manometer indicates the pressure. Pure carbon dioxide is admitted from the eudiometer. The volume of the gas is read off at atmospheric pressure after 45 minutes' contact with material under test. Any alteration of temperature is recorded by the potentiometer. Dry gas can be admitted to the apparatus by inserting three drying tubes—two of calcium chloride and one of phosphorous pentoxide—between the flask and eudiometer.



Apparatus for Determining Adsorption of Carbon Dioxide by Coal

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[1] Received June 4, 1925. Revised paper received March 8, 1926.

[2] *Trans. Inst. Mech. Eng.*, **46**, 563 (1913).

[3] *U. S. Geol. Survey, Bull.* **383**, 60 (1910).

[4] *Bur. Mines, Tech. Paper* **147**, 19 (1917).

[5] University of Illinois, *Bull.* **46**, (1910).

[6] *Proc. Roy. Soc.* (*London*), **78A**, 9 (1906).

[7] *Phil. Mag.*, [6] **18**, 916 (1909); Firth, *Z. phys. Chem.*, **86**, 294 (1914).

Table I—Adsorption by Charcoal

(*A*) *Coconut Charcoal (Absorbite)*

Grade	6–14	14–24	24–48	48–80	80 and finer
Temperature rise, ° C.	4.5	7.2	7.2	4.5	4.5
Volume at N. T. P.,[a] cc.	345	369	360	345	340

(*B*) *Charcoal from Mammoth Vein of Morris Ridge Stripping near Mt. Carmel, Pa. (Anthracite)*

Grade	14	20	28	35	48	65	100	150	200
Temperature rise, ° C.	4.0	4.0	3.9	3.5	3.7	3.0	3.0	3.0	2.7
Volume at N. T. P., cc.	146	159	153	139	127	120	101	100	93

	Per cent	Ash-free Per cent
Volatile matter	3.79	3.83
Fixed carbon	95.23	96.16
Ash	0.98	

(*C*) *Charcoal from Bituminous Coal, Freeport Vein, Indianola, Ind.*

Grade	14	20	28	48	100
Temperature rise, ° C.	1.2	1.2	0.8	0.5	0.9
Volume at N. T. P., cc.	16	20	19	24	24

	Per cent	Ash-free Per cent
Volatile matter	22.34	27.38
Fixed carbon	59.25	72.62
Ash	18.40	

[a] N. T. P. = normal temperature and pressure.

Table II—Adsorption by Anthracite Coal

Mammoth, Forge Split Coal, Nanticoke, Pa.

Grade	14	20	28	35	48	65	100	200
Temperature rise, ° C.	1.4	1.7	3.8	2.5	2.5	2.5	4.0	4.25
Volume at N. T. P., cc.	80	106	146	141	175	190	206	197

	Per cent	Ash-free Per cent
Volatile matter	4.98	5.22
Fixed carbon	90.62	94.78
Ash	4.40	

Table III—Adsorption by Bituminous Coal

(*A*) *Locality Unknown*

Grade	14	20	28	35	48	65	100	200
Temperature rise, ° C.	1.0	1.2	1.0	1.0	0.75	1.0	1.0	0.75
Volume at N. T. P., cc.	15	21	17	28	27	35	59	49

	Per cent	Ash-free Per cent
Volatile matter	35.28	46.80
Fixed carbon	40.10	53.20
Ash	18.40	

(*B*) *Bituminous Coal from Tioga County, Pa.*

Grade	20–40	40–60	60–80	80–100	100–200
Temperature rise, ° C.	1.3	1.0	1.0	1.0	1.0
Volume at N. T. P., cc.	49	54	60	54	55

(*C*) *Bituminous Coal from Miller Seam*

Grade	3–4	4–6	6–8	8–10	10–14	20–40	40–60	80–100	100–200
Temperature rise, ° C.	0.0	0.0	0.0	0.5	0.0	1.0	1.0	1.5	1.5
Volume at N. T. P., cc.	11	13	14	16	19	22	23	22	22

	Per cent	Ash-free Per cent
Volatile matter	19.40	21.15
Fixed carbon	72.29	78.85
Ash	4.31	

Adsorption by Charcoal

The figures for coconut charcoal show that highest temperatures are obtained with grades 14 to 48. The volumes of gas adsorbed in a given time follow the same order as the temperatures.

A comparison of (*A*) and (*B*) in Table I makes it evident that the natural charcoal from the Morris Ridge stripping follows the same order of temperature rise and volume of gas adsorbed as the artificial charcoal.

Although the charcoal in (*C*) was specially selected from the bituminous coal and appeared similar to that obtained from the anthracite given in (*B*) the effects as shown in (*C*) are much smaller. This indicates that charcoal from anthracite is more active than the corresponding charcoal from bituminous coal.

Adsorption by Anthracite Coal

It will be noted that whereas the charcoal from the anthracite (Table I (*B*)) reaches a maximum activity for a grade 20, the anthracite itself increases in activity up to 200 grade. (Table II)

Adsorption by Bituminous Coal

Bituminous, although found to be less active than anthracite, nevertheless shows a similar behavior, as shown in Tables III and IV.

Table IV

Comparison of Bituminous Coal and Charcoal from Freeport Vein

(30-gram samples)

	BITUMINOUS COAL		CHARCOAL	
Grade	80-finer		80-finer	
Rise in temperature	2.6° C.		1.0° C.	
Volume at N. T. P.	112 cc.		45 cc.	
	Per cent	Ash-free Per cent	Per cent	Ash-free Per cent
Volatile matter	30.36	31.34	22.34	27.39
Fixed carbon	66.52	68.66	59.26	72.61
Ash	3.12		18.40	

Adsorption by Cannel Coal

The results with cannel coal are shown in Table V to be similar to those obtained with bituminous coals.

Table V

			Per cent	Ash-free Per cent
Grade	80-finer	Volatile matter	43.56	44.35
Rise of temperature, ° C.	1.0	Fixed carbon	54.67	55.65
Volume at N. T. P., cc.	40	Ash	1.77	

Comparison of Various Anthracites

At this stage a number of anthracites that differed in appearance were examined. These coals were all graded to 80 mesh and finer, to insure a complete homogeneity of the components. Ten-gram samples were used in each test. The following samples were tested:

(1) Lansford, grain free coal
(2) Mineral charcoal from Mammoth Vein, Mt. Carmel, Pa.
(3) Buck Mt. Vein, Lee Split, Nanticoke, Pa.
(4) Mammoth, Nanticoke, Pa.
(5) Primrose, Mills Split, Nanticoke, Pa.
(6) Primrose, Oak Hill, Pa.
(7) Cameron Colliery, Shamokin, Pa.

All the coals are anthracites from the southern, western, middle, and northern fields of Pennsylvania. (1) is the structureless brilliant jet coal commonly used for the manufacture of ornaments. It shows no laminations, and no charcoal layers or lenses. Coals (3) to (7), inclusive, show more distinctness of lamination with various amounts of mineral charcoal. (2) is a pure mineral charcoal from the Mammoth Vein.

It was anticipated that the activity of the anthracites towards carbon dioxide would be proportional to the amount of mineral charcoal contained in them. Yet Table VI shows that (1), no visible charcoal in it, has a greater adsorption of carbon dioxide than (2), which is entirely mineral charcoal. On the other hand, the temperature rise with (2) is greater than with (1).

Table VI

Sample	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Temp. rise, ° C.	2.4	3.6	3.6	3.6	4.8	4.8	4.2
Volume at N. T. P., cc.	160	75	160	156	244	136	80
Analysis (Per cent)							
Volatile matter	3.46	3.79	4.4	4.98	6.82	6.39	12.38
Fixed carbon	93.53	95.23	93.85	90.62	89.39	77.93	75.11
Ash	3.01	0.98	1.75	4.40	3.79	15.68	12.51
Ash-Free Basis							
Volatile matter	3.48	3.83	4.47	5.22	7.09	7.58	14.16
Fixed carbon	96.42	96.16	95.52	94.78	92.91	92.48	85.85

It will be noticed further that the greatest rises of temperature after adsorption are obtained with the coals that are distinctly laminated such as (6) and (7).

It seems clear that charcoal, *per se*, is not the chief factor in the adsorption of carbon dioxide by anthracite; for a definite adsorption is obtained with sample (1), which shows no charcoal, either macroscopically or microscopically.

Comparison between Freshly Mined Anthracite and Old Sample

In order to determine whether there is a difference in activity between a freshly mined sample and a stale one, samples of anthracite were collected in half-inch lumps in the mine and sealed in bottles filled to capacity. The results are given in Table VII.

Table VII

Anthracite, No. 8 Vein from Cameron Colliery

						Per cent
Grade	20	20	28	28	Volatile matter	7.11
State of sample	Fresh	Old	Fresh	Old	Fixed carbon	85.04
Temperature rise, ° C.	0.6	0.9	1.0	0.5	Ash	7.85
Volume at N. T. P., cc.	32	20	38	25		

These figures indicate that the freshly mined sample is a little more active towards carbon dioxide than the old sample.

To confirm these results, 10-gram samples of Morris Ridge stripping (charcoal) were pumped and subjected to the action of oxygen, then repumped and carbon dioxide added. The results were then compared with those obtained by the direct addition of carbon dioxide to the same coal after pumping, the time factor being the same in both cases. The results are given in Table VIII.

Table VIII

Charcoal from Anthracite, Morris Ridge Stripping, Mt. Carmel, Pa.

Grade 150	With O_2	Followed by CO_2	With CO_2
Temperature rise, ° C.	1.5	2.5	3.0
Volume at N. T. P., cc.	14	83	101

Tests with Dry and Saturated Carbon Dioxide

The carbon dioxide employed in the previous experiments was stored over a mixture of equal parts of glycerol and water, and therefore was saturated with water vapor at the temperature of the experiments. To determine the influence of moisture on the rise in temperature dry carbon dioxide and saturated gas were employed in turn (Table IX).

Table IX

Primrose, Mills Split, from Nanticoke, Pa.

(30-gram sample, 80 and finer)

Condition of gas	Dry CO_2	Saturated CO_2
Temperature rise, ° C.	7.7	11.65
Volume at N. T. P., cc.	450	551

From Table IX it is evident that moisture, in the presence of carbon dioxide, plays a part in influencing the rise in temperature.

The increased activity shown by the saturated carbon dioxide over that of the dry gas may possibly be explained by the difference in the chemical nature of the two. In one, dry CO_2 only is employed, whereas in the other we have actually carbonic acid, $CO_2.6H_2O$.

Retention of Carbon Dioxide by Coal

The discrepancy between the amount of oxygen adsorbed and the amount of carbon dioxide produced, a discrepancy commented upon by Winmill, Katz, Chamberlin, and others, and noted in the early part of this paper, was investigated.

Thirty grams of anthracite from Nanticoke, ground to pass 80 mesh, were placed in the apparatus. After evacuation carbon dioxide was admitted until atmospheric pressure was reached. The gas was then pumped back off the coal into the eudiometer. When the pressure over the coal was the same as at the start, the volume was read off. The difference in volume of carbon dioxide pumped back and the amount originally admitted was 75 cc., which represents the amount of carbon dioxide retained by the coal under a vacuum of 0.003 mm. This experiment was repeated, with the same result.

A blank experiment was run to test the tightness of the empty apparatus. The carbon dioxide could be charged into the apparatus and pumped back again with a loss of about 2 cc. From this it would seem that in experiments on the oxidation of coal by the adsorption of oxygen the volume of carbon dioxide recovered is a doubtful index of the amount of oxidation taking place.

Selective Adsorption

It is well known that the most easily liquefied gas is most readily adsorbed by porous substances. From this theoretical consideration it is also well known that carbon dioxide is more readily adsorbed than oxygen. If the difference is sufficiently marked a selective adsorption would be expected from a mixture of carbon dioxide and oxygen. Accordingly, tests were made in which the action of oxygen, and then of mixtures of oxygen with carbon dioxide, were tried. Table X indicates that the adsorption is proportional to the partial pressure of the carbon dioxide in the gaseous mixture.

Table X

Primrose, Mills Split, from Nanticoke, Pa.

(30-gram samples, 80 and finer)

Gas	CO_2	O_2	50% CO_2	25% CO_2	10% CO_2	5% CO_2
Temperature rise, ° C.	6.72	1.0	3.6	2.8	2.0	2.0
Volume at N. T. P., cc.	442	19	290	277	258	192

Conclusions

The greater adsorptive power of anthracitic over bituminous coals appears to lie in the character of the carbon present rather than its quantity. This explanation is suggested by a comparison of the anthracitic coal from Cameron Colliery (7, Table VI) with bituminous coal from Miller Seam (Table III, C) where the fixed carbon obtained by the proximate analyses is almost the same; and yet the adsorptive values are respectively 80 and 22 cc. for 10-gram samples of similar grade. Also the elevation of temperature is of the same order—viz., 4.2° and 1.5° C.

The lower activity of the charcoals from coals as compared with artificially prepared charcoals may be due to an infiltration of bituminous matter into the pores of the adsorbent. Inhibition also may be the result of condensation of oxidation products previously adsorbed in gaseous form. There is also the possibility that the material commonly identified as mineral charcoal is not charcoal.

It has been shown that with coal carbon dioxide will produce elevations of temperature above those obtained with oxygen under similar conditions.

It is suggested, therefore, that carbon dioxide plays an important role in spontaneous combustion, by producing an immediate rise in temperature, through the adsorptive energy between the coal and the gas.

Acknowledgment

The authors wish to thank C. E. Underwood and S. R. Kulp, of the Bethlehem Steel Company, who kindly supplied the analyses of the coals used in this work; also David White, Chief Geologist of the United States Geological Survey, for his suggestions and helpful criticisms during the course of this study.

Oil Extraction in Theory and Practice[1]

By Louis C. Whiton

101 Park Ave., New York, N. Y.

The United States has been singularly behind in the development of the use of solvent extraction for the manufacture of oil from oleaginous-bearing seeds. No doubt this has been due to the fact that in the early days, before a very extended use had been found for vegetable oils, there were considerably larger quantities of oil available in the seed than could be sold. Hydraulic pressing, which recovered a relatively small proportion of the oil, was therefore the logical line of development.

In Europe the same story could be told, but since 1900 the demand for vegetable oils has considerably increased and the conservation of this supply was forced upon the owners of the hydraulic press plants, who had been wasting valuable product and selling it in the meal at about one-fourth of its real value as oil. Many of them turned to solvent extraction, and it is now a highly developed industry abroad, particularly in the Mediterranean countries.

There has been somewhat of an upheaval in the vegetable oil industry in the United States in the last five years. Changed labor conditions due to the war may have had something to do with it, but the fact remains that the development of this industry has reached the stage where it is unprofitable and shortsighted to give away 100 to 150 pounds of an oil worth about 10 cents a pound, with each ton of meal, which sells for only 2.5 cents a pound.

In order that the solvent extraction plant may successfully replace the hydraulic press, it is necessary for it to fulfil the following requirements:

1—It must produce absolutely solvent-free oil and meal so that the former may be used for the refinery and the latter as cattle food.

2—It must be as free from complications as possible, so that expensive technical supervision is not required.

3—The machinery must be such that small plants of the size of the average cotton-oil plant in the South can be run at a profit for a short season.

Anyone who has had occasion to review the patents on solvent extraction has found this process to be one of the favorite playthings of the theorist; but contrary to many types of machinery, solvent extraction resolves itself almost to the crude formula—the fewer the refinements the better the extractor. In other words, the laboratory Soxhlet on a commercial scale is almost the ideal. Some of the complications which seem reasonable to the best engineers until they have had experience in the solvent extraction field are pointed out here.

Freeing Oil and Meal of Solvent

From the point of view of labor and cost of installation it seems reasonable to collect the oil-bearing solvent from a number of extractors and to distil this from a large still. From a practical standpoint it heats the oil too long producing an inferior quality of oil, and requires intensive steaming and heating at the end to eliminate traces of solvent from a large quantity of residual oil. It is far better to use small stills connected with each extractor and to have each still finish off the oil from a single extraction. The oil will thus be less violently treated and of a better quality. Since a still requires practically no labor there is no disadvantage from that standpoint.

The idea that oil cannot be freed of solvent is illogical when one realizes that products much more difficult to remove are eliminated in a refinery deodorizer and that the oil still operates upon the same principle; that is, it must separate an oil, boiling at a high temperature, from a low boiling solvent, which, needless to say, should be properly rectified beforehand.

The elimination of solvent from the meal is also accomplished by steaming. It is a natural conclusion that this solvent can be more easily volatilized if the material is stirred. This is partially true. Nevertheless, the mechanical difficulties of stirring several tons of solid particles of meal that is not surrounded by liquid must be considered. It requires a fair amount of power, offers possible leaks at stuffing boxes, and is a movable part with which it is wise to dispense if possible. The only successful method of avoiding the agitator, used by one of the manufacturers of extractors, consists in draining the meal thoroughly of solvent and then introducing solvent vapors so that there will be a large quantity of vaporous material to steam rather than liquid, which first must be vaporized.

Discharging the Extractor

Discharging the extractor by a mechanical agitator theoretically appears to be worth while. An extractor of the proper size (5000 pounds capacity) can be discharged about as rapidly by hand. The danger of the agitator at this point is considerable. If the meal is improperly deodorized the solvent mixed with the air which enters when the discharging door is open becomes an explosion hazard, as the agitator might strike a spark against a stray stone.

Size Units

Theoretically, it should not be much more difficult to extract 50,000 pounds at a batch than 5000 pounds. It probably is not more difficult, but it is practically impossible to deodorize the residual meal. Several years ago a large flaxseed extraction plant, which attempted to extract immense quantities in each charge, was built in the United States. It was impossible to deodorize the meal properly and this unfortunate experience has probably hindered considerably the development of solvent extraction in the United States. Both the Bataille and the Scott extractors are small, because the European experience upon which

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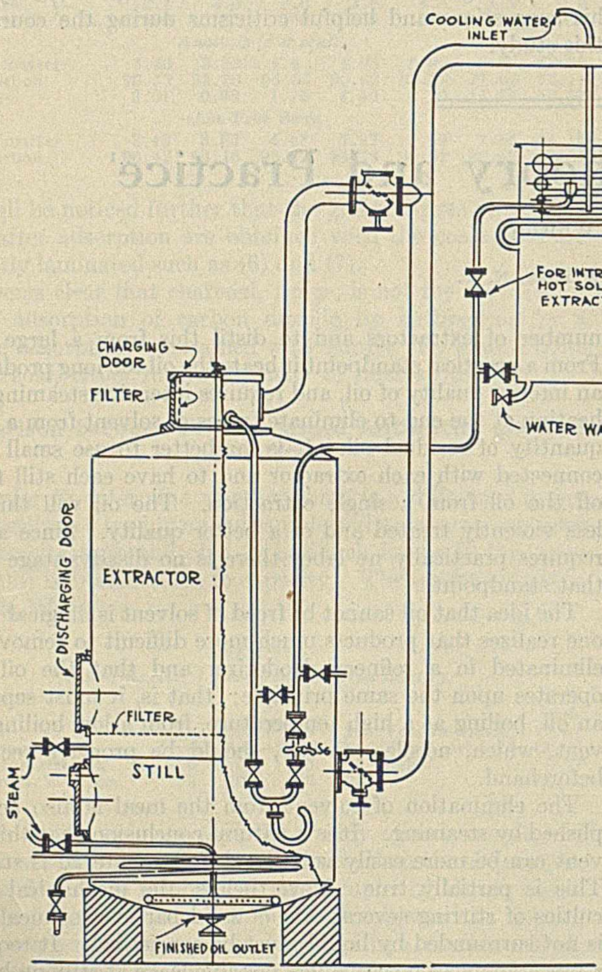
[1] Presented under the title "The Practical *vs.* the Theoretical Side of Oil Extraction," as a part of the Symposium on Cotton and Its Products and Vegetable Oils before the joint session of the Divisions of Biological, Cellulose, Industrial and Engineering, and Agricultural and Food Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

Independent Unit Bataille Extractor, without Agitators, Series Flow, or Circulating Pumps
Circuit of solvent is from solvent tank to extractor, then draining through filter to still, and returning to solvent tank via condenser



their designs are based has indicated that 5000 or 6000 pounds capacity is the maximum size of which an extractor should be built.

Continuous and Series Extractors

The writer knows of only one installation for continuous extraction in this country. Since this plant is no longer in operation, it is probable that continuous extraction has not yet been fully developed. It is doubtful whether it is feasible, because the capacity per dollar invested is probably not so great as the intermittent extractor plant and the complications are manifold.

The semicontinuous or series extractor is an arrangement of four to six in a row with the solvent passing from one extractor to the next. Theoretically, this should save steam by producing a more concentrated oil solution. Practically, it is inadvisable because it means a complicated series of piping and circulating pumps handling hot solvent, both of which increase the solvent loss, which rapidly nullifies any saving in steam. The greatest difficulty is due to the necessity of charging and discharging all the extractors in the series at the same time. This is evidently uneconomical and the practical result is that certain extractors are out of service part of the time awaiting their turn. In addition, if difficulty is experienced with one extractor it holds up the rest of the series. Individual unit extractors, independent one from the other, will be found to turn out a greater amount at the end of the year and operate more economically than the series arrangement.

Extraction Period

The extraction period is comparatively simple provided the extractor is kept filled with solvent and the proper arrangement of filters is used. The solvent that is generally employed in Europe is a cut of gasoline boiling between 60° and 80° C., with neither light nor heavy ends, and which is available almost anywhere on the continent. Trichloroethylene is also in general use because it is not inflammable. Benzene is excellent except that it frequently produces a darker oil. Carbon tetrachloride is not used because it is too easily hydrolyzed and attacks the metal container. Ethylene dichloride is similar to trichloroethylene except that the manufacturers claim that it hydrolyzes less. It has the disadvantage of being slightly inflammable (about one-sixth as much as gasoline), and costs about the same per pound as trichloroethylene.

In conclusion, the extractor having no movable part, no pumps or agitators, which is of a proper size and independent in operation from any other extractor, is the most practical type. It certainly is the type that most appeals to the oil-plant operator who wishes to avoid the use of expensive technical supervision and undoubtedly in the next ten years many of the cotton-oil plants will have adopted such an extractor and thereby recover sufficient oil to pay for the actual operation of their plants.

New Cereal Breeding

The question as to the possibility of raising new cereal varieties, which are able to endure and profit by increased nitrogen fertilization, is a problem of very great importance to future cereal breeding.

By the use of nitrogen superior sorts of cereals with constantly increasing straw-stiffness have been developed to replace the old, local varieties. Plentiful nitrogen fertilization in northern latitudes is known to influence the cereals markedly. The growth becomes luxuriant and the length of the straw and the number of straws per plant increase, while the leaf surfaces also increase in size. The vegetative period becomes longer, but at the same time the plants become more susceptible to certain diseases as yellow rust, powdery mildew, etc.

Cereal breeding, at least in northern districts, must aim at improving the sorts in the direction of greatest possible straw-stiffness, earliness in maturity, and resistance against disease. Breeding work which aims at an increase in nitrogen fertilization, probably goes parallel with the breeding work which drives at an increase in yielding power.

The cereals would no doubt profit in increase in the stiffness of straw, earliness in maturity, and resistance against diseases by an increase in nitrogen application.—[Brief of paper by Dr. Hermann Nilsson-Ehle, director of Swedish Plant Breeding Station, presented at Biarritz, April, 1926.]

Analysis of Boron Alloys[1]

By N. Tschischewski

Academy of Mines, Moscow, Russia

When alloys of boron with iron or other metals are dissolved in acids the boron is converted into boric acid. The existing methods for the determination of this boric acid have been found too complicated and otherwise unsatisfactory. A method used by the author during investigations on the system iron-boron[2] gave very good results but required too much time. The method described in this paper gives exact results and is rapid.

Iron and other metals—manganese, nickel, chromium, etc.—are precipitated from sulfuric acid solution by electrolysis. The resulting solution contains sulfuric and boric acids, which are titrated with caustic soda, making use of the property of boric acid not to react with methyl orange but to be colored by phenolphthalein.

Preliminary Procedure

Sulfuric acid must be used as the solvent, as nitric and hydrochloric acids form compounds which interfere with titration of the boric acid. A flask with a condenser (Figure 1) must be used because of the volatilization of the boric acid.

One half to 1 gram of the alloy is dissolved in 10 to 15 cc. of sulfuric acid (1:3) and heated until a black, flaky precipitate is formed. Three to 5 drops of 30 per cent hydrogen peroxide are then added and the volume is brought up to 100 cc. by the addition of water.

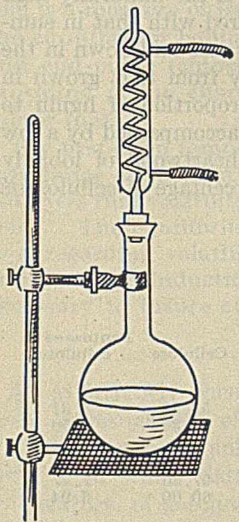


Figure 1

For each test 25 cc. of the solution are taken, any excess sulfuric acid is neutralized with 1 *N* alkali solution free from carbon dioxide, and before electrolysis 3 to 5 drops of strong sulfuric acid are added.

Electrolysis

The Kollock and Schmidt method of electrolysis is used, with the following modifications: Instead of a revolving platinum electrode, a glass stirrer through which a wire was passed is used as an electrode; a larger vessel and more mercury are used since a greater amount of solution—35 cc. instead of 15 cc.—is to be electrolyzed.

The electrolytic apparatus used is shown in Figure 2. Into a glass 6.5 cm. wide and 11 cm. high, mercury is poured to a height of 2.5 to 3 cm. and in the mercury is placed a platinum wire. Another platinum wire, bent into a spiral and passed through a glass stirrer, is used for the electrode. This is attached to a turbine making 350 r. p. m.

This glass is placed in cold water to reduce the heat due to electrolysis and thus prevent volatilization of boron. The temperature is thus kept below 30° C.

With a current of 5 amperes and 10 to 15 volts, after 25 to 30 minutes, iron, manganese, nickel, etc., precipitate completely, forming an amalgam with mercury. The precipitation is complete when no coloration is produced with Gmelin's salt on taking out a small quantity into a capillary tube. Nickel precipitates much more quickly than iron.

When the electrolysis is completed the liquid is siphoned while the electric current is still passing. It is then diluted with water up to 250 cc., from which samples are taken for titration.

Titration

There must be no carbon dioxide in the caustic soda or sulfuric acid. The caustic soda solution should be approximately 0.01 *N* and its titer established by means of fused boron anhydride. The sulfuric acid should have a corresponding strength. For preliminary titration a 0.05 *N* solution of caustic soda is used to avoid too large an amount of liquid. A little glycerol is added to the solution to prevent hydrolysis of sodium metaborate before the complete conversion of all the boric acid into this salt. Methyl orange and phenolphthalein are used as indicators.

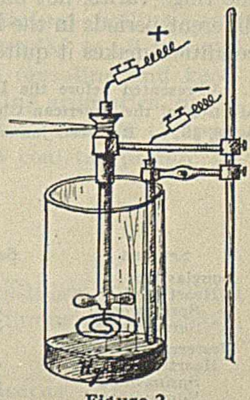


Figure 2

Fifty cubic centimeters of the solution are pipetted out and transferred to a conical flask and 3 to 5 drops of methyl orange added to produce a strong red coloration. A 0.05 *N* solution of caustic soda is then added until the solution becomes a faint rose color. Weak alkali solution is then added until the color changes to orange. The exact moment of completion is noted by comparing the color with a previously prepared standard, and should be carefully determined. In order to get good results it is sometimes better to add a little excess alkali and neutralize with 0.01 *N* sulfuric acid.

All the sulfuric acid is neutralized in this way and the solution contains only boric acid. This is titrated by adding a few drops of phenolphthalein and titrating with caustic soda to the production of a rose color, due to hydrolysis of sodium metaborate. To prevent this hydrolysis glycerol is added, so that the end point of the titration may be determined more easily. Glycerol often shows an acid reaction,

Data on Check Experiments

Total volume of solution, 250 cc.
Volume taken for electrolysis, 25 cc.
Volume after electrolysis, 100 cc.

R. p. m. of stirrer, 350
Current, 5 amperes
E. m. f., 12 volts

Material	Gram	Solution	Soln. taken for titration Cc.	$B(OH)_3$ Present Gram	$B(OH)_3$ Detd. Gram	Temp. ° C.	Time of electrolysis Min.	Remarks
$FeSO_4$ $B(OH)_3$	0.1942 0.1428	H_2O 100 cc. H_2SO_4	50	0.00714	0.00700	40	30	Fe completely pptd.
$FeSO_4$ + $NiSO_4$ $B(OH)_3$	0.2791	H_2O H_2SO_4	50	0.0139	0.00137	30	25	
Fe Ni B(OH)	0.2944 0.2884 0.3428	H_2SO_4 10 cc. H_2O_2 3 drops H_2O 240 cc.	25	0.00153(B)	0.00158(B)	30	25	Ni pptd. first

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[1] Received September 10, 1925.

[2] Tschischewski and Herd, *J. Russ. Met. Soc.*, **1915**, No. 4.

and should be neutralized with caustic soda before being used, using phenolphthalein as indicator.

Check Experiments

A series of check experiments was made to show the accuracy and value of this method. Pure boric acid or fused boric anhydride was dissolved with iron and nickel sulfides and in another experiment boric acid and alloys of iron and nickel were dissolved in sulfuric acid containing a few drops of hydrogen peroxide, in a flask provided with a condenser. The results are shown in the accompanying table.

Chemistry of Wood[1]

IX—Springwood and Summerwood

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

U. S. Forest Products Laboratory, Madison, Wis.

The purpose of the work here reported is to compare the chemical composition of springwood and summerwood in the annual rings of trees.

Springwood differs from summerwood in physical appearance, type of cell structure, density, and thickness of cell wall. It was thought that analysis of the springwood and summerwood of representative species might show characteristic differences in the chemical composition of the two bands of growth and thus afford an additional means of classifying woods. The principal differences discovered were general, however, rather than individual.

Preparation of Samples for Analysis

In separating springwood from summerwood, it is most practicable to cut the bands from thin (3-mm.) cross sections of wood having wide annual rings of growth. The width of the rings varies, not only in different trees, but also during different periods in the history of the same tree. The latter condition makes it quite difficult to obtain suitable rings for springwood and summerwood samples representing a number of consecutive years in both the sapwood and heartwood of a tree. When suitable cross sections and areas of wood have been selected, the springwood and summerwood zones are split apart with a sharp wood chisel and removed separately. This material is ground and sieved to 80- to 100-mesh size.

The methods of analysis are the same as described in the fifth paper of this series.[2] The results obtained for springwood and summerwood of the six representative species chosen for study are recorded in the accompanying table.

Lignin and Cellulose

The outstanding result of this work is the uniformly high yield of lignin in springwood as compared with that in summerwood, showing that the wood substance laid down in the early growing season differs chemically from that grown in the late growing season. The high proportion of lignin to total constituents in the springwood is accompanied by a low percentage of cellulose except in the heartwood of loblolly pine and of red alder, in which the percentage of cellulose is

Analyses of Springwood and Summerwood of Some American Woods

(Results in percentages on oven-dry (105° C.) samples)

			Solubility in								
Species	Sample	Moisture	Cold water	Hot water	1% NaOH	Acetic acid	Methoxyl	Pentosans	Lignin	Cellulose	Pentosans in cellulose
Douglas fir:											
Heartwood:											
Springwood	318	6.92	3.00	4.67	15.10	0.62	3.48	11.97	32.61	55.95	8.31
Summerwood	319	4.82	2.15	3.76	14.56	0.71	3.40	9.89	29.20	59.35	6.50
Western white pine:											
Heartwood:											
Springwood	316	4.78	3.76	5.16	22.08	1.42	3.68	10.07	26.30	57.60	7.27
Summerwood	317	3.47	4.29	5.42	21.47	1.40	3.85	9.82	25.30	60.00	6.94
Loblolly pine:											
Sapwood:											
Springwood	302	2.82	3.28	3.49	11.11	1.28	4.05	11.59	28.12	58.06	8.78
Summerwood	303	3.39	2.18	2.97	11.01	1.41	4.18	11.12	26.78	61.21	8.69
Heartwood:											
Springwood	304	3.13	7.50	7.16	18.14	1.00	6.17	12.77	26.78	53.44	11.52
Summerwood	305	2.16	7.64	6.44	21.19	1.11	6.88	12.12	24.18	52.87	11.20
Catalpa:											
Sapwood:											
Springwood	312	6.76	9.12	12.44	34.45	3.33	4.44	22.39	23.64	50.37	25.94
Summerwood	313	4.04	7.29	10.11	27.97	4.45	4.10	22.35	18.68	56.49	22.09
Heartwood:											
Springwood	314	6.17	7.51	11.65	34.27	3.39	4.97	21.33	24.29	50.38	24.77
Summerwood	315	4.76	2.69	5.26	24.15	4.07	3.37	21.50	19.35	58.45	21.24
Red alder:											
Heartwood:											
Springwood	300	3.25	3.02	4.01	20.49	3.69	5.18	22.37	24.70	58.38	22.80
Summerwood	301	3.16	3.03	4.16	21.15	3.60	5.55	23.36	23.03	57.16	22.90
White ash (sp. gr. 0.68):											
Sapwood:											
Springwood	308	3.93	8.84	10.99	23.71	3.11	5.49	21.45	24.35	49.73	23.14
Summerwood	309	2.89	6.13	8.18	19.32	2.76	5.44	20.51	23.68	54.17	20.15
White ash (sp. gr. 0.71):											
Sapwood:											
Springwood	306	4.52	4.04	4.95	17.71	2.76	6.34	20.34	25.57	53.56	19.50
Summerwood	307	3.51	2.90	3.57	14.57	2.49	6.01	19.35	23.52	57.66	16.97
White ash (sp. gr. 0.81):											
Sapwood:											
Springwood	310	5.34	7.35	8.38	22.95	2.74	5.80	20.17	23.94	52.34	18.56
Summerwood	311	3.54	6.85	7.34	19.64	2.41	5.74	20.52	20.83	57.47	14.33

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[1] Presented before the Division of Cellulose Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924. Received January 28, 1926.

[2] This Journal, **14**, 1050 (1922).

also slightly higher in the springwood. Even here, however, the ratio of lignin to cellulose is higher in the springwood than in the summerwood.

An explanation of why the lignin constitutes a larger percentage of the total wood substance in springwood than in summerwood is already available in a recent paper by Ritter,[3] in which it was shown that the lignin is located partly in the cell wall mixed with the cellulose and partly in the middle lamella with very little, if any, other substance present. If the ratio of lignin to cellulose in the cell wall, exclusive of the middle lamella, is the same in springwood as in summerwood, then the lignin in the middle lamella, which constitutes a greater proportion of the total wood substance in the springwood, would account for the higher proportion of lignin in springwood than in summerwood.

The remaining determinations showed no uniform differences in chemical composition between springwood and summerwood, although a tendency was apparent toward higher percentages of (*a*) pentosans in the springwood, (*b*) pentosans in the isolated springwood cellulose, and (*c*) extractives in the springwood.

Conclusions

1—A higher percentage of lignin exists in springwood than in summerwood. An explanation is offered for the different lignin yields in the two bands of growth.

2—Cellulose forms a larger percentage of the total wood substance in summerwood than in springwood.

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[3] This Journal, 17, 1194 (1925).

Relation between Fuel Deposition Temperature and Equilibrium Boiling Point[1]

By W. A. Whatmough

Friern Watch Ave., North Finchley, London N. 12, England

The determination of "fog points" of combustible mixtures in internal combustion engines under road-running conditions confirms the conclusion of Barnard and Wilson that the equilibrium boiling point of a motor fuel is a measure of its volatility. In the writer's opinion the equilibrium boiling ranks equally with the first-drop and end-point temperature of an Engler distillation in providing prime characteristics for the evaluation of a motor fuel.

The first-drop temperature, or preferably the temperature range of the first 10 or 20 cc. of an Engler distillate, indicates that volatility which gives ease of "starting from cold." The equilibrium boiling point provides information regarding volatility of the motor fuel as a whole, and fixes the induction pipe and mixture temperatures necessary to insure stability of its combustible mixture under normal conditions. Along with the end-point temperature of an Engler distillation, the equilibrium boiling point affords definite criteria in regard to prevention of crank-case dilution. However, it is the equilibrium boiling point that indicates when the induction pipe temperature is dangerously low, irrespective of whether this is due to low volatility of the fuel available, or to prevailing climatic conditions.

The results show that the equilibrium boiling point test for mixture stability can be extended to all types of motor fuels, whether hydrocarbons (gasoline and kerosenes), or mixed motor fuels containing aromatics, naphthenes, and alcohols. The writer has found it to apply also to fuels containing vaporizable coal-tar products—naphthalenes, phenols, and cresols.

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American chemists are already familiar with the investigations of Barnard and Wilson[2] on the vapor pressures of equilibrium solutions prepared from motor fuels, from which data the dew point, or fuel-deposition temperature, of gasoline-air or kerosene-air mixtures can be calculated.

Several years ago the writer[3] determined the "fog points," or fuel-deposition temperatures, in engine manifolds—these being temperatures at which visible droplets of liquid form in a flowing fuel-air mixture made from gaseous components. Fuel is deposited as liquid at the fog-point temperature when the velocity of the mixture is low and if the "induction" pipe is at or below the fuel-deposition temperature.

Figure 1 depicts graphically a somewhat surprising agreement between the results obtained by two researches utilizing methods differing radically in principle. Thus Barnard and Wilson measure, in the absence of air, the vapor pressure of a relatively stationary column of mixed saturated vapors of hydrocarbon gases, which is representative of their equilibrium solution. The author's observations relate to a mixture of fuel gases from an equilibrium distillate admixed with air and flowing as a pulsating stream through the induction pipe of an internal combustion engine.

Arrangement of Apparatus

Figure 2 shows the general arrangement of apparatus used for determining the fog points of motor fuel–air mixtures under road-running conditions. The liquid fuel is evaporated in a "flash"-type balanced pressure boiler under equilibrium conditions—i. e., at the same rate as it is used. This boiler is shown in greater detail in Figure 3 and consists of an outer vessel, *G*, with an internal heater consisting of a metal block, *E*, intersected by vertical saw cuts. The block *E* is continuous with the plate *P*, bearing the staggered pins *C* for collecting heat from the exhaust gases entering at *A*, which pass downwards and then upwards as shown by the direction of the arrow. Heat is transmitted from above downwards, and only the top layer of the liquid fuel is at its boiling point, the liquid being pushed away if gas is generated faster than it is used. The level of the boiling liquid falls or rises to meet any variable demand for fuel gas.

The boiler is part of the Keith-Whatmough system[4] of dry gas carburation for utilizing heavy or nonsprayable

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[1] Received August 15, 1925. Revised paper received April 5, 1926.

[2] *J. Soc. Automotive Eng.*, 9, 313 (1921); 12, 287 (1923); This Journal, 17, 428 (1925).

[3] Keith and Whatmough, *Proc. Inst. Automotive Eng.*, 17, Pt. I, 363 (1922).

[4] English Patent, 184,266 (1922).

motor fuels. The fuel-gas capacity of the boiler, and quality control governor attached, is only a few cubic inches, or sufficient for a few revolutions of the engine. The conditions of gas production are accordingly precisely those used by the writer[5] for determining equilibrium boiling points, inasmuch as fuel is boiled continuously as it is fed from a variable level feed with balance pipe, or pressure-equalizing tube, between the float chamber and boiler. The vaporized fuel from the boiler becomes superheated during its passage towards the governing device used to maintain the combustible mixture at a constant strength. The working temperature of the fuel gas (240° to 260° C.) is ordinarily well above the saturated vapor temperature of motor fuels at pressures approximately atmospheric, the variation being ±1 pound per square inch from prevailing pressure of the atmosphere.

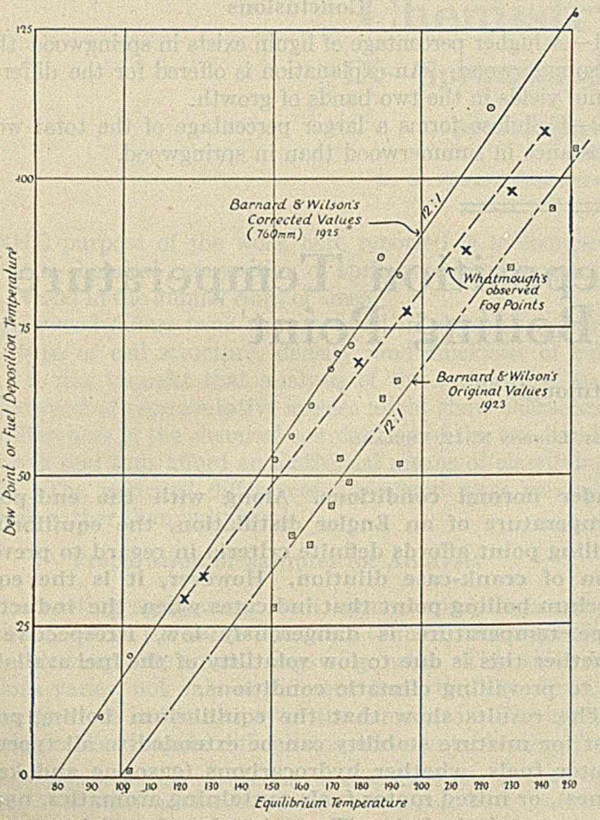

Figure 1—Equilibrium Boiling Point Temperatures of Motor Fuels *vs.* Their Fuel-Deposition Temperatures

For the heaviest fuels, kerosene, and Edeleanu (aromatic) extracts, with equilibrium boiling points above 240° C., an aluminum boiler was found to be advantageous as it enabled the attainment of gas temperatures of 280° to 320° C. The device for maintaining a definite ratio of fuel gas and air in the combustible mixture, independent of variation in engine speed or load, consists of a floating piston attached to a sliding valve, which takes charge of fluctuations of pressure in the boiler and at the same time regulates the pressure of the (governed) fuel gas. The pressure gradient in the fuel gas between that in the piston chamber and the mixing point is the same as that existing in the air flow between the end of the pressure loading pipe to the back of the piston chamber and the point of admixture of fuel gas and air. Accordingly, whatever variations occur in the air stream are reproduced in the gas flow. The quantity of mixture flowing to the engine is regulated by the throttle in the ordinary way. The quality can be set by varying the contracted passageway by the quality control valve between the governed gas pressure and the mixing point, this restricted gas passage being in practice a narrow annulus (and not as drawn). The original paper[3] should be consulted for details of the relationships of the varying flows of air, gas, and combustible mixture.

Tests

Road tests with a Ford van (total weight with load 2800 pounds) was used as a check on fuel efficiency. The mixture strength used was that which gave good power with reasonable economy. The following mileages per British gallon were consistently obtainable on a known test route when using commercial motor fuels in the form of *dry* combustible mixtures: aviation petrol, 30; No. 1 petrol, 32; benzol, 38; paraffin, 35. The weakest possible running mixture (corresponding to 15 air to 1 fuel gas) gave about 20 per cent increase in mileage—e. g., benzol 44 miles per gallon. On this basis the running mixture for economy with power and comfort was probably a close approximation to 12:1 air-fuel ratio.

Thermometers were used for checking the temperatures of the combustible mixture and its gaseous components. The readings available were: (1) temperature of in-going air, (2) fuel gas temperature, (3) mixture temperature before throttling, and (4) mixture temperature after throttling.

Naturally the temperature of the air supply varied according to season and distance of intake from heated surfaces, advantage being taken thereof to vary conditions in order to obtain critical fuel deposition temperatures. Thus a mixture temperature of 40° C. would be made up as follows:

	° C.
Air temperature (atmospheric)	21
Temperature rise due to hot fuel gas	11
Temperature rise due to heating of air supply by surroundings	8
	40

Fog points at temperatures below 40° C. were determined in winter. With petrol mixtures the Venturi mixing nozzle was unheated. A throat heated by exhaust gases was used for relatively heavy nonsprayable fuels with fog points above 60° C. Gain or loss of heat from the induction pipe was prevented as far as possible by lagging.

It is necessary to stress two important points in connection with the determination of dew-point and fog-point temperatures. First, the temperature reading when fuel deposition occurs is due to a wet bulb effect as in hygrometry, and owing to condensation or evaporation the temperature registered by the thermometer may depart considerably from that of the surrounding mixture saturated with vapor, particularly if the latter is stagnant. Induction-pipe temperatures from wet mixtures are misleading owing to evaporation effects when the mixture is receiving external heat. The thermometer bulb is cooled by evaporation of liquid from its surface and frequently registers temperatures 10° C. below that of the mixture. Second, the production of dew or fog depends upon an actual flow of heat which is normally from combustible to mirror or induction pipe. With engine tests a heat balance can be attained between combustible mixture and external atmosphere (heated by engine), this occurring ordinarily in the induction manifold of a Ford engine between 40° and 50° C. Above this temperature insulation by lagging prevents that extreme readiness of fuel deposition which is characteristic of heavy fuels and which increases with heat loss through induction pipe to external air. With very volatile fuels the opposite effect is evident. The great difficulty with the lightest petrols is to exclude external heat because the latent heat of hydrocarbon fuels is so low that a small amount of heat transmission from external air through the induction pipe is sufficient to cause re-evaporation of condensed vapor and prevent fuel deposition. In determining fog-point temperatures these effects are greatly minimized

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[5] This Journal, 18, 43 (1926).

by the large volume of combustible mixture flowing through a well-insulated induction pipe. It is obvious that the temperature registered by the thermometer as the fuel-deposition temperature may deviate from the temperature at which the combustible mixture is fully saturated—i. e., with fuel vapor in equilibrium with liquid fuel—but any error is in the direction at which fuel deposition occurs under road-running conditions.

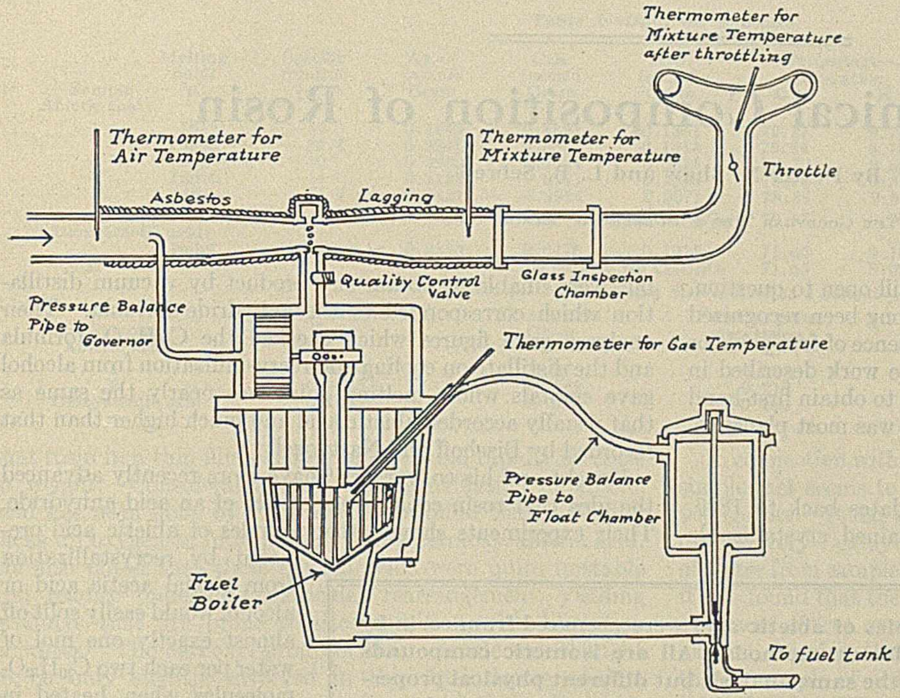

Figure 2—Apparatus for Determining Fog Points

Results

The data in Table I are from actual determinations of both fog-point temperature and of equilibrium boiling point on the same fuel. The percentage position of the latter on the Engler distillation curves is included.

Table I—Relation between Fog Point and Equilibrium Boiling Point

Fuel	Temperature of fog formation ° C.	Equilibrium boiling point ° C.	Approx. percentage position of equilibrium boiling point on Engler distillation curve
Petrol I	29	121	60
Petrol III	33	127	70
Light kerosene (50%) Benzol (50%)	69	179	65
Heavy kerosene (50%) Benzol (50%)	77	196	65
Light kerosene (50%) Light tar oil (50%)	88	215	75
Light kerosene	98	225	80
Heavy kerosene	108	242	85

The actuality of the relationship between equilibrium boiling points and fuel-deposition or fog-point temperatures in an engine manifold is obvious from Figure 1, and from the following considerations:

(1) Fuel was boiled under equilibrium conditions in a balanced pressure boiler.

(2) Mixture of constant quality was maintained automatically.

(3) Fuel gas, air, and mixture temperatures were available as check. Temperatures were not affected by heat changes due to evaporation or condensation until actual fog point was attained.

(4) "Fog" or visible drops of fuel were formed in a moving column of combustible mixture made from gaseous components. Irregularities of temperature readings due to evaporation from the thermometer bulb or condensation of liquid thereon are minimized owing to the flowing mixture cleansing the bulb, as is evident in (6) below.

(5) The critical temperature at which fog is formed (fog point) is readily determined with a motor fuel under running conditions, with an accuracy between 1° and 2° C.

(6) Fog formation is accompanied by deposition of liquid when engine is running slowly. This layer of liquid fuel is snuffed up bodily upon speeding up. When this occurs the engine shows the characteristic signs of bad distribution—staggering or uneven running.

Gruse[6] has determined by a direct method the dew points of gasolines identical with those investigated by Barnard and Wilson, and thereby comparable with the writer's fog points. There is a difference of 20° C. or more between Gruse's "dew-point temperatures and the writer's fog points," and the discrepancy is so great that it is advisable to retain the earlier name "fog point" to indicate formation of visible vapor in the induction manifold of an internal combustion engine. The difference is inexplicable unless metastable conditions of supersaturated vapor are present with Gruse's method, owing to slow heat transmission in a relatively stagnant mixture (see notes on wet bulb effects above). It is agreed that poor admixture and wet (evaporating) fuel gas would tend to give low dew points but these defects are decidedly absent in the experimental procedure used by the writer.

Conclusions

The linear relationship between observed fog points and equilibrium boiling points of the author on the whole agree with those calculated by Barnard and Wilson for light fuels (petrols, gasoline, benzol mixtures, etc.) but diverge steadily on progressing towards heavy fuels, the observed fog point for kerosene being some 10° C. lower than the calculated dew point. This is understandable if it is remembered that fog formation is consequent upon loss of latent heat of vaporization and that this heat loss increases directly according to temperature difference between the fuel mixture and external air. Thus at higher temperature more rapid loss of heat by radiation will result in quicker fog formation. This is in accord with actual conditions during carburation of internal combustion engines.

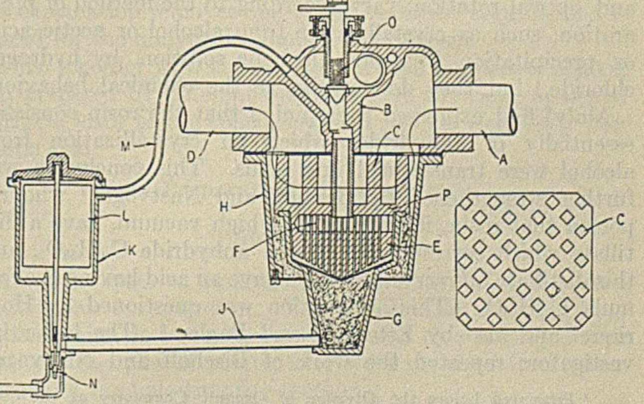

Figure 3—Equilibrium Boiler Employed for Producing Dry Gas from Motor Fuels

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[6] This Journal, 15, 796 (1923).

Table I and the writer's previous article show that the 85 per cent point of an Engler distillation does not represent with sufficient accuracy the equilibrium boiling point of all types of mixed motor fuels. Accordingly, it is desirable to make a direct determination of the equilibrium boiling point. With this exception, the writer's results confirm Barnard and Wilson's conclusions, their corrected 12:1 line on Figure 1 undoubtedly corresponding to ideal mixtures and conditions.

The foregoing data prove that equilibrium boiling point is a real measure of the volatility of a motor fuel under running conditions. Furthermore, the equilibrium boiling point of a motor fuel is an accurate guide to the induction-pipe temperature necessary to maintain a combustible mixture in a stable condition and thereby prevent fuel deposition.

The Chemical Composition of Rosin[1]

By Dexter N. Shaw and L. B. Sebrell

The Goodyear Tire & Rubber Co., Akron, Ohio

Samples of abietic acid were prepared from rosin by five different methods. All are isomeric compounds having the same analysis but different physical properties. Abietic acid readily oxidizes to a monoxy derivative, which on heating readily evolves water forming monoxyabietic anhydride. In the absence of oxygen abietic acid does not evolve water and the corresponding anhydride is not formed.

Rosin must, therefore, be composed of free acids rather than acid anhydrides.

THE exact composition of rosin is still open to question. That it is of an acid nature has long been recognized but whether this is due to the presence of free acids or of acid anhydrides is still disputed. The work described in this paper was carried out in an endeavor to obtain first-hand information as to which of these theories was most plausible.

Historical

The work on the chemistry of rosin dates back to 1826, when Baupe[2] first showed that it contained crystallizable acids. A large amount of work has since been published on the rosin acids and on their relation to the original composition of rosin. Acids of different physical properties have been isolated by different investigators and variously named abietic, pinic, sylvic, sapinic, etc. The empirical formula of these acids was first determined as $C_{20}H_{30}O_2$ by Trammsdorf,[3] who analyzed the copper salt, which formula has now been generally accepted. The physical properties of the acids, such as the melting point and optical rotation, vary according to the method of preparation, such as crystallization from alcohol or acetic acid, or precipitation from an alcoholic solution by hydrogen chloride,[4] but they do not change the chemical behavior.[5]

Maly[6] first expressed the opinion that the rosin consisted essentially of anhydrides which on crystallization from alcohol were transformed into acids. This conclusion was further strengthened by Bischoff and Nastvogel,[7] who reported that rosin, if distilled in a high vacuum, gave a distillate which corresponded to the anhydride $C_{40}H_{58}O_3$, and this distillate on recrystallization gave an acid having the formula $C_{20}H_{30}O_2$. This assumption was questioned by Henrique[8] and also by Esterfield and Bagley.[9] The latter investigators repeated the work of Bischoff and Nastvogel, but were unable to obtain any product by vacuum distillation which corresponded to the anhydride formula. Their analyses gave figures which checked the $C_{20}H_{30}O_2$ formula and the distillate on cooling and recrystallization from alcohol gave crystals whose melting point was nearly the same as that usually accorded abietic acid and much higher than that recorded by Bischoff and Nastvogel.

Knecht and his co-workers[10] have more recently advanced the idea that rosin consists essentially of an acid anhydride. Their experiments showed that samples of abietic acid prepared by recrystallization from glacial acetic acid or alcohol would easily split off almost exactly one mol of water per each two $C_{20}H_{30}O_2$ molecules when heated in an atmosphere of dry carbon dioxide. The residue remaining after the evolution of the water gave on analysis results in accordance with the formula $(C_{20}H_{29}O)_2O$.

Stock[11] concluded that rosin consisted of three free isomeric acids, which he designated as α, β, and γ abietic acids. These he isolated according to the method of Tschirch by means of their metallic salts.

Ruzicka and Meyer[12] and Ruzicka and Schinz[13] were unable to verify the work of Knecht that abietic acid was dehydrated by heating to 190° C. in carbon dioxide for 8 hours. They claimed that in their experiments not a trace of water was liberated under these conditions. Knecht later offered the objection that the acids which Ruzicka investigated were not the same as those which he used for the following reasons: (1) they were prepared by different methods, (2) they were not identical in melting point, and (3) that heat distillation forms a new acid by pyrogenic action which is not present in appreciable amounts in commercial rosin. He offered further experimental evidence of the correctness of his results. Steele,[14] assuming that rosin was composed of the anhydride, developed a method for the preparation of abietic acid by supposedly hydrolyzing the anhydride with glacial acetic acid. On the other hand, Schorger[15] crystallized some vac-

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[1] Presented before the Division of Organic Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925. Received October 28, 1925.

[2] *Ann. chim. phys.*, **1826**, 108.

[3] *Ann. Pharm.*, **13**, 169 (1835).

[4] Fluckinger, *J. prakt. Chem.*, **101**, 235 (1867).

[5] Aschan, *Chem. Ztg.*, **34**, 149 (1924).

[6] *Ann.*, **132**, 249 (1864).

[7] *Ber.*, **23**, 1921 (1890).

[8] *Chem. Rev.*, **1899**, 106.

[9] *J. Chem. Soc. (London)*, **85**, 1238 (1904).

[10] Knecht and Hibbert, *J. Soc. Dyers Colourists*, **35**, 148 (1919); **39**, 338 (1923).

[11] *Farben-Ztg.*, **27**, 156, 221, 287, 353, 416 (1921).

[12] *Helvetica Chim. Acta*, **5**, 315 (1922).

[13] *Ibid.*, **6**, 833 (1923).

[14] *J. Am. Chem. Soc.*, **44**, 1333 (1922).

[15] *Ibid.*, **45**, 1339 (1923).

uum-distilled rosin from anhydrous petroleum ether and found on titration with caustic that it corresponded with the free acid ($C_{20}H_{30}O_2$) and not the anhydride. This, Schorger believed, refuted the work of Knecht, Steele, and others that rosin was composed essentially of the anhydride.

Table I—Data on Samples

Sample	Melting point ° C.	Specific rotation $[\alpha]^{20}_{D}$	Wt. of sample Gram	CO_2 formed Gram	H_2O formed Gram	Percentage composition C	Percentage composition H	Molecular Weights: Wt. sample in alcohol Gram	Molecular Weights: 0.134 *N* NaOH to neut. Cc.	Molecular Weights: Mol. wt.
Abietic acid:										
1	161	−59	0.1545	0.4491	0.1351	79.27	9.78	0.5705	14.05	303.02
2	Indef.	−24.4	0.2247	0.6538	0.1844	79.34	9.12	0.6420	15.85	302.27
3	145	+30	0.0930	0.2684	0.0825	78.70	9.86	(0.3428)	8.45	302.74
4	Indef.	−14	0.2133	0.6291	0.1828	79.79	9.55	0.4845	11.9	303.83
5	161	−81.7	0.3427	0.9914	0.2971	78.89	9.65			
				Calculated for $C_{20}H_{30}O_2$		79.47	9.93			302.24
Dioxyabietic acid:										
	Indef.	Inactive	0.2350	0.6176	0.1925	71.66	9.10	0.3180	7.10	334.26
				Calculated for $C_{20}H_{30}O_4$		71.85	8.98			334.24

Cryoscopic Method Using Stearic Acid as a Solvent

Sample	Wt. of sample Gram	Stearic acid Gram	Freezing point depression ° C.	Cryoscopic constant	Mol. wt.
Abietic acid:					
1	0.5759	21.976	0.39	4.5	302.34
2	0.3015	21.549	0.210	4.5	302.16
Dioxyabietic acid	0.1520	20.063	0.100	4.5	342

The tendency of abietic acid to undergo oxidation has not thus far been mentioned in connection with the dispute concerning the composition of the rosin. Weger[16] first showed that rosin in a thin film exposed to air would rapidly increase in weight. Considerable work on the oxidation of abietic acid has been done by Fahrion,[17] who found that it readily picks up oxygen to form a dioxy and a tetraoxy abietic acid. He also noted that these oxygen acids were quite unstable and readily underwent molecular rearrangement, yielding products that are prone to decomposition with liberation of water. The carboxyl group of the molecule was thought to be only slightly involved in this final decomposition. The process is essentially one of autoxidation. It is interesting in connection with the work described in this paper to note that among the oxidation products of abietic acid Aschan[5] has isolated an oxy acid which he believes is monoxy abietic acid, $C_{20}H_{30}O_3$.

The great tendency for abietic acid to undergo oxidation is further shown by the recent work of Veitch and Sterling,[18] who found that autoxidation of rosin had begun on storage for a week at ordinary temperature. Knecht[10] has also verified the work of Fahrion[17] and found that the abietic acid readily takes up two atoms of oxygen per each mol of acid.

Purpose of Present Work

From this brief review of the literature[19] it seems difficult to decide whether rosin consists of free acids or whether these are not formed from their anhydrides by the method of preparation. The present investigation was concerned with establishing the exact composition of natural rosin for commercial purposes and to determine if possible the cause of the differences in the results obtained by Knecht and those obtained by Ruzicka and Shinz.

In the present work the authors have prepared five samples of abietic acid by as many different methods.[19] It was their intention to show that all the samples were identical in chemical composition but that their physical properties varied with the method of preparation used. In this, they have been successful. They wished, also, to ascertain why those who believe that rosin consists essentially of abietic anhydride could evolve water from abietic acid, by heating at 180° C. in an atmosphere of dry CO_2, while other investigators, failing to obtain such results, claim that rosin is essentially free abietic acid.

The analysis and physical properties of the acid which the writers prepared by crystallization from alcohol agrees well with the sample described by Knecht, while the sample obtained by distillation under high vacuum checks the one reported by Ruzicka and Meyer.

In connection with this evolution of water on heating, a very simple fact seems to have escaped the attention of other investigators. It has already been noted that rosin reacts with oxygen very readily. In attempting to check the evolution of water from samples of abietic acid heated in carbon dioxide, it was found that the gas must be carefully purified to remove all traces of free oxygen; otherwise the acid readily absorbs oxygen, forming the monoxyabietic acid. The results show that a sample of abietic acid heated in dry commercial carbon dioxide will readily evolve the theoretical amount of water necessary to form the monoxyabietic anhydride. The residue gives an analysis corresponding to this anhydride. This experiment was repeated using the same sample and the same source of carbon dioxide, which had first been carefully freed from oxygen, but under the same conditions as before no water could be driven off. The sample after heating analyzed for unchanged abietic acid.

It is believed that these facts explain the difference in the results noted by Knecht and Hibbert and those reported by Ruzicka and Schinz. The writers have shown that abietic acid in the absence of oxygen is not readily dehydrated and this explanation removes one of the strongest arguments advanced for the anhydride composition of rosin.

This, together with the fact that all the samples of abietic acid prepared by different methods gave the same analysis, $C_{20}H_{30}O_2$, leads to the conclusion that rosin is essentially free abietic acid.

Preparation of Samples

Abietic Acid

American rosin of the grades known as WWX and N was used in this investigation. The WWX rosin was the best grade obtainable while the grade N was of a slightly lower quality. Samples of abietic acid were prepared from rosin by each of the following five methods:

1—Recrystallization from glacial acetic acid after boiling for 2 hours, and further recrystallization from alcohol
2—Vacuum distillation of the acid prepared in (1)
3—Recrystallization from alcohol
4—Vacuum distillation of rosin
5—Material prepared as in (4) was recrystallized from alcohol

No attempt was made to secure the maximum yield by each of these processes. Recrystallization from acetic acid as

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[16] *Chem. Rev.*, **5**, 236 (1898).

[17] *Z. angew. Chem.*, **20**, 356 (1907).

[18] This Journal, **15**, 576 (1923).

[19] Since the completion of this paper an article by Dupont and Uzac (*Chimie & industrie*, Sp. No., 482-3, September (1925)) has appeared which confirms the conclusion that rosin is composed of free abietic acids.

described below gave 56 per cent of crystalline abietic acid; alcohol gave only 45 to 50 per cent, while by vacuum distillation 80 to 85 per cent of the rosin distilled over as abietic acid. It is reasonable to assume that the original rosin contained a much higher proportion of the free abietic acid but that the presence of small amounts of resinous material inhibited the crystallization of larger amounts. The larger amount obtained on vacuum distillation supports this conclusion.

The details of these preparations are as follows:

Sample 1. Grade WWX rosin was boiled for 2 hours with 98 per cent acetic acid. Upon cooling crystals separated, which were filtered and washed with alcohol. The product was subsequently purified seven times from alcohol.

Sample 2. Grade WWX rosin was heated with 98 per cent acid for 2 hours. Upon cooling crystals separated out, which were recrystallized once from alcohol. These crystals were then distilled at 15 mm. pressure and the portion collected which distilled between 230° and 250° C. The product set to a yellow, transparent glass without crystallizing. Owing to its supercooled condition there is no true melting point.

Sample 3. Grade WWX rosin was dissolved in hot alcohol and water was added until a slight turbidity resulted. Crystals formed after the solution was allowed to stand for some time. These crystals were filtered and recrystallized seven times from alcohol.

Sample 4. Grade N rosin was three times fractionally distilled in vacuum and the portion on the third distillation which boiled between 225° and 235° C. at 4 mm. pressure was collected. The mass set to a yellow, transparent glass with an indefinite melting point.

Sample 5. Grade N rosin was fractionally distilled three times and the portion on the third distillation which boiled between 225° and 235° C. at 4 mm. pressure was collected. The distillate was dissolved in alcohol and recrystallized six times from this solvent.

The data for the preparation of these samples together with their composition and physical properties, are given in Table I. From this table it will be seen that all the products prepared from rosin by each of the five different methods have the same empirical composition. The analyses all agree for the free acid instead of the acid anhydride.

Dioxyabietic Acid

The dioxyabietic acid, which has been previously described by Fahrion,[17] was prepared by dissolving the pure abietic acid in alkali and reprecipitating in a very dilute solution by dilute acid. This gave an extremely fine product which was dried very slowly in the air. It was then three times redissolved and reprecipitated in the same manner. This is necessary to obtain the whole sample as the dioxy acid.

Dioxyabietic acid had no definite melting point. At 78° C. the mass softened and at 94° C. it became a liquid.

The analysis and molecular weight, as well as its insolubility in petroleum ether, identify this acid with the dioxyabietic acid prepared and analyzed by Fahrion. The data on this acid are given in Table I.

Evolution of Water

Samples prepared by the five different methods given above were heated in a combustion tube for several hours at 180° C. The temperature was carefully controlled and the water evolved was collected in calcium chloride drying tubes. The first determination on each sample was made by passing dry commercial carbon dioxide over the samples, while in the second the free oxygen was first removed from the carbon dioxide by passing the gas over red-hot reduced copper spirals. In the first case water was evolved but in the second not a trace of water was found. The residue left in the tube was analyzed in both cases. In the former case the analyses corresponded to the monoxyabietic acid anhydride and in the second case the unchanged abietic acid was found. The presence of the monoxyabietic acid anhydride supports the fact that oxygen is needed for dehydration. These data are given in Tables II and III.

Table II—Evolution of Water in Commercial Carbon Dioxide

Sample	Wt. of sample Gram	Wt. of H_2O Gram		H_2O to form $C_{40}H_{58}O_5$ Per cent
Abietic acid:				
1	0.4312	0.0132		3.05
2	0.5472	0.0156		2.85
3	0.4535	0.0124		2.74
4	0.4496	0.0127		2.82
5	0.4738[a]	0.0144		3.04
			Calcd.	2.83
Dioxyabietic acid	0.3670	0.0242		6.5[b]
			Calcd.	2.69

[a] Heated 8 hours.
[b] Some dioxyabietic acid sublimed over into $CaCl_2$ tube.

Table III—Evolution of Water in Pure Carbon Dioxide

Sample	Wt. of sample Gram	Time of heating Hours	Wt. of H_2O Gram	Percentage composition C	H	ANALYSIS OF RESIDUE Residue Gram	CO_2 Gram	H_2O Gram
Abietic acid:								
1	1.2013	7	None	79.27	9.78	0.1545	0.4491	0.1351
2	0.9960	10	None	79.79	9.55	0.2133	0.6241	0.1826
3	0.9960	8	None					
4	1.8824	8	None					
5	0.7783	8	None					
Calcd. for anhydride				81.91%	9.89%			
Dioxyabietic acid	0.5382		0.0469[a] (8.70%)					

[a] Due partly to sublimed acid but water collected in cold part of tube.

Analysis of Residue of Samples Remaining after Evolution of Water

It has already been shown that when no water is evolved the residue remaining is unchanged abietic acid. Therefore, in order to prove that the samples from which water was evolved upon heating in commercial carbon dioxide were oxy acids instead of the straight acids the residues remaining after the heat treatment were analyzed, as shown in Table IV. The monoxyabietic anhydride must therefore hydrolyze on titration to the free acid.

Table IV—Analysis of Residue Remaining after Evolution of Water

COMBUSTION				MOLECULAR WEIGHT BY TITRATION			
Wt. of sample Gram	CO_2	Per cent C Calcd.	Per cent C Found	Wt. of sample Gram	0.13 *N* NaOH Cc.	Mol. wt. Calcd.	Mol. wt. Found
Monoxyabietic anhydride							
0.1864	0.5311	77.6	77.69	0.1961	4.6	318	318
Dioxyabietic anhydride							
0.2236	0.6666	73.99	74.55				

Potash Agreement Favors French Producers

The success of the provisional Franco-German potash pact, which expired May 1, in stimulating foreign sales and stabilizing production and prices paved the way for the recent preliminary conferences which led to a new agreement, according to the Department of Commerce. Trade Commissioner William T. Dougherty at Berlin, reports that the general scheme of the new agreement, which is for a period of ten years, follows that of the preliminary world agreement, except that France will be permitted to increase its share of the world market.

The 70:30 ratio of sales division between Germany and France is continued, up to combined foreign sales of 840,000 metric tons pure potash. Provision is made for a special extra 3000-ton delivery in the following year by the French Syndicate in case total sales reach only 825,000 tons. Any deliveries above 840,000 will be met by German and French syndicates on an equal basis.

If in the first four years the total foreign sales do not reach 840,000 tons, the French producers will receive in the fifth year a preference delivery of 8000 tons in place of the 3000 tons bonus. Provided the maximum of 840,000 tons is not reached in the fifth year, then the amount sold in excess of the highest previous annual sales will henceforth be divided on a 50:50 basis. For example, if after four years of the agreement, peak annual sales reached only 700,000 tons, and if in the fifth year they reached 800,000, the 100,000 tons would be apportioned on an equal basis to each country.

Some Factors Influencing the Weathering of Vulcanized Rubber[1]

By N. A. Shepard, Stanley Krall,[2] and H. L. Morris

The Firestone Tire & Rubber Co., Akron, Ohio

"Sun-cracking" has always been a factor in the compounding of rubber for use in articles exposed to sunlight or weather. Especially is this true where the rubber article is exposed in a stretched condition, as in the case of inflated spare tires.

This susceptibility of vulcanized rubber to crack or check when in a stretched or strained condition has been utilized in formulating an accelerated checking test for studying the deterioration of rubber compounds when exposed to the weather. This test has been used in determining the influence of cure, sulfur bloom, color, grade of rubber, reclaimed rubber, several filler pigments, several kinds of softeners, accelerators, and an antioxidant.

This work has shown that by the selection of the proper pigments, together with certain specifically protective materials, much can be done to improve the weathering of most types of rubber compounds.

IT HAS long been known that rubber deteriorates rapidly when exposed to the action of direct sunlight, especially if the rubber is under strain. The surface becomes crazed or more or less covered with checks or cracks, perpendicular to the direction of the strain. These cracks not only produce a very unsightly appearance, but also may even become so deep as to affect materially the useful life of a rubber product.

Cracking under the influence of light or weather is not the only type of cracking to which rubber products are susceptible. When vulcanized rubber, especially that compounded with large amounts of filler pigments, is subjected to repeated stresses—i. e., to flexing—cracking results, again perpendicular to the stress, which may closely resemble sun-checking. These two types of cracking must not be confused, as they are of quite different origin, the one arising from exposure to light and the other from repeated stretching or flexing.

Historical

The literature contains many references to the action of light on rubber. In 1902 Weber[3] wrote:

> The liability of India rubber goods of various descriptions, but more particularly tire covers, to develop, often to a very disagreeable degree, the defect known as sun-cracking is very generally recognized. It is the result of the oxidation of the India rubber by the atmosphere. The term "sun-cracking" might therefore appear to be a misnomer, but, as a matter of fact, it emphasizes very expressively the marked hastening of this oxidation through the influence of direct sunlight.

Work on this subject, however, pre-dates 1902 by more than thirty-five years. As far back as 1865 Spiller[4] investigated the changes produced in rubber under atmospheric conditions. It was he who proved that oxygen functions in the change. Burghardt,[5] in 1883, made the following statement:

> One fact has been amply verified by experiment and research—that is, that the destruction of India rubber, however brought about, is simply a more or less degree of oxidation of the mass entering into the composition of the rubber goods. *** Light also exerts an injurious action, but only in conjunction with other destructive agents, which it assists in their action; alone, it probably would not produce any injury to perfectly good normal vulcanized caoutchouc.

Fickendey[6] has demonstrated that this last conjecture of Burghardt's is correct, at least as far as raw rubber is concerned. Fickendey exposed his samples to direct sunlight in sealed tubes filled with oxygen, nitrogen, hydrogen, and carbon dioxide, respectively. To quote his words: "Even after weeks, the rubber in the hydrogen, in the nitrogen, and in the carbon dioxide was unchanged. The rubber in the oxygen, on the other hand, had become sticky."

Aside from the action of sunlight there are several other factors, such as heat, which have a direct bearing on the rate of oxidation of rubber. Heil and Esch,[7] in writing of soft vulcanized rubber, state that "the oxidation is favored by the action of sunlight and high temperatures as well as by admixtures which increase the porosity of the rubber." Ahrens[8] corroborates this statement in regard to the effect of temperature, finding that "warming accelerated the action very much."

The relative speed of oxidation of raw rubber as compared with that of vulcanized rubber has been studied by several investigators. Ahrens[8] states that vulcanization with sulfur alone retards the oxidation but that many compounding ingredients tend to accelerate it. This statement agrees with the findings of Peachy and Leon[9]—namely, that vulcanized rubber, whether resinous or resin-free, oxidizes far less rapidly than the corresponding raw rubber, although the amounts of oxygen ultimately taken up are of the same order in the two cases. Henri[10] also finds that

> When one subjects to the action of ultra-violet light pure gum sheets vulcanized either in the cold or hot, one sees immediately a very great difference; at the end of twenty hours (which time is sufficient to produce a marked change in the unvulcanized rubber), there is no appreciable change in the vulcanized rubber. It is necessary to prolong the action of the rays to 48 and even to 72 hours in order to observe a change in the surface of the rubber; this surface then cracks and the rubber loses likewise its elasticity. Thus vulcanization of rubber protects it to a great extent against the action of ultra-violet rays.

It is thus an established fact that sun-checking or sun-cracking is an oxidation process aided by both light and heat.

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[1] Presented before the joint meeting of the Division of Rubber Chemistry and the Akron Section of the American Chemical Society, Akron, Ohio, February 22 and 23, 1926.

[2] Fisk Rubber Co., Chicopee, Mass.

[3] "The Chemistry of India Rubber" **1902**; cf. 4th Impression, p. 229 (1912). Chas. Griffen & Co., Ltd.

[4] *J. Chem. Soc. (London)*, **18**, 44 (1865); cf. *Bull. soc. chim.*, **4**, 231 (1865).

[5] *J. Soc. Chem. Ind.*, **2**, 119 (1883).

[6] *Kolloid-Z.*, **9**, 81 (1911).

[7] "The Manufacture of Rubber Goods," **1909**, p. 22. Chas. Griffin & Co., Ltd.

[8] *Kunststoffe*, **3**, 478; cf. *C. A.*, **8**, 1515 (1914).

[9] *J. Soc. Chem. Ind.*, **37**, 56T (1918).

[10] *Caoutchouc & gutta-percha*, **7**, 4372 (1910).

The part played by ozone in the deterioration of rubber has long been recognized,[11] but that it specifically functions in sun-checking has only recently been demonstrated. Early in 1925 Asano[12] pointed out the deleterious action of ozone, and the part it plays in the deterioration of rubber under the influence of light. Later Haushalter,[13] in measuring the corona effect on rubber, called attention to the cracking or checking produced, and attributed it to ozone. His views are supported by experimental evidence. Still more recently Peritor[14] suggested ozone for use in testing rubber goods. Williams[15] demonstrated the connection between ozone and sun-checking in this laboratory in 1923.

Some work has already been published on the effect of different compounding ingredients on the oxidation of rubber. Henri,[10] during the progress of his work on unvulcanized rubber with ultra-violet light, found that

> In general, sheets of rubber containing different mineral fillers suffer change much more slowly than pure rubber. However, this change depends on the nature of the filler; certain substances, such as litharge, retard the deterioration of the rubber by the rays, while others, such as antimony sulfide, accelerate the change.

Traces of copper salts have been shown to be extremely active in bringing about the deterioration of rubber in both the raw and cured condition.[16] Powdered glass, according to Ditmar,[17] exerts a protective influence against oxidation which is directly proportional to the amount present. This same investigator found also that the presence of zinc oxide in vulcanized rubber increases the oxidation tendency. He was unable, however, to find any regularity between the percentage of zinc oxide and the degree of oxidation. It is of interest in this connection that pure zinc oxide has been found to have no effect on the rate of oxidation of linseed oil.[18]

In addition to mineral compounding ingredients and other filler pigments, some work has been published with reference to the influence of oils and resins. It is well known that vulcanized[19] rubber, as well as raw rubber[20] from which the resin has been removed, oxidizes extremely rapidly. Addition of such materials might be expected to be protective. This was early found to be true, especially in the case of vaseline, paraffin, and similar petroleum products. In 1881 Kreusler and Budde made a paraffin treatment of vulcanized rubber the subject of a patent.[21] This consisted in dipping the finished product into a paraffin bath at 100° C. and holding it there for a few seconds up to several minutes, depending on the size of the article. Articles so treated are claimed to be highly resistant to light and atmospheric influences, and not subject to hardening or cracking. Himmelbauer & Company[22] recommend a similar process, using vaseline or ceresin wax.

The first investigator to refer to the use of paraffin and such materials in compounding was Weber,[3] who mentions that there was a material on the market for the prevention of sun-checking which consisted of a mixture of paraffin with sulfur and small quantities of beeswax and tallow. He also mentions paraffin alone, stating that its effect is to "reduce the liability of India rubber to oxidation in general and to sun-cracking in particular." Ahrens[22] stated that in 1899 he added ceresin to a tread stock on the mixing mill and then exposed tires with half-and-half treads, one-half containing ceresin and the other none. The protective action in the presence of ceresin he ascribed to the chemically inert bloom or coating of ceresin. Vaseline and paraffin are classed with ceresin in their protective action. Chertoff[23] attempts to cover by patent certain vegetable oils (including palm oil, rosin oil, pine oil, and turpentine) in admixture with resins (including rosin, dammar, and copal), to prevent rapid deterioration and hardening of rubber with age. Paraffin, mineral, and other nondrying oils are also suggested by Repony.[24]

Numerous other materials, such as nitrogen compounds (aniline[25] and related substances), phenolic bodies (beta-naphthol, resorcinol,[26] and tannin,[27]) and nitro compounds[28] have been advanced for use in the protection of rubber, crude and synthetic, raw and vulcanized, against oxidation. Many of these materials fall into the class of substances known as "antioxidants," and as such should be of interest in the prevention of sun-checking. However, as far as the writers are aware, nothing has been published concerning the specific influence of these materials on sun-checking.

The work recorded in this paper is confined chiefly to a series of exposure tests covering the influence of various compounding ingredients on sun-checking. These ingredients include several fillers, softeners, accelerators, and an antioxidant. In addition, reclaimed rubber has been compared with several grades of raw rubber.

Procedure

Most of the work recorded in the literature was carried out with oxygen gas, working with very thin films of rubber. The experimental details were laborious and the purely surface phenomena, in which there is the greatest interest, were not readily observable. Weber,[3] in order to avoid the long, tedious process of making exposure tests for prolonged periods in direct sunlight with the uncontrollable conditions of weather and season, devised a wet oxidation with acetone peroxide. This method also has its limitations —the reagent is highly explosive in the dry state, and Weber admits that the method is only a fairly reliable measure of the relative susceptibility of the samples to sun-cracking.

It appeared to the writers that direct-exposure tests would be of the most practical application provided the action of the weather could be accelerated, because these tests would be carried on under conditions more nearly approximating the actual weathering conditions of the rubber in service. Various references to the rapid deterioration of rubber when stretched are found in the literature. In his early experiments on the oxidation of rubber threads, Thomson[29] finds that "rubber threads, which are stretched or pinched or strained in any way, are more easily oxidized at the parts subjected to such strain than threads in their normal condition." The same author points out that ozonized air has but little action on unstretched or unstrained rubber but that it acts very rapidly on rubber in the stretched or strained condition. Heil and Esch[7] find that rubber rapidly absorbs oxygen when exposed to its action, either in solution or when distended by a solvent, or when kept stretched.

Preliminary experiments proved very quickly the value of exposing the test samples in a stretched condition. Stretch-

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[11] *J. Soc. Chem. Ind.*, **4**, 710 (1925); *Gummi-Ztg.*, **14**, 687 (1900).

[12] *India Rubber J.*, **70**, 395 (1925).

[13] *Ibid.*, **70**, 899 (1925).

[14] *Gummi-Ztg.*, **40**, 95 (1925).

[15] This Journal, **18**, 367 (1926).

[16] *Kolloid-Z.*, **4**, 232 (1909).

[17] *Gummi-Ztg.*, **21**, 243 (1906); *C. A.*, **1**, 491 (1907).

[18] This Journal, **18**, 30 (1926).

[19] *India Rubber J.*, **52**, 373 (1916).

[20] *Ibid.*, **56**, 235 (1918).

[21] D. R. P. 18,740 (August 26, 1881).

[22] *Chem. Ztg.*, **36**, 1441 (1912).

[23] U. S. Patent 1,379,743 (May 31, 1921).

[24] *Rubber Age*, **5**, 5 (1919).

[25] D. R. P. 221,310 (1908).

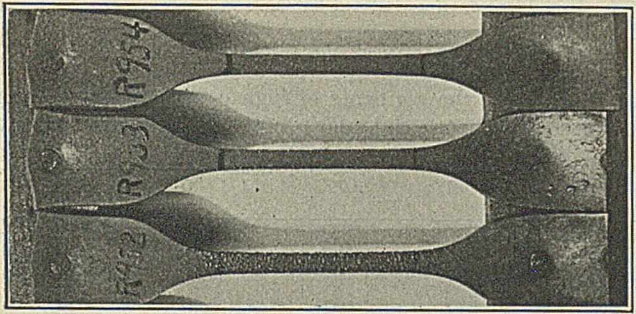
[26] Badische, D. R. P. 330,741 (1918).

[27] *Kolloid-Z.*, **9**, 81 (1911); Badische, D. R. P. 266,153 (1912).

[28] Badische, D. R. P. 332,305 (1918).

[29] *J. Soc. Chem. Ind.*, **4**, 710 (1885).

ing to an elongation of 12.5 per cent proved sufficient to produce checking of susceptible samples within 24 hours, while unstretched samples were not checked for months, when exposed to sunlight. This elongation was selected as a standard after it was found that increasing the elongation beyond this amount did not accentuate the checking,[30] but produced a larger number of finer checks which were less visible. Working at very low elongations produces a larger crack, but may lead to erroneous conclusions in stocks of high permanent set, as a result of the loss in stress.



R 952, no softener; R 953, 2.0%; R 954, 4.0%
Cure, 75 minutes at 290° F. Exposure, 39 days. Elongation, 12.5%; for photographing, 50%

Figure 1—Stretching Frame and Influence of Vaseline

Dumb-bell strips such as are used for tensile testing, cut from slabs approximately 5 mm. thick, were of uniform width and easily fastened on the stretching frames. These frames were made of wood of sufficient thickness to support a considerable number of test pieces without bending. The test strips were tacked to these frames. By marking the test strips with the usual marks 1 inch apart, as in tensile testing, it was a simple matter to stretch them to the desired elongation (Figure 1).

The frames, suspended from a rope, were exposed upon the roof. They revolved in the wind and in this way all the surfaces of the strips received approximately the same exposure. A control stock was included in each series and the exposure was continued until marked checking could be observed with the naked eye. Although this test was qualitative, reliable conclusions were assured by running the tests in duplicate and evaluating independently by two observers.

In order to determine the behavior of a stock when cured in combination with other stocks—as, for example, a tread stock in contact with a cushion stock—it was necessary to build up composite slabs in which the ratio of the thickness of one stock to that of the other approximated that in the cured article. This was essential because of the tendency for certain compounding ingredients, especially oils and resins, to migrate to adjacent stocks during cure and on aging and thus give rise to erroneous conclusions.

Cure

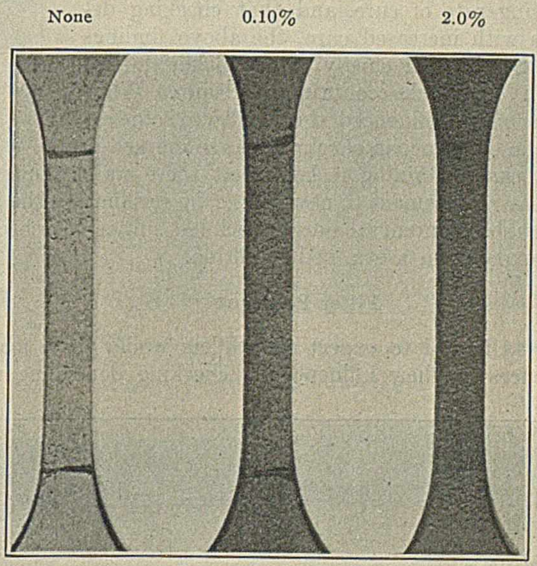
When a range of cures is exposed, it is almost always observed that with increase in cure the resistance to checking increases. For example, an appreciable difference in checking was observable on the 90-, 120-, and 150-minute cures at 287° F. (141.7° C.), on a gray sidewall stock, accelerated with hexamethylenetetramine and pigmented chiefly with whiting and zinc oxide. In order to determine whether this difference was due simply to increased state of cure or was influenced by the duration of the vulcanization period—i. e., by the heat treatment—this same stock, which contained 0.25 per cent of accelerator and 5.25 per cent of sulfur to the rubber was compounded with twice the amount of accelerator. The samples for test were both cured for 75 minutes at 287° F. (141.7° C.). After exposure for 2 days in June the stock with the higher concentration of accelerator was entirely free from cracks, while the other was noticeably checked.

Sulfur Bloom

The protective influence of heavy bloom was demonstrated by exposing two strips from the same slab of a blooming tread stock, from one of which the bloom was mechanically removed. After 16 days' exposure in June there was an appreciable difference in the amount of checking in favor of the bloomed stock. The protective influence is probably due to the film of sulfur acting as a covering more or less impervious to light or to ozone.

Color

Exposure tests have proved conclusively that a white stock loses much in resistance to sun-checking when made gray or black; even a dirty spot on a white stock becomes checked more rapidly than where the surface is clean and white. As little as 0.1 per cent of gas black added to a white stock to make it gray increases checking. The same stock made black with 2 per cent of gas black loses still more in resistance to checking. There was a definite gradation in sun-checking resistance, the white stock heading the list, with the gray stock intermediate (Figure 2). This result was to be expected since dark stocks unquestionably absorb more light than white as any dark body absorbs more light than a white one.



Cure, 75 minutes at 290° F. Exposure, 6 days. Elongation, 25%; for photographing, 50%

Figure 2—Influence of Gas Black

Kind of Rubber

Smoked sheet, pale crepe, blanket crepe, and rolled brown crepe were compared in the following formula:

Zinc oxide	19.0
Sulfur	3.5
Gas black	18.0
Hexamethylenetetramine	0.25
Palm oil	3.0
Rubber	56.25
	100.00

After 28 days' exposure in September distinct differences were observed in the stocks containing the different rubbers.

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[30] Experiment conducted by D. J. Beaver.

The stock containing rolled brown crepe was in the best condition. It was notably better than the stock containing blanket crepe, which, in turn, was better than the stocks containing smoked sheet or pale crepe. The latter stocks were both equally bad in degree of checking. It is therefore clear that the lower grade, off-color rubbers are not more susceptible to sun-checking than the high-grade rubbers.

Reclaimed Rubber

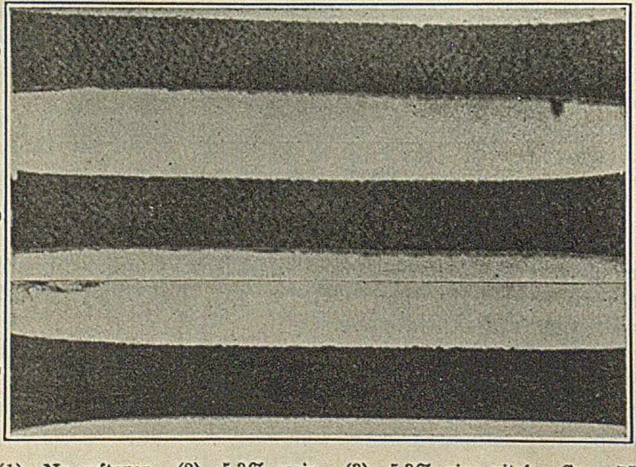
Several reclaimed rubbers—namely, two whole tire alkali reclaims, acid-reclaimed uncured frictions, and motor tire reclaim—were introduced into a tread formula in place of 10 parts of rubber. The replacement was based on the rubber content of the reclaim and zinc oxide was removed from the formula to compensate for the pigment in the reclaim. The interpretation of the results is difficult, owing to the variation in the scrap and the possible effect of the reclaiming agents used in the preparation of the reclaims, but it is significant that in every case the resistance to cracking was much greater than that of the control containing only smoked sheet. After 26 days' exposure in September the stocks containing whole tire reclaim and acid reclaim were classified as "good," while the control was stated to be "very bad." In no case, however, were the stocks containing reclaim completely protected.

Knowing the influence of reclaimed rubber in increasing rate of cure, and that checking decreases with increased cure, the above findings might be ascribed chiefly to the higher state of cure in the stocks containing reclaim. While this probably influenced the results to some extent, the difference in checking was so marked in the stocks containing reclaim that there was no question but that replacement of new rubber by reclaim (on the basis of its rubber content) makes a stock less subject to checking when exposed in a strained condition.

Filler Pigment

It was logical to expect that fillers would show marked differences in their influence on checking depending upon their covering power. This did not prove to be the case. When several pigments were introduced to the extent of 13.5 volumes (22.25 per cent to the rubber by volume) into a stock accelerated with hexamethylenetetramine and containing only sufficient zinc oxide for activation of the accelerator (zinc oxide 2, sulfur 3.5, hexamethylenetetramine 0.25, rubber 56.25 parts) they showed the following order of increasing resistance to checking:

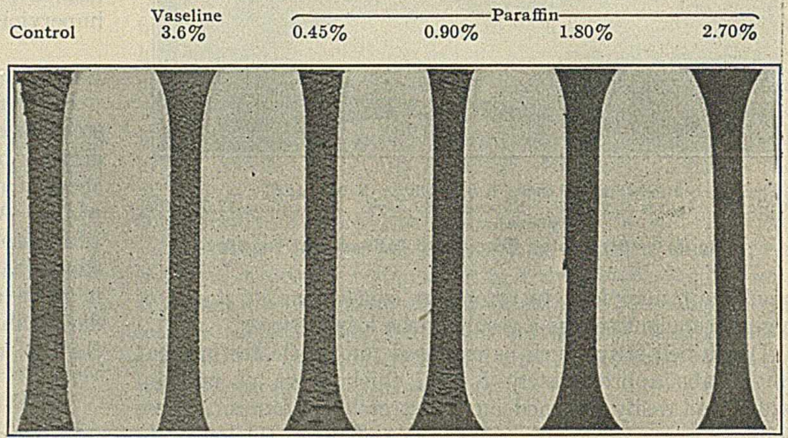
Control (no pigment)
Gas black
Lithopone ($BaSO_4$ and ZnS)
Zinc oxide
Whiting (precipitated $CaCO_3$)
Blanc fixe (precipitated $BaSO_4$)
Clay
Magnesium carbonate (basic $MgCO_3$)



(1) No softener. (2) 5.3% rosin. (3) 5.3% pine pitch. Cure, 75 minutes at 287° F. Exposure, 29 days. Elongation, 12.5%; for photographing, 50%. Photograph enlarged

Figure 3—Influence of Rosin and Pine Pitch

In other words, the pigments of high covering power—zinc oxide and lithopone—did not protect to the same extent as such pigments as whiting and clay, which are of notably low covering power. The behavior of gas black might indicate that the absorption of light by this pigment plays a part.



Cure, 75 minutes at 290° F. Exposure, 12 days. Elongation, 12.5%; for photographing, 50%

Figure 4—Influence of Paraffin and Comparison with Vaseline

In connection with the low resistance to checking observed in the stock containing gas black, it is of interest to note the statement of Goodyear[31] with reference to lampblack, that it "is often used to cause the gum to endure the effects of the sun and weather." Whether under the conditions of this checking test lampblack will differ from gas black has not been determined.

Softeners

The following classes of softeners were tested: asphaltic bodies, resins and pitches, vegetable oils, petroleum products, and waxes.

Mineral rubber and other asphaltic substances tested in a tread stock showed no protective action and can therefore be classed as "poor" from the standpoint of preserving a rubber stock against sun-checking.

Rosin and pine pitch were both found to have a detrimental influence on rubber from the standpoint of checking when introduced in a tread stock to the extent of 5.3 per cent on the rubber. Unlike most oils and resins these substances not only have no protective influence, but make a stock even less resistant to sun-checking (Figure 3).

The vegetable oils tested included palm and cottonseed oils. These glycerides influenced checking but slightly. They were tested in a tread formula and, although 3 per cent on the stock, or 5.3 per cent on the rubber, was added, the differences in the checking were very small. It was impossible to differentiate between the stock containing

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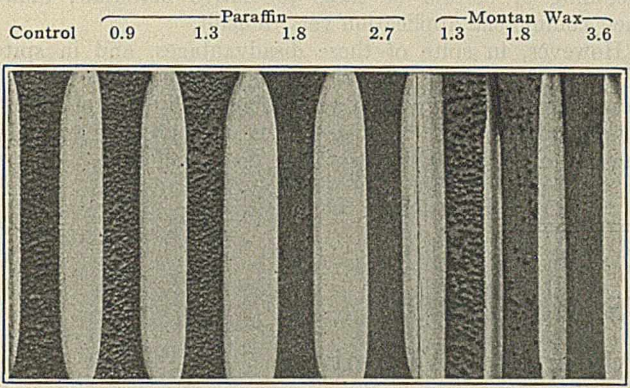
[31] "On Gum Elastic," Compounding Section, 1855.

cottonseed oil and the control containing no oil, while the stock containing palm oil was barely distinguishable as the best of the three. These two oils were also tested in a gray sidewall formula, with similar results; the margin in favor of the palm oil was greater, however.

The findings on petroleum products corroborate the statements in the literature. Figure 1 shows the effect of introducing vaseline into a gray sidewall stock. These strips were exposed for 39 days in October and November.

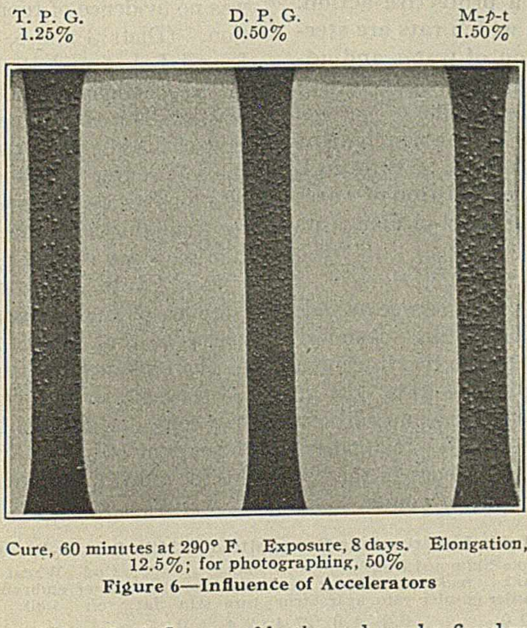


Cure, 75 minutes at 290° F. Exposure, 27 days. Elongation, 12.5%; for photographing, 50%

Figure 5—Comparison of Paraffin and Refined Montan Wax

Paraffin has a much stronger protective action than vaseline, as is seen in Figure 4, in which the comparison was made in a nonblooming tread stock. This exposure was very severe, owing to the time of year at which it was conducted (July). It is clear that more than 2 per cent of paraffin to the rubber was necessary to give complete protection; also that even 3.6 per cent of vaseline gave only slight protection, and no more than 0.9 per cent of paraffin.

Among other petroleum products tested was a light engine oil. This was found to be protective but inferior to vaseline.



Cure, 60 minutes at 290° F. Exposure, 8 days. Elongation, 12.5%; for photographing, 50%

Figure 6—Influence of Accelerators

On studying the influence of both crude and refined montan wax, it was found that the crude wax is but little, if any, better than asphaltic softeners. The refined wax, however, gives marked protection, being intermediate between vaseline and paraffin (Figure 5).

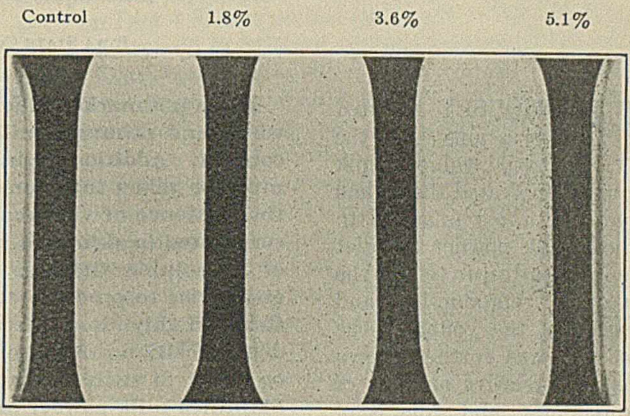
Though these materials as a class are very effective in protecting against sun-checking, their commercial application for this purpose is often very difficult. Paraffin, for example, not only blooms to the surface of cured articles, but also to the surface of raw stock. The former results in a very unsightly appearance, while the latter seriously interferes with factory processing.

Materials, such as paraffin, which are soluble in rubber, not only give trouble from blooming, but also are in a measure ineffective on account of their migration to other stocks. Thus, a tread stock containing ample paraffin for complete protection when cured alone, will lose so much to the breaker, cushion, and carcass, through migration, that it will check readily on a cured tire. For example, starting with a concentration of 4.6 per cent of paraffin to the rubber in the tread and 4.7 per cent in the sidewall, it was found that the concentrations based on the rubber in the various parts of a 33 × 4.5 inch, 6-ply cord tire, after cure, were as follows:

	Per cent
Tread (near surface)	1.4
Sidewall	1.2
Cushion	0.7
Top ply skim	0.6

Furthermore, the paraffin had actually migrated into the rubber between the lower plies and into the fabric itself.

The solubility of a material in rubber thus plays a prominent part in its value as a protective agent. Without solubility and the resultant migration to the surface no film of thickness sufficient for protection can be formed; too high a solubility, however, is detrimental, owing to the excessive amounts of material that must be used in order to produce a film, and owing to the amount of migration to adjacent stocks.



Cure, 75 minutes at 290° F. Exposure, 7 days. Elongation, 12.5%; for photographing, 50%

Figure 7—Influence of Benzidine

Accelerators

Several common organic accelerators were compared as to their influence on sun-checking. Among these were triphenylguanidine, diphenylguanidine, and methylene-*p*-toluidine. They were introduced into a typical tread formula in approximately equivalent quantities, as judged by the time required to reach optimum modulus. Figure 6 shows that there is little choice between these accelerators from the standpoint of improving resistance to checking.

Preservative or Antioxidant

Benzidine was studied in the following tread stock:

Zinc oxide	20.25
Sulfur	1.625
Gas black	18.
Softener	3.32
Triphenylguanidine	1.18
Rubber	55.625
	100.00

Concentrations of 1.0, 2.0, and 2.75 per cent to the stock (1.8, 3.6, and 5.1 per cent to the rubber, respectively) were used. From Figure 7 it is seen that more than 3.6 per cent to the rubber was necessary to give complete protection for one week. The price of this material, together with its tendency to bloom and discolor fabric[32] and other materials with which it comes in contact, make this specific antioxidant of doubtful commercial interest in the control of sun-checking.

Conclusions

Through the proper selection of rubber, reclaim, and compounding ingredients, it is possible to reduce to a marked extent the tendency for rubber products to crack and check. The maximum results from a checking standpoint would be obtained by using, in rubber compounding, only those materials that are protective in their action, but, unfortunately, selective pigmentation cannot usually be resorted to, without the sacrifice of desirable physical properties. Gas black, for example, has no protective action, and, even in small quantities, offsets the protective influence of other pigments, but for stocks such as tread stocks this pigment is highly desirable from the standpoint of toughness, resistance to tear, and abrasion. Other characteristics, such as the blooming of certain of these protective materials, make their commercial application very difficult.

However, in spite of these disadvantages, and in spite of certain limitations imposed by physical properties, much can be done to improve the weathering of all types of rubber compounds, and in some cases it is even possible to make them completely resistant for long periods of time.

[32] Weber, *J. Soc. Chem. Ind.*, **19**, 546 (1900).

Milk Powders as Food[1]

II—Observations on the Existence of Vitamin E

By L. T. Anderegg and V. E. Nelson

Iowa State College, Ames, Iowa

There is a marked difference in the nutritive value of whole and skimmed milk powders aside from the fat content. Additional observations are recorded which must be taken into consideration in connection with the existence of vitamin E. When cod-liver oil is incorporated in skimmed milk powder diets, as a source of fat-soluble vitamins, it undergoes decomposition giving rise to products strongly suggestive of acrolein. Other highly desiccated materials also induce this decomposition. Addition of ethyl alcohol, wheat oil, or water to such mixtures exerts a protective action. Skimmed milk powder diets, upon which rats are sterile, were so changed by the addition of water and administering the cod-liver oil separately that fourth generation young have now been obtained.

These results indicate that some of the conclusions previously drawn relative to the existence of vitamin E are now no longer tenable. The mere addition of water to a highly desiccated diet may markedly influence its nutritive value.

PREVIOUSLY reported observations[2,3] on the nutritive value of milk powders indicated that when iron citrate was added to whole milk powder the diet became adequate for the growth, reproduction, and rearing of the young of the rat. It was further shown that the relative amount of protein, fat, and salts is of great importance, and that reproduction may be greatly influenced by the amount of iron salt added. It was concluded that the whole milk powder employed was adequate as concerns the protein and vitamins necessary for growth, reproduction, and the rearing of the young of the rat. Other observers have since reported success with reproduction on whole milk powder diets.[4,5,6]

During this work a marked difference was observed between the nutritive value of whole milk powder and skimmed milk powder. This difference cannot be attributed solely to a difference in the fat content, for when skimmed milk powder was suitably supplemented so that the resulting diet conformed in chemical composition to one of whole milk powder, on which very good results concerning reproduction were obtained, the outcome on the skimmed milk powder diet was entirely different. The data for Lots 1 and 2, on Diets 1 and 2, as indicated in the respective tables, illustrate this point. Also, on a diet of skimmed milk powder 60.0, iron citrate 0.2, agar-agar 4, butter fat 5.0 (or cod-liver oil 5.0), and dextrin to 100, rats grew normally, but there was no evidence of reproduction. (Diets 3 and 6, Table I, and Lots 6 and 16, Table II.) Although skimmed milk powder diets containing 5 per cent of filtered butter fat as the sole source of fat-soluble vitamins were unfavorable for reproduction, the addition of 5 per cent of filtered butter fat to an oats diet as the only source of added vitamins A and D supplied sufficient of these chemical complexes so that rats could be reared to the fourth generation. The oats diet had the following composition: oat groats 93 per cent, sodium chloride 1 per cent, calcium carbonate 1 per cent, and filtered butter fat 5 per cent. It appears that 5 per cent of butter fat supplies a sufficiency of these vitamins for growth, reproduction, and rearing of young.

Table I—Percentage Composition of Milk Powder Diets

Diet	Whole milk powder	Skimmed milk powder	Iron citrate	Agar-agar	Dextrin	Salt mixture	Casein	Butter fat	Cod-liver oil	Wheat embryo oil	Harris yeast
1	60.0		0.2	4.0	27.4	2.4	6.0				
2		65.0	0.2	4.0	13.8	1.0		16.0			
3		60.0	0.2	2.0	32.8			5.0			
4		50.0	0.2	2.0	38.8				2.0	5.0	2.0
5		50.0	0.2	2.0	47.8						
6		60.0	0.2	2.0	32.8				5.0		

Evidently, these observations show that further investigations on the nutritive value of skimmed milk powder might lead to interesting and useful results, both from a practical

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[1] Reported at the Intersectional Meeting of the American Chemical Society at Iowa City and before the joint session of the Divisions of Agricultural and Food Chemistry and Biological Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] Anderegg, *J. Biol. Chem.*, **59**, 587 (1924).

[3] Anderegg and Nelson, This Journal, **17**, 451 (1925).

[4] Matill, Carman, and Clayton, *J. Biol. Chem.*, **61**, 729 (1924).

[5] Maze, *Compt. rend.*, **180**, 1683 (1925); *C. A.*, **19**, 2693 (1925).

[6] Woods, *J. Biol. Chem.*, **66**, 57 (1925).

Table II—Growth, Reproduction, and Rearing of Young on Powdered Milk Diets

Lot	Diet	Generation	Males	Females	Growth	Litters	Young born	Young weaned	Remarks
1	1	1	2	5	N	17	139	132	
2	2	1	3	5	N	6	32	7	Only 1 litter reared
3	3	1	2	3	N	4	26	15	Whole liquid milk in diet
4	3	1	2	3	N	2	12	7	Cream in diet
5	3	1	2	4	N	3	19	9	Orange juice in diet
6	3	1	2	4	N	0	0	0	No addition
7	4	1	2	4	N+	4	28	20	
8	5	1	2	3	N	3	21	5	2.0 uncertified cod-liver oil and 2 yeast separately
9	5	2	2	3	N	0	0	0	2.0 uncertified cod-liver oil and 2 yeast separately
10	5	1	2	3	N	1	0	0	2.0 uncertified cod-liver oil separately, no yeast
11	5	1	2	4	N	4	7	5	Basal ration wetted and then dried 7.0 uncertified cod-liver oil and 2.0 yeast added
12	5	1	2	4	N	4	13	10	Basal ration wetted and then dried 2.0 uncertified cold-liver oil and 2.0 yeast added
13	5	1	3	3	N+	6	37	33	5.0 water incorporated 2.0 certified cod-liver oil and 2.0 yeast separately
14	5	2	4	5	N+	10	54	37	5.0 water incorporated 2.0 certified cod-liver oil and 2.0 yeast added
15	5	3	3	7	N+	7	46		5.0 water incorporated 2.0 certified cod-liver oil and 2.0 yeast added
16	6	1	3	5	N	0	0	0	

and from a theoretical viewpoint. The value of such information to the producers and consumers of these products is sufficiently obvious.

Previously, butter fat had served chiefly as the source of the fat-soluble vitamins. In the experiments to be considered at this time cod-liver oil was also employed to furnish these substances. Since the results concerning reproduction were decidedly abnormal when skimmed milk powder was supplemented with butter fat and iron salts, it was suggested that possibly some change had occurred in the butter fat. The nutritive value of the fat as it occurs in whole milk might be different from the filtered butter fat as it was employed in making up the diets. If such a change took place it might account for the differences in nutritive value between whole milk powder diets and similarly composed skimmed milk powder diets. Such a change could be due to the destruction or the removal of a necessary dietary principle. It is also possible that the difference might be due to a dietary factor other than vitamins A, B, C, and D—namely, a vitamin having to do specifically with reproduction, and which is present in whole milk powder but not in skimmed milk powder.

Effect of Addition of Certain Substances on Nutritive Value of Skimmed Milk Powder

If the nutritive value of the butter fat was impaired by the various treatments it received, positive results might obtain if liquid whole milk, or cream, were added as a further supplement. Orange juice was also tried, as it is a potent source of certain vitamins. Diet 3 was employed in these experiments. The feed containers were about half filled with the dry mixture, after which enough of the liquid supplement—whole milk, cream, or orange juice—was added so that the thoroughly stirred mixture became a thin paste. Positive results were obtained (Lots 3, 4, and 5, in Table II), while no reproduction was obtained with Lot 6, which was on the experiment at the same time and under the same general environmental conditions as Lots 3, 4, and 5. This group served as a control. Reproduction has never been observed on this diet (Diet 3), although a large number of animals have been employed. From the observations on the oat diets it appears that a sufficiency of fat-soluble vitamins is present in Diet 3. The results of these four experiments indicate that the liquid supplement, whether whole milk, cream, or orange juice, exerted a beneficial action when incorporated in the skimmed milk powder diet. On the skimmed milk powder diet alone without supplement results on reproduction and rearing of young were negative.

Effect of Certain Diets on Added Cod-Liver Oil

When cod-liver oil was added to supply the fat-soluble vitamins in earlier experiments, a peculiar and characteristic decomposition was observed. The diets are usually prepared in quantities of a kilogram, and are then stored in 2-quart mason jars. Under these conditions some of the material may remain unconsumed for a period of 10 days if the number of rats fed thereon is small. Under such conditions, when cod-liver oil was a component of the diet, very pungent and penetrating odors strongly suggestive of acrolein were produced. However, when wheat embryo oil had also been added to such a diet no such decomposition was observed. On such diets, when wheat embryo oil was incorporated, reproduction and rearing of young occurred. Lot 7 on Diet 4 illustrates this statement. The efficiency of wheat embryo oil in inducing reproduction has been pointed out by Evans[7] and also by Sure.[8] Among their experiments Evans and Bishop[9] included in one of their diets cod-liver oil to the extent of 24 per cent and, since reproduction was not augmented, concluded that this oil did not contain the reproductive vitamin which has recently been designated vitamin E by Sure,[10] and Evans and Burr.[11] Evans and Bishop[9] also employed yeast to the extent of 25 per cent of the ration. In summarizing their findings they say, "Whole milk, fresh or dried, cod-liver oil, orange juice, and yeast fail to act as curative agents when added to the basic diet." Evans and Burr[11] state that "whole milk powder may constitute one-third of the ration by weight and sterility result." The writers have previously shown that reproduction occurred on a synthetic diet when all the vitamins were furnished by whole milk powder present to the extent of 15 and 30 per cent by weight of the diet. The first of these diets contained about 4.1 per cent of butter fat while the second contained about 8.3 per cent. Both of these diets, on which reproduction and rearing of young occurred, contain smaller amounts of butter fat than the basal ration of Evans and Bishop,[9] which contains 9 per cent of butter fat. The basal ration of Evans and Bishop[9] also contains 15 per cent of lard, whereas no lard was used in the diets containing 15 and 30 per cent of whole milk powder mentioned above.

The writers have made some very limited observations employing practically the basal ration of Evans and Bishop[9]—namely, casein 18, dextrin 54, lard 15, butter fat 9, salts 4. Four lots of animals were kept under similar environmental conditions and observed for about 4 months. In addition to the basal diet one lot received yeast only, the second yeast and butter added separately, the third yeast and cod-liver oil separately, and the fourth yeast and wheat embryo oil separately. There was no evidence of pregnancy among the females of any of these lots of animals.

Sure[10] also failed to get reproduction on skimmed milk powder diets supplemented with 2 per cent of cod-liver

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[7] *Science*, **60**, 20 (1924).

[8] *J. Biol. Chem.*, **62**, 371 (1924).

[9] *J. Met. Res.*, **3**, 233 (1923).

[10] *J. Biol. Chem.*, **58**, 693 (1924).

[11] *Proc. Nat. Acad. Sci.*, **2**, 336 (1925).

oil. Addition of various extracts of wheat embryo, yellow corn, and several other substances gave positive results, and Sure[10] interpreted these findings to prove the existence of a vitamin specific for reproduction which he named "vitamin E."

Decomposition of Cod-Liver Oil

Cod-liver oil was mixed with a number of dry substances in order to determine whether similar decomposition would occur. Stoppered wide-mouth bottles of about 800-cc. capacity or quart mason jars were used as containers. To 200 grams of material 5 per cent of cod-liver oil was added and the whole thoroughly mixed and placed in the glass container, which was then tightly closed. Whole milk powder, skimmed milk powder, starch, and finely ground dextrin were tried and induced similar decompositions of the added oil. The addition of anhydrous ether, chloroform or benzene to the extent of 5 per cent did not prevent the decomposition, while such substances as 95 per cent alcohol, wheat embryo oil, and water exerted a protective action increasing in the order given. Moreover, the protection due to the water varied with the quantity added. With 10 per cent of added water no decomposition of the oil was evident even after several months. Mustiness and discoloration ensued, but the odor so characteristic of the other decompositions could not be discerned. The 5 per cent of added wheat embryo oil prevented noticeable decomposition for about a month. Although decomposition was noticeable with whole milk powder, the amount and rate of decomposition was markedly less than with skimmed milk powder.

In the light of these observations it appeared that the lack of successful reproduction on skimmed milk powder diets might be attributed to the action of the highly desiccated material upon the added fats. Should this theory be well founded, then better results might obtain if the fats were fed separately, or if the diet were moistened before adding the fat.

Effect of Moistened Diets and Feeding the Fat Separately

All experiments described were made with rats of an initial weight of 50 to 60 grams, selected from the breeding colony, which consists of a very healthy, vigorous stock of animals. Two brands of cod-liver oil purchased locally were employed. The yeast was obtained from the Harris Laboratories. Dextrin was prepared by autoclaving cornstarch moistened with a 1 per cent citric acid solution at 1 atmosphere (15 pounds) pressure for about 3 hours, with subsequent drying over steam coils and then grinding to a moderately fine powder. The skimmed milk powder was obtained from the Merrell-Soule Co., Syracuse, N. Y. The animals were kept under as nearly identical environmental conditions as possible and were observed daily. In order to reduce the labor involved, a basal diet of skimmed milk powder 50.0, agar-agar 2.0, iron citrate 0.2, and dextrin 47.8 was prepared. Added cod-liver oil, yeast, or water was then calculated to this mixture as a basis.

Lots 8 and 9 received this basal diet, Diet 5, with 2 per cent of uncertified cod-liver oil and 2 per cent of yeast fed separately. The yeast and oil were mixed with a little water and placed in a petri dish. These portions were readily consumed by the animals. On this diet, the first generation, Lot 8, grew normally, reproduced, and reared young. The second generation, Lot 9, though under observation for 9 months has not reproduced. Lot 10 received a similar diet save that the yeast was omitted. Although growth was comparable in these experiments, only one female of Lot 10 was obviously pregnant. She died before the young were born; autopsy revealed 6 fetuses. Altogether, the results on these diets were not very satisfactory.

On the supposition that the physical condition of the milk powder might have some influence on its nutritive value, the basal ration was treated with water until a thin paste was formed. This was dried, coarsely ground, and the cod-liver oil and yeast added to the ground material. Lot 11 received this diet, containing 7.0 per cent of added uncertified cod-liver oil and 2.0 per cent of yeast. Lot 12 received a similar diet, except that the added oil was reduced to 2.0 per cent. Each female of both groups became pregnant. In Lot 11 two females died at parturition and two gave birth to young. Of these latter one consumed the young before they could be counted, while the other reared 5 of her 7 young. Quite similarly, two females of Lot 12 died at parturition, the two remaining ones gave birth to litters of 5 and 8, of which 2 and 8 were reared. The young were inferior at weaning. In Table II all litters are indicated, but the number of young refers only to those actually born. In these experiments the decomposition of the added cod-liver oil was not entirely averted. It is now believed that this was because the material was too thoroughly dried after having been wetted. The odors characteristic of the decompositions described above were noticed several times.

The best results so far obtained on skimmed milk powder diets are illustrated by Lots 13, 14, and 15. The dextrin, agar-agar, and iron citrate were mixed, 5 per cent water incorporated, after which the milk powder was thoroughly mixed into the moistened mass. More than 5 per cent of added water makes the mixed mass too sticky to handle easily. Certified cod-liver oil to the extent of 2 per cent and yeast 2 per cent were fed separately. It so happened that one of the three females of Lot 13, the first generation, was sterile throughout. The other two females each gave birth to three litters of young. Of 37 young born 33 were reared. The second generation, Lot 14, likewise grew normally. The females reproduced and reared young. Of 54 third generation young born 37 were weaned. The females of Lot 15, third generation, have just had their first litters. In all, 7 females of this lot have had young which constitute the fourth generation. The total number of fourth generation young was 46. From the appearance of the young there is every reason to believe that they will be weaned and grow normally.

Reproduction and rearing of young are occurring on a diet which has hitherto been considered inadequate in this respect, on a diet, in fact, which has been employed to adduce proof for the existence of a vitamin specific for reproduction. It is now believed that a highly desiccated diet may have a very deleterious action on some of the added components. The mechanism of the destructive action, while under investigation, is not understood. It is now further believed that some of the conclusions previously drawn from observations of the reproduction of rats on skimmed milk powder diets, with reference to the existence of a vitamin specific for reproduction, are no longer tenable. Further, the simple expedient of adding water to certain highly desiccated diets, which, as such, are unsatisfactory because of lessened palatability and because of destruction of certain components, may greatly improve their nutritive value.

Acknowledgment

The writers desire to thank the Merrell-Soule Company for supplying some of the materials used in this investigation.

Willard Gibbs Medal Award

The Willard Gibbs Medal has been awarded to Sir James C. Irvine, of The University of St. Andrews, Scotland. The medal will be presented to him at the meeting of the Chicago Section which will be held on Friday evening, September 17, 1926. Dr. W. Lee Lewis is in charge of the committee planning the award and will present the medal.

Preparation and Colloidal Properties of Pectin[1]

Preliminary Report

By Mary A. Griggs and Ruth Johnstin

Wellesley College, Wellesley, Mass.

In the preparation of pure pectin from lemon albedo the following points are emphasized. The albedo is treated with alcohol before grinding, and this extraction must be rapid and at a definite temperature. Dialysis of the pectin sols is the best method of removing electrolytes, especially calcium salts. The pectin is precipitated by the dropwise addition of alcohol to the pectin sol, and not vice versa, the gelatinous precipitate flocculated in an electric field, and filtered through silk cloth.

Some colloidal properties of pectin solutions are discussed. These include the optical properties, the charge on the particles and their precipitation, the fact that pectin does not dialyze, the viscosity, and a discussion of alcohol-pectin gels and sugar-acid-pectin gels. In describing the sugar-acid-pectin gels it is pointed out that heat and evaporation are not necessary for gelation, that there is a time factor in gelation, and that there is probably no compound formation.

The writers have indicated in this report the course along which their investigations will proceed. It seems probable that with a standard method of preparing pectin free from impurities, reproducible and valuable results can be obtained. A thorough knowledge of the colloidal behavior of pectin sols must furnish the scientific basis for the commercial utilization of the enormous quantities of pectin now available.

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The ability of pectin sols to form gels is unquestionably the most interesting and important characteristic of these substances. A number of investigators have studied the conditions governing the gelation of sugar-pectin-acid mixtures, but it is difficult to bring this work together into any sort of uniformity because in no two cases is the pectin used the same and in only one instance[2] has there been any attempt to work with a highly purified pectin.

Pectin in water constitutes a colloidal system resembling in some respects the lyophilic sols of gelatin and also of agar-agar. Apparently the pectin-water system differs from these in that the transition from sol to gel state can be effected only by the addition of a third substance or sometimes a fourth. It has been stated repeatedly in the literature that sugar and acid are both necessary for the formation of pectin gels. Certain observations made on sols containing pectin of a much higher degree of purity, and of a much lower ash content than any previously used, have led the authors to believe that the gelation of pectin sols is a simpler process than one is led to believe from a consideration of the complex pectin-sugar-acid-water systems.

In order to study the behavior of colloidally dispersed pectin it seemed desirable to prepare a product of a high degree of purity the physical constants of which could be well defined.

Preparation of Pectin

These studies present several new procedures used in the preparation of pectin which have proved to be of real value in removing impurities and in handling this extremely difficult material. Some modifications may still be necessary before an entirely satisfactory method of preparation is established.

The material was obtained from the skin of lemons by first removing the outer yellow rind with a stainless steel knife. The albedo was then carefully peeled off so that no pulp adhered and was immediately soaked in alcohol for about 10 minutes. This treatment hardens the skin so that it can be ground in a meat chopper without any of the darkening due to oxidation and to the action of the metal.

Extraction of Organic Impurities—The extraction of organic impurities, such as oils, terpenes, resins, etc., with alcohol and then with ether under a reflux condenser, first suggested by Bourquelot and Hérissey,[3] was carried out as rapidly as possible. If fresh portions of alcohol are added frequently, especially during the first day, readsorption by the albedo of alcohol-soluble material is prevented and the time required for complete extraction is lessened. The completeness of this extraction can be judged from the final form of the pectin, for it cannot be produced as a white powder unless free from these alcohol-soluble and ether-soluble substances. When the extracts become entirely colorless the albedo is dried at not more than 65° C. According to von Fellenberg,[4] this treatment converts much of the insoluble protopectin to soluble pectin. The albedo loses about 85 per cent of its weight on extraction and drying.

It should be noted in passing that this preliminary extraction with alcohol and ether is of special value in the preparation of apple pectin, in which it has not been generally used. This treatment removes those substances from the apple pulp which oxidize so readily in the air to form sticky dark brown compounds, which when once formed can hardly be separated from the pectin. Pectin prepared from apple pomace or commercial pectin solutions cannot be expected to be free from these organic impurities.

Extraction of Pectin from Albedo—The temperature of extraction and the hydrogen-ion concentration of the extracting medium are the conditions which should be carefully defined during this process, since variations in either may profoundly affect the physical state of the resulting product.

The effect of heat alone on pectin is not well known, but it has been shown[4] that boiling with acid brings about hydrolysis of the pectin to pectic acid and long heating at a lower temperature has the same effect. It therefore seems necessary at least to define the temperature of preparation. Ninety degrees Centigrade has been chosen in this work as the maximum temperature to which the pectin is ever submitted and the solutions are always brought to this temperature rapidly in order to avoid long heating. This is probably below the temperature of much hydrolysis, and yet it is great enough to prevent bacterial action and also to allow fairly rapid filtration of the solutions. The preparation of pectin in the cold would be of interest as possibly yielding a product of different properties, but this could only be accomplished with the addition of preservatives.

The procedure employed in this work was as follows: 15 grams of the albedo prepared as above were extracted

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[1] Received November 27, 1925.

[2] Sucharipa, *J. Assoc. Official Agr. Chem.*, **7**, 57 (1923).

[3] *J. pharm. chim.*, [6] **7**, 473 (1898).

[4] *Biochem. Z.*, **85**, 118 (1918).

successively with three portions (750 ml., 500 ml., 500 ml.) of 0.01 *N* hydrochloric acid at 90° C. The first portion of acid was added to the albedo cold, stirred for 15 minutes, and then heated with stirring to 90° C. The final yield of purified pectin was about 27 per cent of this albedo, or about 4 per cent of the original albedo. It should be borne in mind that this is an acid-treated pectin.

Removal of Inorganic Impurities—The problem of lowering the ash content of pectin has been attacked by various workers in different ways. Since the ash contains about 95 per cent of calcium oxide, many workers have attempted to remove it with oxalate ions, either extracting the pectin from the albedo with dilute oxalic acid or ammonium oxalate or precipitating with an oxalate solution. In order to precipitate calcium completely as the oxalate, the solution must be alkaline and pectin hydrolyzes to pectic acid very readily in alkaline solution. Again, calcium oxalate is such a fine precipitate that it will not be retained by filter paper, which also allows the passage of pectin sols.

Reprecipitation has been found by some workers, notably Sucharipa,[2] to be quite effective for reducing the mineral content. Three reprecipitations, however, from water solutions containing several grams of pectin have left pectin with an ash content of 2.60 per cent, while three reprecipitations from dilute hydrochloric acid solutions have left 0.69 per cent ash. This is not only large but it leaves the pectin with considerable adsorbed acid. These difficulties have led, in this work, to the use of dialysis as the most effective method.

Dialysis—The pectin sol containing 1 gram in 300 or 400 ml. is dialyzed in a parchment bag with 0.01 *N* hydrochloric acid. It is heated every 24 hours to about 90° C. to prevent bacterial action. A fresh portion of acid is used daily until it no longer gives a test for calcium. This usually requires a week. The acid can then be dialyzed out with distilled water in 4 or 5 days with daily heating. By this method, however, ash in pectin has been reduced in duplicate dialyses from 2.60 per cent to 0.18 per cent and the pectin has only a slightly acid reaction. About 20 per cent of the pectin is lost in the dialysis.

Precipitation—The method of precipitating pectin determines the degree of dispersion of the resulting product, which the writers believe to be the controlling factor in gelation.

Not only is complete precipitation of the pectin desirable, but the precipitate should be in a form which is easily filterable and carries down a minimum amount of adsorbed material. The use of dilute solutions—1 gram in 300 or 400 ml.—is important. Two volumes of 95 per cent alcohol should be added to the pectin sol dropwise with thorough stirring at room temperature. If the pectin sol is added to the alcohol as suggested by Tarr[5] and by Halliday and Bailey,[6] the pectin comes down completely, but in a gummy mass which must adsorb many impurities. Precipitation at a high temperature results in a gelatinous rather than a flocculent precipitate. Flocculation is aided by the presence of electrolytes, so as these diminish the pectin becomes more gelatinous. This gelatinous mass can be flocculated in a very satisfactory way at the anode on electrolysis with 110-volt d. c. for about 2 hours with platinum electrodes. The effect is identical with that produced by the addition of positive ions without the complication of added electrolytes. At least one reprecipitation is always advisable.

The precipitated pectin can be filtered easily by suction through heavy silk cloth stretched over a funnel. It is sucked and pressed as dry as possible with a porcelain spatula, removed from the filter, thoroughly mixed with alcohol for washing, and again pressed dry on the filter. This should be repeated about four times. After the last precipitation the washing with alcohol is followed by similar treatment with ether. The pectin is constantly worked with a porcelain spatula, as suggested by Wendlemuth,[7] on the silk filter with suction, and when it becomes thoroughly dry it is a snow-white hard powder. It contains about 11 per cent moisture and 0.18 per cent ash. Its specific rotation is +230 at 23° C., which agrees closely with Poore's[8] results. It has only a slightly acid reaction unless acid is used in the precipitation.

Colloidal Properties

There is no doubt that pectin in water solution is colloidally dispersed. The water solutions are opalescent in reflected light and clear in transmitted light. The Tyndall effect has been observed by the authors in a 1 per cent pectin solution with variations in the intensity of the ray with crossed Nicols. In the ultra-microscope the sols show Brownian movement.

It is usually thought that the colloidal particles bear negative charges in water solution. This is borne out by the precipitation of pectin from water solutions by some metallic ions. Lead ions have been found the most effective of many positive ions for this coagulation. A few drops of very dilute (0.01 *N*) lead nitrate solution immediately converts a 1 per cent pectin sol to a clear, hard gel. On the other hand, strong alkalies and, on standing, strong acids produce opaque white gels due to hydrolysis of the pectin to pectic acid. The fact that iron and aluminum ions having a valence of three are less effective precipitants suggests the possibility that the precipitation is not due solely to a negative charge on the pectin. Moreover, in electrolyzing water-pectin sols practically free from electrolytes, pectin has been found deposited on the cathode, which should indicate a positive charge. However, the addition of alcohol to the nearly pure pectin sols often produces a soft gel in which there is no doubt that the pectin is a negative colloid, for it forms as a solid gel on the anode when electrolyzed.

Studies on the dialysis of pectin sols and gels have shown that pectin is but slightly dialyzable and that electrolytes such as acids and calcium salts may be separated from pectin by this method. This leads one to question whether pectin as it occurs in the cell wall is a stable calcium compound, as is often assumed.

The viscosity of pectin sols seems to be much greater than the viscosity of gelatin sols of equal concentration. In a preliminary study of this property the following values for the specific viscosity of lemon pectin sols at 25° C. have been found:

Pectin Per cent	Specific viscosity at 25° C.
0.10	1.348
0.25	1.834
0.50	2.899
0.65	4.018
0.80	5.190
1.00	7.235

The Ostwald viscometer is used to determine the viscosities, and the densities are determined by means of the Sprengel tube. Since viscosity is one of the most important properties of pectin sols, a series of experiments is planned to show the effect on the viscosity of such factors as concentration, pH, age, sugar, alcohol, temperature, method of preparation, etc.

At the present time, the conditions governing pectin sol–gel transformation are not well understood and the structure of the resulting gels has been given very little attention. By means of X-ray and ultra-microscopic studies the authors

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[5] Del. Agr. Expt. Sta., *Bull.* **134** (1923).

[6] This Journal, **16**, 595 (1924).

[7] *Kolloidchem. Beihefte*, **19**, 115 (1924).

[8] U. S. Dept. Agr., *Bull.* **1323** (1925).

hope to be able to throw some light on this very interesting phase of the subject. At present precipitation seems to be closely related to gelation. By controlling temperature and concentration it has been found possible to produce gels with many of the reagents ordinarily thought to be precipitants of pectin. The alcohol-pectin gels have been prepared quite as successfully as the sugar-acid-pectin gels and they allow the formation of Liesegang rings of both ferric ferrocyanide and silver chromate.

The usual pectin gels—containing pectin, water, sugar, and acid—are complicated because of the large number of constituents and the very ease of gelation, which may occur under varying conditions. The four components are essential for this type of gels, and yet Goldthwaite[9] has prepared satisfactory gels by substituting glycerol for the sucrose. The authors have substituted 50 per cent dextrose for sucrose and obtained a gel, but only when the solution was heated.

That heat is not a necessary factor in the building up of this type of gel structure the writers have shown conclusively by preparing a series of gels containing 50 per cent sugar, 0.5 per cent citric acid, and from 0.125 to 0.5 per cent pectin without any heating. Further, evaporation seems to play no important part, as has often been assumed, because these gels were left covered and the loss in weight was negligible.

It seems probable that the important factors in pectin gel formation are the degree of dispersion of the pectin and the time required for the building up of the gel structure. It has been found that as the percentage of pectin decreased the time required for gelation increased.

The high jellying power of this purified pectin should be noted because some authors state that repeated purifications decrease the jellying power. This is doubtless true when the methods of purification bring about the hydrolysis of pectin to the forms containing fewer methoxyl groups.

Both Tarr[5] and Chernoff[10] have recently suggested the possibility of the formation of definite chemical compounds in sugar-pectin-acid gels in explaining the building up of a structure. Sucharipa,[2] however, succeeded in washing out most of the sugar and acid from a gel with 75 per cent alcohol, leaving, he believed, the pectin with too little sugar or acid to indicate a chemical compound. The writers have confirmed this repeatedly by dialyzing out from the gels so much sugar that the residue was tasteless and so much acid that a gel could only be made from the residue with the addition of acid as well as sugar.

[9] This Journal, 1, 333 (1909).

[10] *Am. Food J.*, 18, 200 (1923).

Nature of Vegetable Tannage[1,2]

Tanning with Mixtures of Gallotannin and Quinone

By Arthur W. Thomas and Margaret W. Kelly

Columbia University, New York, N. Y.

PREVIOUS investigations[3] of the change in rate of vegetable tannin fixation by hide substance as a function of the pH values of the solutions have shown that (1) a minimum is always obtained in the region of pH 4 to 5, and (2) the curves rise from this minimum to a maximum at pH 2 (sometimes pH 1) on the acid side and to a maximum at pH 7 to 8 on the alkaline side of the point of minimum rate of fixation.

Composite curves of results obtained with six commercial vegetable tanning extracts are shown in Figure 1. The explanation of the complex paths in these graphs in the pH range of 1 to 8 was offered[3] on the basis of the Procter-Wilson theory of tanning and the postulate of two forms of collagen, the anions of the complex, high-molecular-weight tannin acids combining with collagen cations to form the insoluble substance, leather or "collagen tannate."

It was expected that there would be no tannin fixed from solutions more alkaline than pH 8. However, tannin was fixed even up to the pH value of 12. This could not be accounted for by the Procter-Wilson theory, and since it was more noticeable with tanning extracts rich in nontans, it was suggested[3] that the tanning action observed in the alkaline solutions might be attributable to substances of the character of quinone which are capable of oxidizing amino groups in alkaline solution and combining therewith. That the "leathers" tanned in acid and alkaline solutions are different in nature was demonstrated by alcoholic extraction.[4]

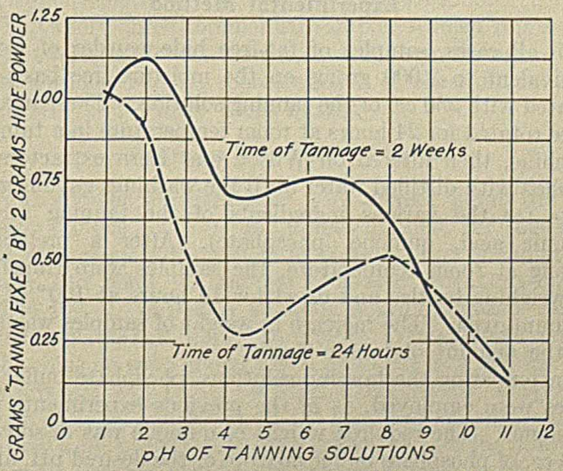

Figure 1—Rate of Tanning as a Function of pH Value

The 24-hour curve is the average of eleven measurements of six commercial tanning extracts—hemlock bark, quebracho, wattle, gambier, oak bark, and larch bark, the average concentration being 55 grams total solids per liter. The 2-week curve is the average of six measurements with same extracts, the average concentration being 39 grams total solids.

If the suggested hypothesis for tannage in alkaline solutions is correct, then tannic acid, which is practically devoid of nontannins, should show no tanning action in solutions more alkaline than pH 8. This was tested and found to be true.[5] To be sure, there was a slight degree of tannage in tannic acid solutions at pH 9 to 12, but it was small in comparison to that obtained with vegetable tanning extracts. It must not be overlooked that there is a certain amount of decomposition of tannic acid in alkaline solutions due to oxidation. This

[1] Presented under the title "Tannage with Mixtures of Gallotannin and Quinone" before the Division of Leather and Gelatin Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924. Received October 30, 1925.

[2] Contribution No. 497 from the Department of Chemistry, Columbia University.

[3] Thomas and Kelly, This Journal, 15, 1148 (1923).

[4] *Ibid.*, 16, 31 (1924).

[5] This Journal, 16, 800 (1924).

is evident from the dark color of such solutions, and substances so produced, different in nature from tannic acid, account for the slight degree of "tannin" fixation at pH 9 to 12. If quinone-like bodies were responsible for the tannage in alkaline solutions as postulated, then benzoquinone should certainly tan in alkaline solutions. This was found to be true.[6]

The fixation of tannin by hide powder from solutions of tannic acid and of quinone separately is shown in Figure 2. While this experimental evidence supported the hypothesis for the nature of tannin fixation in alkaline solutions, it was deemed of value to test it further by tanning with mixtures of tannic acid and benzoquinone.

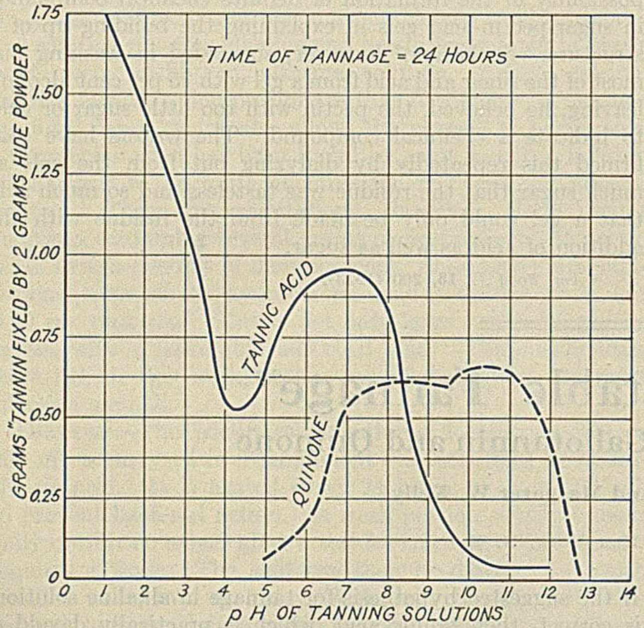

Figure 2—Typical Tannic and Quinone Rates of Tannage as a Function of pH

Concentration of tannic acid, 40 grams per liter. Concentration of quinone, 13.7 grams per liter (saturated solution).

Experimental Method

In all cases, samples of fat-free hide powder of weights equivalent to 2.000 grams on the moisture-free basis were treated with 250 cc. of the tanning solution. These mixtures were rotated for 24 hours at room temperature in a tumbling machine, then filtered on Wilson and Kern extractors and washed with distilled water until the washings gave negative tests for the various ingredients of the tanning solution (tannic acid, quinone, phosphate). After a preliminary drying at room temperature, the samples were transferred to weighing bottles and dried for 16 hours at 100° C. in a vacuum oven. The increase in weight of samples was taken as the amount of tannin fixed.

In preparing the tanning solutions, phosphate buffer mixtures were employed, as in the previous experiments using quinone.[6] The required weight of quinone was dissolved in 200 cc. of phosphate buffer mixture of the desired pH, and to this solution were added 50 cc. of tannic acid solution of the same pH and of such strength as would give, on dilution to 250 cc., the desired concentration of tannic acid. The adjustment of the tannic acid solution to the required pH was made by dilution to 50 cc. of a sample of a stock solution (400 grams tannic acid per liter), after the addition of varying amounts of hydrochloric acid or sodium hydroxide, these amounts having been previously determined by electrometric titration of a sample of the stock solution. In each instance there was an excess of tannic acid and quinone present.

Results

The results are summarized in the accompanying table. Experiments I to V are arranged in the order of increasing ratio of quinone to gallotannin, the amount of 3.425 grams of quinone constituting a saturated solution in distilled water.

Tannin Fixed by 2 Grams Hide Powder from 250-Cc. Solution

Original pH of tanning soln.	I Tannic acid, 10 g. Grams	II Tannic acid, 10 g. Quinone, 0.8 g. Grams	III Tannic acid, 10 g. Quinone, 2.0 g. Grams	IV Tannic acid, 10 g. Quinone, 3.425 g. Grams	V Tannic acid, 5 g. Quinone, 3.425 g. Grams
2.0	2.59	2.58	...[a]	...[a]	...[a]
3.0	1.76	1.85	...[a]	...[a]	...[a]
4.0	0.67	0.75	0.98	...[a]	...[a]
5.0	0.66	0.52	0.48	0.56	...[a]
6.0	1.02	0.92	0.84	0.73	0.68
7.0	1.07	0.99	0.91	0.98	0.97
7.5	0.95	0.92	0.87	1.00	1.01
8.0	0.82	0.86	0.84	0.96	0.98
9.0	0.21	0.28	0.36	0.47	0.71
10.0	0.10	0.14	0.22	0.47	0.47
11.0	0.11	0.14	0.18	0.27	0.36
12.0	0.09	0.13	...	0.23	0.27

[a] These results were rendered valueless on account of the formation of an abundant red precipitate of an unknown compound of tannic acid and quinone, thus precluding the determination of tannin fixed by the Wilson and Kern method. It is interesting to note that this precipitate looked just like the well-known "reds" or phlobaphenes encountered in certain natural vegetable tannin solutions. In addition, it was noted that, together with the separation of this precipitate, a gas was formed, which was especially evident after the addition of hide powder.

The results given in the table and in Figure 3 show increasing amounts of fixation in the alkaline range of pH 8 to 12, thereby approximating the typical vegetable tanning curve. In the region of pH 8 to 5 it is seen that quinone effects a retardation of tanning. This is not unexpected when it is recalled that nontans generally retard the rate of combination of tanning with hide substance;[7,8,9] quinone acts, relatively speaking, like a nontan in this pH range.

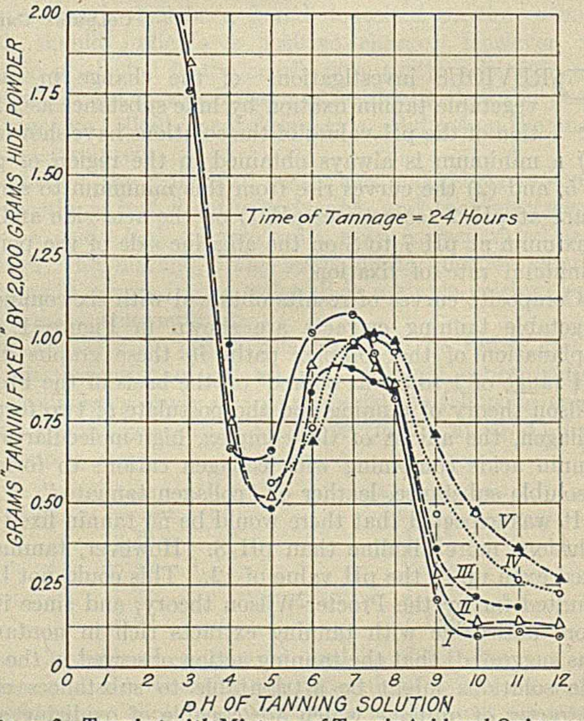

Figure 3—Tanning with Mixtures of Tannic Acid and Quinone

The designations on the curves are explained in the table.

The evidence submitted supports the view that the tanning action of vegetable extracts in the range of pH 8 to 12 is due to substances of the nature of quinone.

The authors are indebted to A. F. Gallun and Sons Company for grants in aid of this investigation.

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[6] This Journal, 16, 925 (1924).

[7] Wilson, *J. Am. Leather Chem. Assoc.*, 15, 374 (1920).

[8] Thomas and Kelly, This Journal, 14, 292 (1922).

[9] *Ibid.*, 17, 41 (1925).

Standardization of Agalma Black 10B[1,2]

By Wm. D. Appel, Wallace R. Brode, and I. M. Welch

BUREAU OF STANDARDS, WASHINGTON, D. C.

A series of samples of agalma black 10B from foreign and domestic manufacturers has been evaluated independently by means of titanous chloride titration, spectrophotometric measurements, and practical dyeings. The possibility of writing specifications for and establishing one or more trade standards for the dye is discussed.

THE lack of uniformity in strength, quality, and money value of commercial dyes from different sources is well known to the trade. Inherited from the pre-war industry, this condition has been continued perforce, for the American dye manufacturers have been fully occupied with problems of production. With it has continued the multiplicity of names, the appearance of old dyes under new names, and the talk of trade "secrets,"—pre-war practices designed to stimulate business. It may be said with assurance that such practices work no permanent good for the dye industry. Certainly, unscrupulous dealers have profited by them and legitimate industry has suffered corresponding loss. The establishment of trade standards for the more important and better known dyestuffs would not only tend to prevent such loss, but would simplify and clarify the trade for both manufacturer and consumer.

This standardization need extend to only a few of the more important technical dyes to be of great benefit to the industry. Thus the first ten dyes in the order of quantity produced in the United States during 1924 made up 65 per cent of the total. The quantity sold amounted to 64 per cent, with a value of 33 per cent of the total.[3] In the accompanying table are given the production and value for 1924 of the more important dyes. The money value of a number of dyes which are made in lesser quantity far exceeds that of other dyes which are made in larger amounts. Auramine, which is number 21 in the order of production, is number 7 in the order of value. Not only the dyes of large production or of high value, but also those produced by a number of different manufacturers should be standardized. The number of American manufacturers of each dye listed is also shown in the table.

Some dyes are already reasonably well standardized for strength. Indigo and the vat dyes are sold on a definite strength basis in terms of the dry powder, which is normally a concentrated product. The different manufacturers' standards of some of the common water-soluble dyes agree reasonably well in strength. Certain dyes, such as the sulfur colors and some of the complex azo dyes, offer peculiar difficulties to standardization because of the variability in constitution or difficulty of test, and much work is required before satisfactory standards for them can be established.

Studies of some of the important dyes from the standpoint of commercial standardization are in progress. This paper is the first of three reporting the results of such studies of agalma black 10B. In it are compared three independent methods for the estimation of the strength of commercial samples of the dye—namely, titanous chloride titration, spectrophotometric analysis, and comparative dyeing.

Agalma black 10B ranks fifth in the order of importance of the commercial dyes, nearly $1^1/_3$ million pounds with a value of $780,000 having been produced by thirteen manufacturers in the United States in 1924. It dyes wool and silk a greenish black from an acid bath and is the basis of nearly all the black acid dye mixtures on the market. Vegetable fibers are unstained by it.

The preparation of agalma black 10B is well known. A neutral solution of H-acid (8-amino-1-naphthol-3,6-disulfonic acid) is added to an equivalent amount of diazotized *p*-nitroaniline, the mixture containing free mineral acid at all times. When the acid coupling is complete, diazotized aniline is coupled in alkaline solution to the monoazo dye formed. In practice, the couplings are not strictly molecular and red monoazo dyes are also formed and to a greater or lesser extent are present in the finished product.

These subsidiary dyes modify the clear green-black shade of dyeings of pure agalma black 10B and introduce difficulties in the estimation of strength of commercial samples. Their quantitative estimation is the subject of another paper.

Materials

Two laboratory preparations of agalma black were used to check the standardization of the titanous chloride solution and for standard spectrophotometric measurements. They were prepared by the method outlined above, using molecular equivalents of the components. One sample was purified by recrystallization, the second sample by recrystallization and then dialysis. The first sample contained 91 per cent of anhydrous dye, 2.2 per cent of moisture, and 6.3 per cent of salt; the second, 99.2 per cent of anhydrous dye and not over 0.2 per cent of salt. Spectrophotometrically the two samples agreed when allowance was made for the difference in strength. The mother liquor of dyeings made from them gave the same spectrophotometric curve as the original solution.

The twenty-three commercial samples studied represented about twenty different sources, five of them foreign. They were considered to be representative of the different manufacturers' and dealers' stock quality dye.

Titanous Chloride Titration

Titanous chloride titrations[4] were carried out in the presence of sulfuric acid by the indirect method, the blue-green color of a reduction product with ferric iron giving a satisfactory end point. A sample equivalent to about 350 cc. (300 to 400 cc.) of 0.05 N titanous chloride solution was dissolved in water and diluted to 1000 cc. To a 100-cc. portion of the solution were added 25 cc. of 40 per cent sulfuric acid. The mixture was boiled to expel dissolved air, swept with carbon dioxide, and 50 cc. of the standard titanous chloride solution were added. The mixture was boiled for 5 minutes and then titrated hot (under carbon dioxide) with 0.05 N ferric alum solution to the appearance of a blue-green color. The end point in most cases was sharp.

Spectrophotometric Measurements

The spectrophotometric measurements[5] were made on the Keuffel & Esser color analyzer. The quantity measured

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[1] A preliminary report of this work was given under this title before the Division of Dye Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925. Received February 26, 1926.

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

[3] Statistics given in this paper are taken from the Census of Dyes and Other Synthetic Organic Chemicals, 1924, by the U. S. Tariff Commission.

[4] Knecht and Hibbert, "New Reduction Method in Volumetric Analysis," Longmans, Green & Co., 2d ed., **1925**; and Calcott and English, THIS JOURNAL, **15**, 1042 (1923).

[5] For general information, see "Spectrophotometry," Report of Progress Committee for 1922–3, *J. Optical Soc. Am.*, **10**, 169 (1925).

was the transmittancy—viz., the transmission at selected wave lengths of the solution in a given cell relative to that of the solvent in a similar cell. Thicknesses of 5 cm. were used for solvent and solution and the concentration of the latter was 3.33 mg. of pure dye per liter of solution on the basis of the titanous chloride titration. This concentration was obtained by dissolving the required amount (1 to 3.5 grams) of the commercial sample and diluting to a volume of 500 cc., diluting 25 cc. of this solution to 250 cc. and 10 cc. of this to 300 cc. The solvent was an aqueous buffer solution containing 0.01 gram molecule each of sodium acetate and acetic acid per liter and having a pH of 5.0.

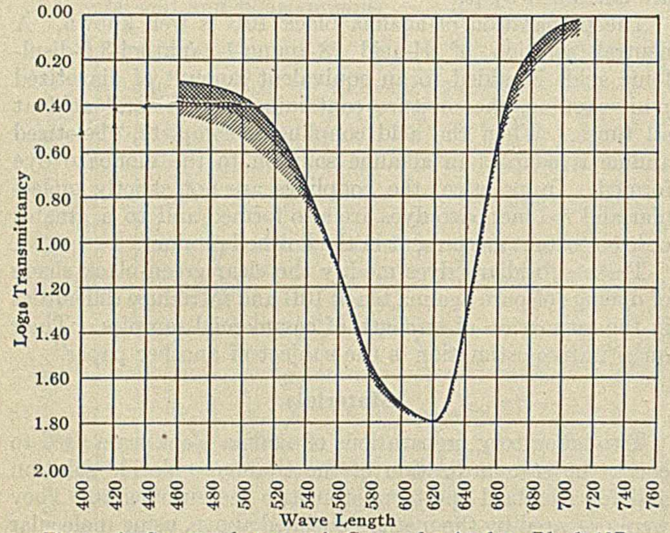

Figure 1—Spectrophotometric Curves for Agalma Black 10B

The inside line is the curve for the pure dye 10 mg. per liter, thickness of solution 2 cm., temperature 25° C., in acetate buffer solution, pH 5.0. The curves of the 23 commercial samples lie within the shaded area, the majority of them within the heavily shaded area.

The negative logarithms of the spectral transmittancies are quantities ordinarily proportional to the amount of dye in solution. Accordingly, if they are plotted against wave length, the area between the curve so obtained and the wave-length axis will be proportional to the amount of dye in solution. Calling this area for a commercial sample and for the pure dye, respectively, A and B, and the weights taken, respectively, C and D, then the percentage purity $= A/B \times D/C \times 100$. Wave-length limits of 540 and 670 mμ were chosen as boundaries of the area as the measurements on this particular dye are the most reliable within this range. The percentage purity was also calculated from the value of the curve at 620 mμ, the wave length of maximum absorption. The average of the two values is the final spectrophotometric value which was used in Figure 2.

In Figure 1 the solid line represents the curve for the pure dye and the shaded area covers the spectrophotometric curves for all twenty-three samples reduced to the same value at the wave length of maximum absorption. The lightly shaded area is necessitated by a few of the samples only; the majority fall within the heavily shaded area. This composite curve shows the remarkably good agreement among the samples and affords an excellent means of defining the dye type and maximum allowable deviations in color from it.

Comparative Dyeing Tests

Comparative dyeing tests were made under controlled conditions in the apparatus described elsewhere.[6] Four-tenths per cent dyeings on the basis of dye content were made on fine white wool flock. Four grams of wool flock from a large supply previously thoroughly mixed and bottled were placed in the 6 × 23 cm. test tube used as a dye bath and wet out by stirring with 100 cc. of boiling water for 5 minutes. The temperature was maintained by boiling water in the outer jacket of the dye bath. The requisite amount of the dye solution used for the titanous chloride titration was diluted to 30 cc. and added to the dye bath. Ten cubic centimeters of rinse water, 4 cc. of 10 per cent sodium sulfate solution, 4 cc. of 10 per cent acid sodium sulfate solution, and 12 cc. of rinse water were then added in order. Dyeing was continued for 15 minutes. The dyed fiber was separated from the mother liquor on a wire screen and squeezed in a press between blotting paper. It was then dried in an air bath, conditioned in an atmosphere of 65 per cent humidity, and bottled.

Dyeings were made on the basis of the titanous chloride determinations and also on the spectrophotometric figures. Additional dyeings were made as needed to insure careful evaluations.

The relative strengths of these dyeings were judged by visual comparison with dyeings of Sample 13 (Figure 2), a good quality commercial product containing 60 per cent coloring matter, rather than with those of the pure dye. Dyeings of the pure dye were not so satisfactory for judging strength since they were much purer in color than those of the commercial samples. The variations in hue of dyeings from No. 13 were also noted and are given in Figure 2.

Comparison of Results

The results of these strength determinations are given in Figure 2. In fifteen out of the twenty-three cases the spectrophotometric and titanous chloride evaluations agree with the dyeing results within the limits of accuracy of the dyeing results, which has been taken as ±2 per cent and indicated by the size of the circle. The precision of the spectrophotometric and titanous chloride evaluations is better than this, as is indicated by the size of the circles in the figure. In three cases the spectrophotometric evaluations agree with the dyeing, but the titanous chloride titrations are high, indicating the presence of *p*-nitroaniline or other reducible material.

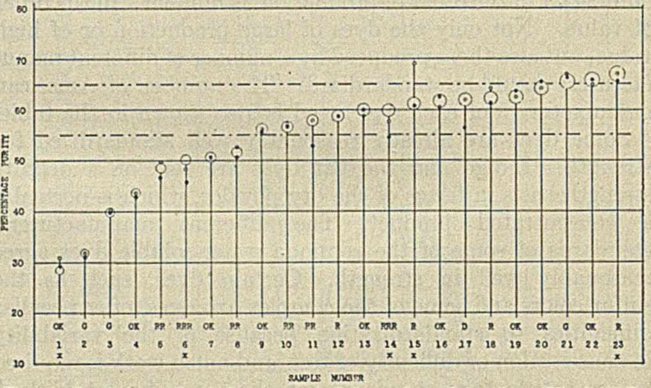

Figure 2—Strength of Commercial Samples of Agalma Black 10B

○ Strength by dyeing test
∘ Titanous chloride titration
· Spectrophotometric method

Above the sample number is given the "Shade" of dyeing as compared with Sample 13

OK = Same as 13
G = Greener
R = Redder
D = Duller
X = Foreign sample

In three cases the titanous chloride titrations agree with the dyeing results, but the spectrophotometric evaluations are low. In two instances both titanous chloride titrations and spectrophotometric evaluations are low.

The five last-mentioned cases are of especial interest. Although a dye sample may contain less pure dye than the spectrophotometric and titanous chloride evaluations show, it cannot contain more pure dye than they show. Therefore, it is evident that Samples 5, 6, 11, 14, and 17 are abnormal. They cannot contain more true agalma black than is indicated by the spectrophotometer. The first four of these samples

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[6] Appel, *Am. Dyestuff Rep.*, **13**, 507 (1924).

Production and Value of Some Important Dyes Produced in the United States in 1924

					SALES			
No.	NAME	Schultz No.	No. of mfrs.	Production Units of 100,000 lbs.	Quantity Units of 100,000 lbs.	Value Units of $50,000	Price per lb.	Per cent total value
1	Indigo, 20% paste	874	3	199.9	179.8	78.3	0.22	11.2
2	Sulfur black	720	5	117.3	111.9	42.6	0.19	6.1
3	Direct deep black EW	462	9	54.7	49.5	37.6	0.38	5.4
4	Alizarin saphirol B	858	4	...	2.5	16.5	3.30	2.4
5	Agalma black 10B	217	13	12.7	11.8	15.1	0.64	2.2
6	Methyl violet	515	8	5.4	5.4	12.1	1.13	1.7
7	Auramine	493	5	3.9	4.0	12.1	1.52	1.7
8	Nigrosine W. S.	700	6	12.4	12.3	11.8	0.48	1.7
9	Sulfur brown		14	14.0	14.1	10.8	0.38	1.5
10	Methylene blue	659	3	4.1	3.6	9.0	1.26	1.3
11	Oxamine black	333	9	7.7	6.9	9.0	0.65	1.3
12	Salicine black U	181	13	7.7	8.8	8.4	0.48	1.2
13	Benzamine brown G	476	10	8.2	8.3	8.0	0.49	1.1
14	Orange II	145	8	11.6	12.2	8.0	0.33	1.1
15	Chrysophenine G	304	5	5.1	4.5	7.5	0.84	1.1
16	Chicago blue 6B	424	5	2.4	2.7	6.8	1.26	1.0
17	Alkali blue	536	8	1.2	1.3	6.5	2.56	0.9
18	Benzo fast scarlet	279	4	1.9	1.7	6.3	1.91	0.9
19	Benzopurpurine 4B	363	6	4.5	4.0	5.9	0.73	0.8
20	Direct yellow R	9	8	4.5	4.4	5.8	0.66	0.8
21	Metanil yellow	134	6	3.3	3.9	5.7	0.72	0.8
22	Eosine	587	4	1.3	1.5	5.6	1.85	0.8
23	Chrysoidine	33	9	5.6	5.6	5.5	0.49	0.8
24	Malachite green	495	4	1.8	1.6	5.5	1.70	0.8
25	Bismarck brown 2R	284	10	5.6	5.4	5.4	0.51	0.8
26	Amaranth (food)	168	5	1.0	1.0	5.4	2.77	0.8
27	Benzo blue 2B	337	12	7.0	6.9	5.1	0.37	0.7
28	Sulfoncyanine G	257	4	2.7	2.7	4.7	0.89	0.7
29	Fast light yellow	19	5	0.9	0.9	4.7	2.64	0.7
30	Azo rubine	163	9	2.9	3.0	4.7	0.79	0.7

give dyeings of a very red shade and obviously contain a considerable amount of a red impurity. The fifth sample gives a dull dyeing and is distinctly not the same quality as the remaining samples.

It is of interest to note that over half of the samples have a dye content between 55 and 65 per cent, indicating that for most manufacturers the compliance with a definite standard such as 60 per cent would not be difficult.

Conclusions

It appears that neither the spectrophotometric nor the titanous chloride method is entirely satisfactory for the evaluation of commercial samples of agalma black 10B in respect to strength. However, a combination of the two methods seems to give a satisfactory means of specifying a standard commercial type, since where the two methods agree the result is that obtained by the usual dyeing test. Over half of the twenty-three samples examined satisfy this requirement.

A standard of 60 per cent purity by titanous chloride and spectrophotometer would necessitate but slight shift in the strength of the standards of a majority of manufacturers.

Preparation of Cyanamide Hydrochloride[1]

By L. A. Pinck and H. C. Hetherington

Fixed Nitrogen Research Laboratory, Washington, D. C.

Cyanamide, H_2CN_2, possesses considerable interest as the natural starting point in a large number of organic syntheses, and although at present it has little or no commercial value, it is by no means certain that uses would not soon be found for it were it not for its extremely hygroscopic nature and its tendency to polymerize, even in the solid state and at room temperature.

For these reasons the salt cyanamide hydrochloride, $H_2CN_2.2HCl$, which is known to be far less hygroscopic and more stable than cyanamide itself, should be of greater interest. Cyanamide hydrochloride is a white crystalline compound, stable at ordinary temperature when dry but hydrolyzing readily in aqueous solution. It may be heated safely to 70°–80° C., but decomposes rapidly when heated above 100° C., yielding hydrogen chloride and mellon.

Two methods have previously been proposed for the preparation of cyanamide hydrochloride. The earlier[2] of these consists in passing dry hydrogen chloride gas into an absolute ether solution of cyanamide. The success of the preparation depends upon the complete absence of moisture, for in the presence of even a very slight amount of water the hydrochloride forms a sticky mass which is difficult to dry and which invariably clogs the gas inlet.

The other recorded method[3] consists in dissolving cyanamide in concentrated hydrochloric acid and evaporating the solution in a vacuum desiccator. This method is open to several objections, chief of which is the difficulty of obtaining a dry product, free from uncombined hydrogen chloride. Moreover, there is considerable danger of contamination of the product with urea formed by hydrolysis of cyanamide in the aqueous solution of hydrogen chloride.

Since the elimination of water is the principal difficulty in the foregoing methods, it was believed that the preparation might be more satisfactorily carried out in solvents such as ethyl alcohol, methanol, or acetone, which through their miscibility with water would prevent the salt from taking up all the moisture in the system.

Qualitative experiments were first made to determine whether or not ethyl alcohol would itself react with the other constituents. That such a reaction might occur was indicated by the reported preparation of alkyl isourea from cyanamide and alcoholic hydrogen chloride.[4] It was found, however, that this reaction is too slow to take place to a measurable extent during the preparation of cyanamide hydrochloride. A somewhat similar behavior was observed in the case of acetone. While no side reactions occurred when cyanamide hydrochloride was prepared in this solvent, a compound corresponding to tri-isopropyl diurea or triacetonyl diurea was formed when a solution of cyanamide

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[1] Received March 19, 1926.

[2] Dreschel, *J. prakt. Chem.*, [2] **11**, 315 (1875).

[3] Hantsch and Vagt, *Ann.*, **314**, 366 (1901).

[4] Stieglitz and McKee, *Ber.*, **33**, 807 (1900).

hydrochloride in acetone was allowed to stand for several weeks.

Experiments were made to determine the yield and quality of product obtainable when cyanamide was added to an alcoholic solution of varying hydrogen chloride and water content. It was found, as would be expected, that the solubility of $H_2CN_2.2HCl$ in alcohol was materially reduced by the presence of a slight excess of hydrogen chloride, and that the salt could satisfactorily be prepared in alcohol containing as much as 10 per cent of water.

Yields of 98 to 99 per cent, based on the cyanamide used, are obtainable by the method finally adopted when the salt is made in several lots and the mother liquor from the first lot is used for those succeeding, but when one preparation only is made the solubility of the salt reduces the yield to about 94 per cent.

Although methanol and acetone were found to be fairly satisfactory, the higher solubility of cyanamide hydrochloride in these solvents materially reduced the yields as compared with those obtained from ethyl alcohol.

Method Adopted

Dry hydrogen chloride is passed into ethyl alcohol (95 per cent) until the solution contains about 40 per cent HCl. To this solution solid cyanamide is gradually added in quantity sufficient to react with about 95 per cent of the hydrogen chloride. Proper cooling is supplied so as to keep the temperature at 45° C. or less, thus preventing the escape of hydrogen chloride and alcohol. The reacting mixture is agitated for a short time (5 to 10 minutes), filtered, and washed, preferably with a saturated alcoholic solution of cyanamide hydrochloride or ether, to remove the excess hydrogen chloride. The salt can be safely dried at 80° C. The mother liquor, if no ether has been used, is made up to the original volume with the required amount of fresh alcoholic hydrogen chloride, and hydrogen chloride is further added until the required concentration (approximately 40 per cent) is obtained. Cyanamide is then added to the solution as in the first cycle of operation. The yield is thus made practically theoretical and the process may be continued in this manner until the volume of water introduced with the cyanamide and that due to absorption from the atmosphere has risen to a point where difficulty is experienced in obtaining a dry product. The percentage of water may rise to about 10 per cent without interfering with the isolation of the hydrochloride in practically pure and dry condition. From the nature of the preparation, it will be seen that there is no limitation to the scale on which it may be carried out.

Apparatus for Wet Ashing[1]

By William A. Turner

Bureau of Dairying, Washington, D. C.

In ashing organic materials in the wet way—i. e., with sulfuric and nitric acids, the prolific escape of sulfuric and nitric oxide fumes is liable to become a considerable nuisance. To obviate this as much as possible, the apparatus illustrated was devised and has been used with satisfaction for the past three years. Hay, grain, blood, milk, feces, and urine have been ashed with very little annoyance.

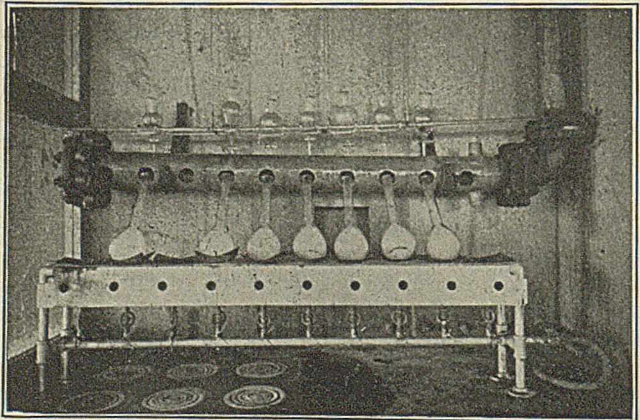

Plate 1

The apparatus, shown in detail in Figures 1 and 2 and in actual operation in Plate 1, consists of a tube similar to the conventional lead tube used in Kjeldahl determinations, except that it is constructed of acid-resistant Duriron and has, in addition to the large openings at the side for the Kjeldahl flasks, small openings at the top for the introduction of nitric acid into each flask. The tube is accompanied by a burner rack similar to that used for Kjeldahl determinations. As installed by the writer the apparatus was placed in a hood and a special fan was inserted in the Duriron tube which led to a good flue.

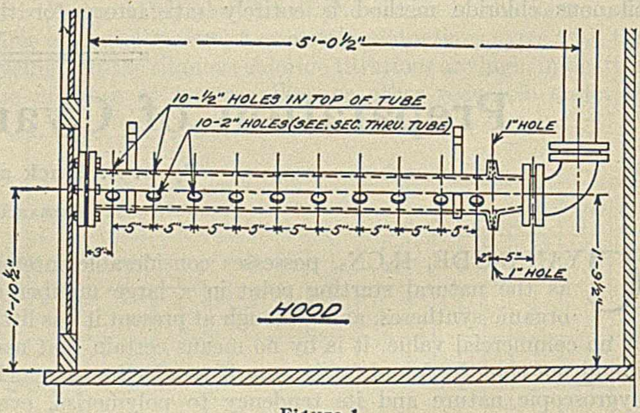

Figure 1

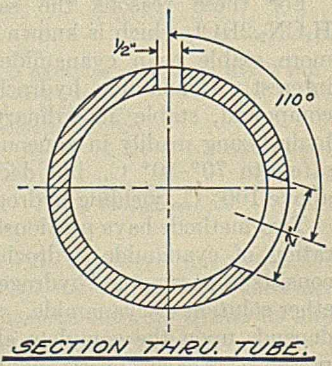

Figure 2

The ashings are ordinarily conducted in 500-cc. long-necked Kjeldahl flasks, and the nitric acid is introduced from dropping funnels, supported on heavy glass rods to avoid the use of corrosive metal. The delivery tubes of the dropping funnels are bent so as to enter the mouths of the flasks. There is an opening at the end of the Duriron tube for the escape of condensed moisture and acids. The ashings may be conducted as fast as desired with due regard to proper precautions.

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[1] Received March 4, 1926.

The Freeness of Sulfite Pulp[1]

By D. S. Davis

Bureau of Tests, International Paper Co., Glens Falls, N. Y.

The data and plots presented are intended to enhance the usefulness of the Williams freeness tester. A method of duplicating orifice settings is outlined. Curved-line and straight-line plots and an equation are given for the purpose of converting freeness values obtained with an orifice of one size to those obtained with an orifice of another. The effect of change of consistency upon freeness is discussed and charts are given for converting freeness values from one consistency to another, the use of the charts eliminating a portion of the experimental manipulation.

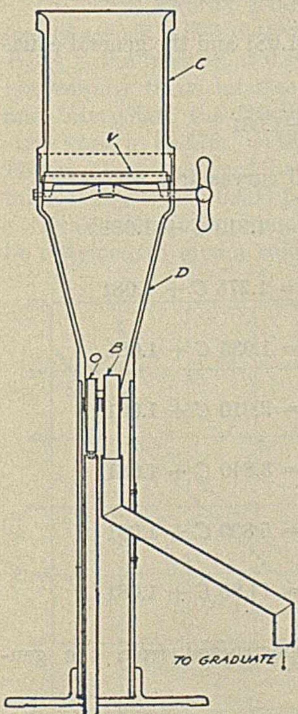
It is pointed out that freeness, as measured by the Williams tester, is not an additive property of the stock and a method is outlined for converting Williams freeness to additive freeness. The type of mathematical treatment employed is equally applicable to orifices of other sizes and to modifications of the procedure to suit individual needs.

ONE of the most important properties of stock for paper-making purposes is the rate of drainage of water from the fiber on the wire of the paper machine. This rate of drainage is called "freeness" and influences, to a marked degree, the strength, uniformity, and finish of the paper and the operation of the machine.

In regard to freeness, Buncke[2] says:

> If there is very much coarse fiber and insufficient filler (fine, fluffy fiber) in the stock, the fiber mat will not pack well; it will be of open texture, the water will pass through quickly, and the stock will be called free stock. On the other hand, if there is a large amount of fiber that is short, mixed with fiber with frayed ends, a more dense mat of fiber will be made. The water will then pass through the fiber mat more slowly, and the mixture will be known as slow stock.

In mechanical pulp freeness is influenced almost entirely by two operations: grinding, the action of the pulpstone upon the pulpwood; and jordaning, the cutting action of the jordan engines upon the pulp suspension. In chemical pulp freeness is also largely dependent upon two operations: beating, the hydrating and fraying actions of the beaters; and the jordaning of the beaten stock.



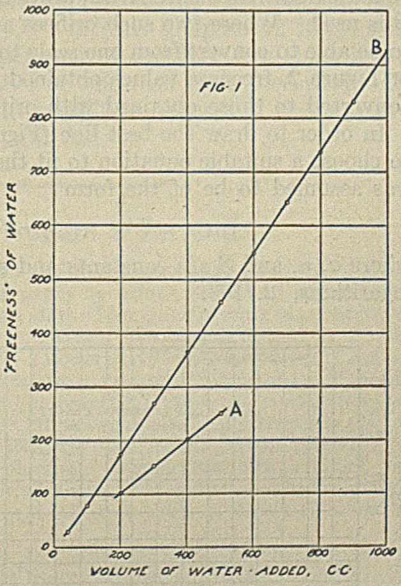
Freeness Tester for Sulfite Pulp

Since freeness is of such importance, close control of the grinding, beating, and jordaning operations is desirable; that is, it is essential to know when to sharpen the pulpstones, how long to beat the stock, and how to set the jordans. Such information is best given by testing the freeness of the stock under consideration. For this purpose several types of freeness testers have been developed. Recent experimental work conducted at this laboratory has brought to light several interesting facts concerning the nature of freeness of sulfite stock as determined by a tester essentially of the Williams type.

Apparatus

The apparatus consists of four units: a motor-driven centrifuge, a motor-driven stirrer, an electric heating coil which fits into the centrifuge, and the tester proper which is a slightly modified form of the Williams Model 50–50 freeness tester.[3]

The freeness tester as modified by Mr. Williams for use in this laboratory is shown in the accompanying diagram. At the upper part of the tester is a 1-liter cup, *C*, with a screen bottom against which a flat plate or foot valve, *V*, fits. One liter of a pulp suspension of 0.400 per cent consistency is poured into the cup. On tripping the valve the water drains from the pulp through the screen into a conical chamber, *D*. At the bottom of this are two outlets, one, *B*, which leads to a graduate, and the other, *O*, through which the water goes to waste. The half-inch measuring outlet, *B*, is slightly the higher so that as the level of the water in the conical chamber drops, the flow into the graduate is cut off sharply. The water which continues to drain slowly from the fiber runs out through the lower outlet. The volume of water passing to the graduate will be called the Williams freeness number and will be designated by *F*.



Some of the tests were made with a quarter-inch instead of a half-inch outlet. The smaller orifice will be denoted by *A* and the freeness values so obtained by *f*. The procedures in the cases of the two outlets were exactly the same except that when *A* was used only 500 cc. of 0.400 per cent pulp suspension were required.

Method

Sufficient stock of somewhat more than 24 grams bone-dry weight is made up to 6 liters. This is agitated in a pail with the motor-driven stirrer and 500 cc. of the stock are

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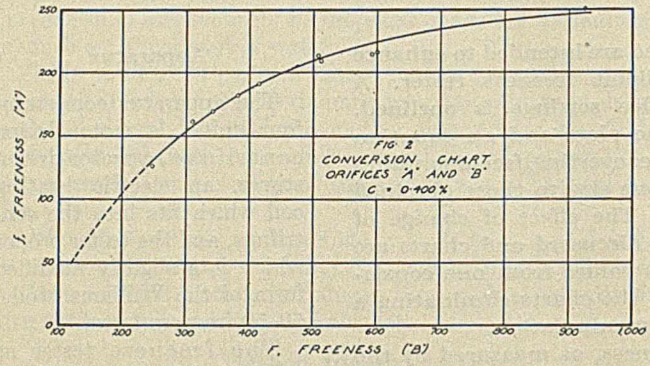
[1] Received January 12, 1926.

[2] "The Manufacture of Pulp and Paper," Vol. III, § 3, p. 7. McGraw-Hill Book Co., 1922.

[3] Williams, *Pulp Paper Mag. Can.*, **23**, 443 (1925).

brought to the bone-dry condition in the centrifuge with the aid of the heating coil. The bone-dry lap is removed, weighed rapidly, reheated, and reweighed. The amount of water to add to the remaining 5.5 liters to give a consistency of 0.400 per cent on the bone-dry basis is then calculated. This is added and the stock is again agitated.



One liter or 0.5 liter of this stock is poured into the cup according to whether orifice B or A is used.

Duplication of Orifice Settings

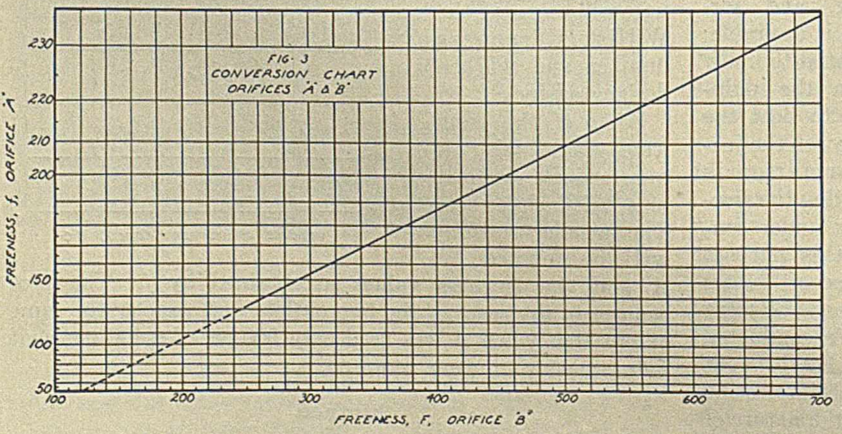
Of the water passing through the screen, orifices A and B divert about 50 and 90 per cent, respectively, to the graduate. The volumes of water passing into the graduate for various amounts of water poured into the cup are plotted in Figure 1. With this graph it is possible to duplicate any previous setting of the measuring orifices.

The use of the larger orifice serves to expand the freeness scale; that is, two stocks which differ only slightly in freeness as measured with orifice A will differ more markedly if orifice B is used. Where two such orifices are in use it is desirable to be able to convert from one scale to the other. By means of Figure 2, freeness values obtained with orifice A may be converted to those obtained with orifice B.

In order to draw the best line (Figure 2) it was necessary to choose a suitable equation to fit the data. This equation was assumed to be of the form

$$e^{nF + a} = S - f$$

where a, n, and S are constants and e is the base of natural logarithms, 2.7183.



The equation of the conversion curve is

$$333.6\ e^{-0.00395\,F} = 255.3 - f$$

or the more convenient form

$$F = 1470 - 583 \log (255.3 - f)$$

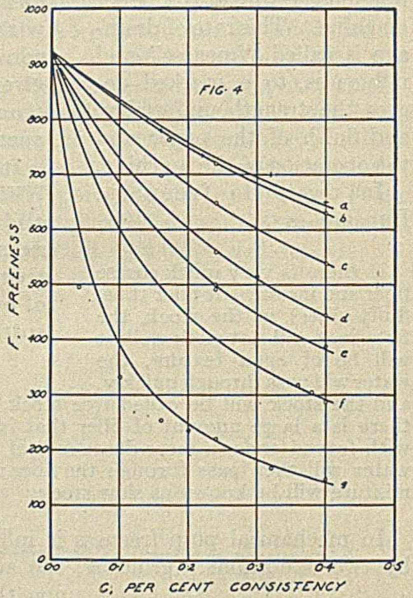
Figure 3 is for the same purpose as Figure 2 but the equations of the functions plotted along the axes are

$$x = mF$$
$$y = p \log(255.3 - f)$$

and so the curve is a straight line.

Effect of Change of Consistency

From a consideration of the nature of freeness, it is evident that freeness increases with decreasing consistency. The manner of this increase is shown by Figure 4.



From the positions of the plotted points and the fact that the curves must all pass through 925, the freeness of stock at zero consistency, or water, it is evident that the most convenient curves representing the data are hyperbolas.

The general form of the equations is

$$\frac{H}{F} = KC + A$$

where A, H, and K are constants.

H is chosen to be 1000 for convenience and, since all the hyperbolas have a common intersection at 0, 925, we may substitute these values for C and F, respectively, in the general equation and solve for A. The value of A is 1.081 and the general equation becomes

$$\frac{1000}{F} = KC + 1.081$$

The equations of the individual curves are,

$$(a) \qquad \frac{1000}{F} = 1.219\ C + 1.081$$

$$(b) \qquad \frac{1000}{F} = 1.275\ C + 1.081$$

$$(c) \qquad \frac{1000}{F} = 1.935\ C + 1.081$$

$$(d) \qquad \frac{1000}{F} = 2.910\ C + 1.081$$

$$(e) \qquad \frac{1000}{F} = 3.840\ C + 1.081$$

$$(f) \qquad \frac{1000}{F} = 5.850\ C + 1.081$$

$$(g) \qquad \frac{1000}{F} = 14.96\ C + 1.081$$

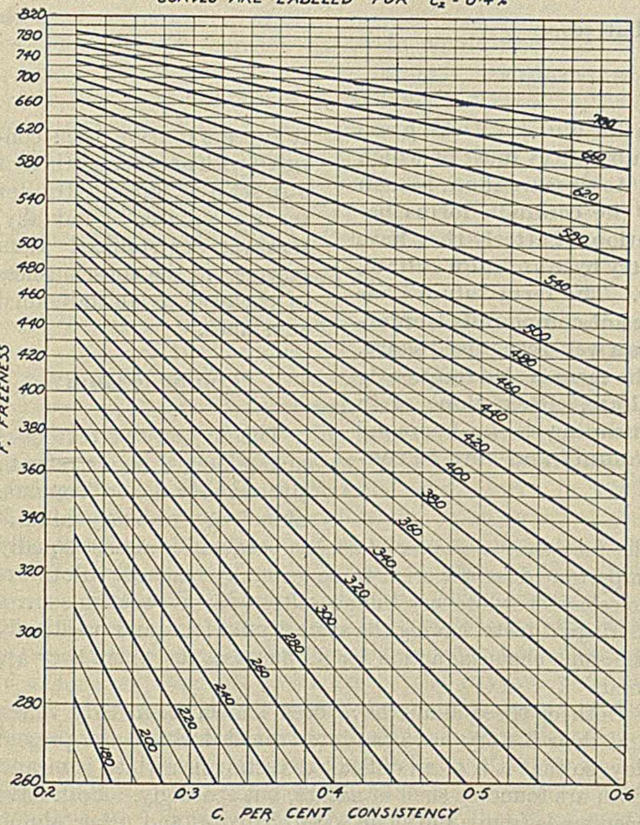
Figure 5 was constructed from the general equation,

$$\frac{1000}{F} = KC + 1.081$$

and since the equations of the functions plotted along the axes are

$$x = qC$$
$$\text{and } y = r\left(\frac{1000}{F}\right)$$

FIG. 5
CHART FOR CONVERTING FREENESS AT C_1 TO FREENESS AT C_2 PER CENT CONSISTENCY
CURVES ARE LABELED FOR $C_2 = 0.4\%$



the curves are all straight lines with a common point of convergence.

The use of Figure 5 is outlined as follows: Given the freeness of a stock as 500, determined at 0.360 per cent consistency. What is the freeness at 0.400 per cent? Follow the 500 line horizontally to its intersection with the 0.360 per cent line and interpolate the freeness at 0.400 per cent, along the slant lines, to be 476. What is the freeness at 0.300 per cent? Follow along the slant lines from the 0.360 per cent, 500, intersection to the 0.300 per cent line, and read 557.

Occasionally, in running a sample, not enough stock would be obtained to give a sufficient quantity of 0.400 per cent suspension to handle readily and sometimes errors would be found in the calculation of the amount of water to add to dilute to 0.400 per cent. By the use of Figure 5 such determinations were not lost, for the apparent freeness at the consistency used could be easily converted to the standard 0.400 per cent.

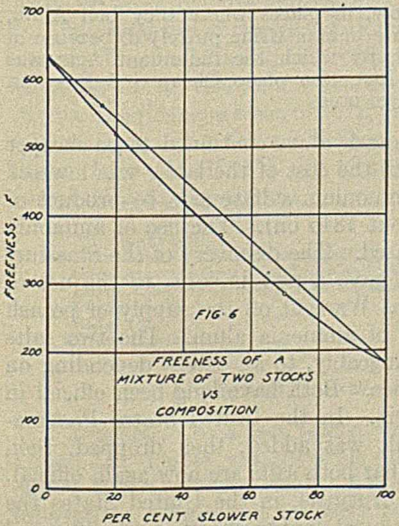


FIG. 6
FREENESS OF A MIXTURE OF TWO STOCKS VS COMPOSITION

A plot of the type of Figure 5 also enables one to dispense with the dilution to 0.400 per cent. It is possible to judge the amount of thick stock to be taken to make a suspension of 0.3 per cent to 0.5 per cent. The consistency need not be adjusted, for with its value known the freeness at 0.400 per cent may be read from the chart.

Conversion of Williams Freeness to Additive Freeness

In common with many other physical properties, freeness, as defined and measured at present, is not an additive property of the stock. Equal volumes of stocks of freenesses of 635 and 181 give a mixture not of a freeness of 408, the arithmetic mean, but of 370. This is shown in Figure 6, a plot of the freeness of a mixture of two stocks against the percentage by volume of the slower stock. The curve resembles the boiling point-composition plots for binary mixtures.

The freeness values plotted were obtained with the larger orifice, *B*, and are designated by *F*. A plot of the freeness, *f*, against the percentage composition would be very much like Figure 6, but the line would be concave in the opposite direction. Thus it is seen that neither freeness scale is additive.

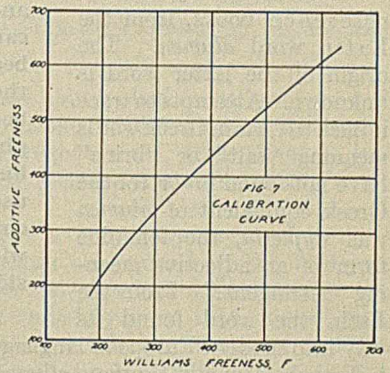


FIG. 7
CALIBRATION CURVE

The freeness scale may be arbitrarily made additive in the following manner: Two stocks are chosen, one very free, the other very slow. Mixtures of these two are made up and the volumes of water separating are measured. These volumes are calibrated to give the calculated additive freeness.

Figure 7 is a plot of additive freeness numbers against Williams freeness numbers, *F*, and was obtained from the data of Figure 6. In this illustrative case, stocks of freeness values of 635 and 181 were chosen as the very free and very slow stocks, respectively. A mixture composed of 40 per cent of the slower and 60 per cent of the very free stock has a Williams freeness number of 420, read from the heavy line, Figure 6. The calculated additive freeness of this mixture is 453, read from the light line.

New Sugars from Old

At the May 13th meeting of the Washington Chemical Society C. S. Hudson presented a paper by Alfons Kunz and himself, describing a new chlorination method for transforming sugar acetates to chloroacetyl derivatives. When lactose octaacetate in chloroform solution was heated 2 hours at 65° with an excess of active aluminum chloride a crystalline yield was obtained of about 30 per cent of the well-known α-chloroacetyl lactose (m. p. 120, $[\alpha]_D = +84$ in $CHCl_3$) and about 20 per cent of a chloroacetate (m. p. 182, $[\alpha]_D = +71$) of an isomeric disaccharide, which proves to be a new sugar called neolactose. Neolactose was oxidized by bromine to neolactobionic acid which yielded on acid hydrolysis *d*-galactose and *d*-altronic acid; the new sugar is thus a galactosido altrose.

In a second paper by Dr. Hudson, a similar chlorination of cellobiose octaacetate was described, which yielded about 20 per cent of ordinary α-chloroacetyl cellobiose (m. p. 184, $[\alpha]_D = +73$) and 18 per cent of a chloroacetate (hexagonal plates, m. p. 136, $[\alpha]_D = +60$) of a new sugar, celtrobiose. The action of aluminum chloride upon glucose pentaacetate produced α-chloroacetyl glucose (m. p. 71, $[\alpha]_D = +166$). The possibility that isomerization of glucose to another hexose may occur in this reaction is being studied at the Bureau of Standards and likewise the structure of celtrobiose and the action of aluminum bromide upon sugar acetates. The action of the aluminum halides upon sugar acetates apparently furnishes a method for carrying out remarkable transformations in sugar structures. It is hoped that some of the rarer sugars may be conveniently producible from the more accessible ones, as well as other new sugars from such compound sugars as maltose, gentiobiose, melibiose, etc.

The History of the Word "Alum"[1,2]

By Austin M. Patterson

Antioch College, Yellow Springs, Ohio

"Alum" is derived from the Latin "alumen," which was applied to several astringent substances most of which contained aluminum sulfate. As time went on, potash and ammonia alums became the common forms because of their ready crystallization. Latterly they have been largely displaced in industry by aluminum sulfate, though still used in pharmacy. The term "alum" has been extended to a whole series of compounds isomorphous with potash alum; this is a well-recognized sense, but a rather technical one. The term is also frequently used to mean "aluminum sulfate, either alone or in combination." The latter meaning is in harmony with the history of the word "alum" and may be considered entirely justifiable.

THE English word "alum" is derived, as is stated by various reference books, from the Latin word *alumen.* The origin of the latter word is unknown. Attempts to trace it back to certain Greek words meaning "salt" or "brine" have not found favor, for the Greek equivalent of *alumen* was *stypteria*, the feminine form of an adjective meaning "astringent." From the Latin the word found its way into modern European languages: *alum* in English, *alun* in French, *Alaun* in German, *allume* in Italian, etc.

The Early History of Alum

The ancients seem to have applied the terms *stypteria* and *alumen* to a number of substances of astringent taste, some light in color, some dark. The chemistry of that time was so primitive that the most superficial likeness was sufficient to cause very different compounds to be classed together under the same name. It is a matter of dispute whether they were acquainted with any of the series of crystallized double sulfates technically called "alums" by modern chemists. For example, Meyer, in his "History of Chemistry" (Chapter I), says:

> Under στυπτηρια or *alumen* of the ancients must be understood substances of astringent properties generally, although alum itself is what is usually meant; being prepared from alum shale, it contained green vitriol as an impurity.

But the Encyclopaedia Britannica (11th ed., "Alum") states that:

> The alumen of the ancients, then, was not the same as the alum of the moderns. It was most commonly an iron sulphate, sometimes probably an aluminium sulphate, and usually a mixture of the two. But the ancients were unacquainted with our alum.

We have no definite information on the earliest meaning of "alum" in English, but one may reasonably suppose that it was applied in the same general way to several astringent salts. The first citation for the word in Murray's Oxford English Dictionary is dated about 1325: "As alum and alkatran [pitch], that angre arn bothe." Sir John Mandeville's Travels (1366) contains the passage: "And fro Jerico, a 3 Myle, is the dede See. Aboute that See growethe moche Alom and of Alkatran." The word occurs about 1386 in Chaucer's Canon's Yeoman's Tale (a most amusing story of a quack alchemist): "Of tartre, alum, glas, berme, wort and argoille."

It seems certain that crystallized alum was known to the medieval chemists, or alchemists, though even at that time it appears to have been confused with another astringent substance, green vitriol or ferrous sulfate. Gradually, however, crystallized alum emerged in the consciousness of chemists as an individual substance.

"Common Alum"

The majority of textbooks and reference books refer to *potash alum* as "common alum" or "ordinary alum;" the fact that *ammonia alum* has been and is almost equally important does not seem to be generally realized. Both are colorless or white crystalline salts, with a sweetish-sourish astringent taste, having the same crystal form and practically the same chemical action for all purposes for which they are used.

Both of these alums have been known from early times, and their history has been intertwined down to the present day, so that it is often difficult to distinguish which is meant. Both are found as such in nature, but sparingly. Both have been made from alum shale, clay, bauxite, and other aluminous materials. Both have been used in medicine and such arts as tanning, dyeing, paper-sizing, and water purification.

The fact that these particular alums could be made from well-known materials and easily obtained in a pure condition by crystallization accounts for their centuries of usefulness. Ammonia alum could be made from alum shale by the addition of decomposed urine. If the ammonia were replaced by potash (which can be obtained from the ashes of most plants), potash alum resulted. Potash alum could also be made directly from the mineral known as alum stone or alunite.

Meyer is authority for the statement that the alum of the iatrochemical period (about 1550) was essentially ammonia alum, and James, in his Medical Dictionary (1743), says:

> Formerly, and even now, in places where they boil Alum, instead of Pot-ash, they use human Urine putrefy'd, because of the Urinous volatile Salt, by which the redundant Acid was temper'd; but since the Invention of so Cheap and Easy an Expedient, Urine is no longer used.

From James's time potash alum continued to be cheaper than ammonia alum until the cost of the latter was lowered by the production of ammonium sulfate as a by-product of the gas-works (from about 1845 on). The use of ammonia alum then greatly increased. The discovery of the Stassfurt potash deposits in 1861 gave a new impetus to the use of potash alum. The Great War cut off the supply of potash and stimulated the use of ammonia alum. The two salts have been used interchangeably, to an extent depending on their relative market price. Both have long been official in the British Pharmacopeia. In the United States Pharmacopeia the ammonia salt was added, then dropped, then (1916) added again, so that both salts are now again official. According to wholesale druggists, in the United States the two are at present employed in pharmacy in about equal quantities. Hence, it is scarcely correct to say that "common or ordinary alum" means potash alum, especially since

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[1] Received March 12, 1925.

[2] In December, 1923, the author was employed to make an unbiased study of the meaning of the word "alum." The result of this study was given a small circulation in the form of a copyrighted pamphlet entitled "The Meaning of the Word Alum," and also embodied in testimony before the Federal Trade Commission in 1924. The subject is treated here from a standpoint of general scientific interest. (In their decision the commissioners upheld the meaning of the word "alum" as herein developed.—*Editor.*)

both the latter and ammonia alum have largely lost their industrial importance, as will be seen below.

As compared with potash alum and ammonia alum, *soda alum* (or sodium alum) is much more soluble and less easily crystallizable and therefore harder to obtain free from impurities. Its very existence was formerly questioned, but this is now fully established.[3] Soda alum made its appearance in industry much later than either potash alum or ammonia alum. Ure's Dictionary, 6th edition, 1867, states that it "is not an article of commerce nor is it used in the arts." Since then, however, it has come into use to a certain extent, and there are several patents for manufacturing it.

The Alum Series

As chemists well know, potash alum is a potassium aluminum sulfate of the formula $KAl(SO_4)_2.12H_2O$ (also written $K_2SO_4.Al_2(SO_4)_3.24H_2O$), and ammonia alum is exactly the same except that ammonium replaces potassium. Both crystallize in octahedra of the regular or isometric system.

As chemistry developed other salts were discovered, of analogous composition and the same crystal form, in which other elements replace the potassium or ammonium, and even the aluminum and sulfur, of potash or ammonia alum; and "alum" was applied as a generic term to the whole series. Thus we have cesium alum, iron alum, chrome alum, ammonia iron alum, and so on. In the most extended sense it is possible to have an alum containing none of the elements of potash or ammonia alum except the oxygen, plus the water of crystallization! All of these alums belong to the same crystal system and may crystallize together in all proportions, or the crystals may be made up of layers of the different salts. This is, of course, an extension of the original meaning of "alum." It will be observed that it is based, not on sameness of chemical action, but on analogy in composition and sameness of crystal system (isomorphism).

Replacement of Potash and Ammonia Alums in the Arts

As has been mentioned previously, potash and ammonia alums formerly had many uses. In practically all, if not all, of these uses their value depended on their aluminum sulfate and not on their potassium or ammonium sulfate. Hence other soluble forms of aluminum sulfate would answer as well or better if these forms could be obtained pure enough and cheap enough. Attention was first turned to soda alum, but its technical preparation was not then satisfactorily solved. Then came the possibility of pure aluminum sulfate, prepared from bauxite and sulfuric acid, and from that day the industrial use of the earlier alums began to wane.

According to Ullman, the replacement was first made in sizing for paper, then in mordants for dyeing. The Encyclopaedia Americana, edition of 1918, under the heading "Alum," quotes figures for the production of alums in the United States from the 1914 U. S. Census reports as follows (in round millions of pounds):

Aluminum sulfate	142
Alum cake (crude aluminum sulfate)	23
Concentrated alum (aluminum sulfate)	43
Burnt alum (desiccated potash or ammonia alum?)	23
Potash alum	13
Sodal alum	14
Other alums	56

Aluminum Sulfate as "Alum"

It appears to be a fact that aluminum sulfate has largely driven the double sulfates with potassium and ammonium out of industry. The effect of this on the use of words is interesting. There is a tendency to apply the familiar term "alum" to the newer and stronger reagent. This tendency seems most pronounced in paper-making and water purification, but is far wider than that. In the following citations "alum" means aluminum sulfate in all cases:

Water purification: "Water company makes its own alum and chlorine" [*Eng. News*, September 7, 1916].

Paper sizing: "Aluminum sulfate (alum) is used in paper manufacture . . . " [Aldons, "Paper and Its Constitutents," p. 30].

Agriculture: "The effect of alum on silicate colloids" [Scofield, *J. Wash. Acad. Sci.*, **2**, 438 (1921)].

Fireproofing: "The fabric had been so seriously affected by the alum solution as to be easily torn apart by the fingers [Silbey, THIS JOURNAL, **13**, 676 (1921)].

Analysis: "Introduce 10 cc. of the alum solution" [*C. A.*, **16**, 2093 (1922)].

The following phrases are also applied to various forms of aluminum sulfate in the chemical trade: concentrated alum, extra concentrated alum, patent alum, filter alum, papermakers' alum, pearl alum, pickle alum, sizing alum, alum cake.

In alum baking powders a dehydrated form of sodium aluminum sulfate (sometimes abbreviated in the trade to "S. A. S.") has displaced the potash and ammonia alums formerly used. It is contended by some that this is not a true double salt, but merely a mixture; whatever it is, it would be easy to show by citations that it has been called "alum" by manufacturers, chemists, and the public.

Furthermore, there are certain minerals, called "feather alum," "plume alum," and "manganese alum," which do not belong to the isomorphous series of alums but which do contain aluminum sulfate; and miners refer to "alum deposits" in the same broad way.

There is, then, a considerable body of usage which can be cited to show that "alum" may mean, not only "any of a certain series of isomorphous double sulfates," but also "*aluminum sulfate, whether alone or in combination.*" Is the latter a justifiable use? The history of the term seems to indicate that it is. Most of the early forms of "alum" are believed to have contained aluminum sulfate; they were valued because they contained it. The entry of twelve molecules of water, and even of potassium or ammonium sulfate, into the concept of "alum" was incidental. In fact it was not till 1791 that alkali sulfates were found by Chaptal and Vauquelin to be combined with the aluminum sulfate. It is the aluminum sulfate that has always done the work that is expected of alum. The phrase "concentrated alum" as applied to this salt is a true one, for it has the valuable chemical properties of alum in a high degree. We may with propriety use the term "alum" in the crystallographic sense and talk of "iron alums," "selenium alums," and what not, but we should not forget that this is after all a rather special and technical meaning. The older, more widely spread concept employed by Pliny, Chaucer, Pope, and Tennyson, the man in the street, and the chemist alike will, when stripped of nonessential features, be found to involve little more or less than aluminum sulfate. We might even go further than this, and suggest that its center of gravity is a good deal nearer the "aluminum" than the "sulfate." but as no other aluminum salt is likely to be substituted for the sulfate and called "alum" we need not go beyond recorded usage.

It is true that many chemists do not call a substance "alum" unless it belongs to the isomorphous alum series. It is also true that some chemists who distinguish between aluminum sulfate and "alum" when they are thinking of *crystal system* do not hesitate to call any form of aluminum sulfate "alum" when thinking of its *chemical action.* It seems to us that the latter criterion is the better one and is historically justified. If so, the paper-maker, the water chemist, or the dealer in chemicals is not guilty of incorrectness or trade slang in his use of this interesting old word.

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[3] Smith, *J. Am. Chem. Soc.*, **31**, 245 (1909).

Recommended Specifications for Analytical Reagent Chemicals

Part I

Acetic Anhydride, Acetone, Glacial Acetic Acid, Hydrofluoric Acid, Perchloric Acid, Aluminum and Potassium Sulfate, Ammonium Acetate, Ammonium Carbonate, Ammonium Chloride, Ammonium Persulfate, Ammonium Sulfate, Amyl Alcohol

By W. D. Collins, H. V. Farr, Joseph Rosin, G. C. Spencer, and Edward Wichers

Committee on Guaranteed Reagents, American Chemical Society

The specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. It is not intended that any limit or method of examination shall be recommended except after independent testing by several members of the committee. Suggestions for improvement of the specifications will be welcomed by the committee.

The requirements specified are of two kinds. Some, like the strength of acids, are absolute requirements, regardless of the method of testing; others are merely that the chemical shall pass the test given, and the suggested limit may show only approximately the quantity of the impurity in question.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in the previous publication[2] from the committee. A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Corrections for four of the specifications published[2] in 1925 are given at the end of Part II.

Acetic Anhydride

Requirements

Assay—Not less than 90 per cent $(CH_3CO)_2O$.

Nonvolatile Matter—Not more than 0.003 per cent.

Chloride (Cl)—Not more than 0.0005 per cent.

Sulfate (SO_4)—Not more than 0.0005 per cent.

Phosphate (PO_4)—Not more than 0.001 per cent.

Substances Reducing Permanganate—To pass test.

Heavy Metals—To pass test (limit about 0.0005 per cent lead, about 0.001 per cent iron).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble material would interfere.

Assay—Weigh about 2 grams in a 200- or 250-cc. glass-stoppered Erlenmeyer flask, cool in ice, add 5 cc. of freshly distilled aniline, immediately stopper, shake vigorously, and allow to stand at room temperature for half an hour. Add 50 cc. of ice cold water, pouring it in so as to rinse down the sides of the flask; mix well and titrate with normal alkali, using 3 drops of phenolphthalein indicator. The titration should be carried to a point where the red color persists after standing for 10 minutes.

In a second flask weigh about 2 grams of the sample, add 50 cc. of water, allow to stand for half an hour, and titrate with normal alkali to the same end point with phenolphthalein indicator. Calculate the number of cubic centimeters of alkali used in each of the titrations to the basis of 1 gram of the sample. The difference between the two calculated titrations multiplied by 2 is the number of cubic centimeters of normal alkali equivalent to the anhydride in 1 gram of the sample.

Nonvolatile Matter—Evaporate 30 cc. on the steam bath, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 5 cc. in 25 cc. of water, add 2 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.025 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Sulfate—To 25 cc. of the sample add 25 cc. of water and 0.01 gram of sodium carbonate and evaporate to dryness on the steam bath. Take up in water, filter, and make up to a volume of 10 cc. in a test tube. Add 1 cc. of hydrochloric acid (1 volume strong acid in 20) and 1 cc. of 10 per cent barium chloride solution. The turbidity after 10 minutes should not be greater than is produced by 0.13 mg. of sulfate (SO_4) in an equal volume of solution containing the quantities of sodium carbonate, hydrochloric acid, and barium chloride used in the test.

Phosphate—Evaporate 10 cc. on the steam bath. Take up the residue with 10 cc. of nitric acid and dilute with 50 cc. of water. Nearly neutralize with ammonium hydroxide, cool slightly, add 50 cc. of ammonium molybdate solution, shake (at a temperature of about 40° C.) for 5 minutes, and allow to stand for half an hour. Any yellow precipitate should not be greater than is formed from 0.1 mg. of PO_4 in an equal volume of solution containing as nearly as possible the quantities of nitric acid, ammonium hydroxide, and ammonium molybdate used in the test.

The ammonium molybdate solution is prepared as follows:

Solution (1). Mix thoroughly 100 grams of 85 per cent molybdic acid with 240 cc. of water and then add 140 cc. of ammonium hydroxide. Filter and add 60 cc. of concentrated nitric acid.

Solution (2). Add 400 cc. of concentrated nitric acid to 960 cc. of water.

When the two solutions have cooled, add solution (1) to solution (2), stirring constantly. Then add 0.1 gram of ammonium phosphate dissolved in 10 cc. water. Stir the solution and allow to stand 24 hours before filtering out the yellow precipitate.

Substances Reducing Permanganate—Dissolve 2 cc. of the sample in 10 cc. of water and add 0.4 cc. of 0.1 *N* potassium permanganate. At the end of 5 minutes the pink color should not be entirely discharged.

Heavy Metals—Dissolve 5 cc. of the sample in 45 cc. of water, pass hydrogen sulfide through the solution, and make just alkaline with ammonium hydroxide. No brown color should be observed. Any green color should not be greater than is produced by 0.05 mg. of iron in alkaline solution to which ammonium sulfide is added.

Acetone

Requirements

Assay—Not less than 99.5 per cent.

Boiling Range—From 55.5° to 57.5° C.

Nonvolatile Matter—Not more than 0.0013 per cent.

Solubility in Water—To pass test.

Acids (as acetic)—Not more than 0.003 per cent.

Alkaline Substances (as NH_3)—Not more than 0.001 per cent.

Aldehyde—To pass test.

Substances Reducing Permanganate—To pass test.

Tests

Assay—Test according to the U. S. Pharmacopeia X.

Boiling Range—Test according to the U. S. Pharmacopeia X, using a sample of 100 cc.

Nonvolatile Matter—Evaporate 100 cc. and dry at 105° to 110° C. The weight of the residue should not exceed 0.0010 gram.

Solubility in Water—Mix 25 cc. with 25 cc. of carbon dioxide-free water. The solution should remain clear for 30 minutes.

Acids—Add 2 drops of phenolphthalein indicator solution to the solution prepared in the preceding test. Not more than 0.1 cc. of 0.1 *N* sodium hydroxide should be required to produce a pink color.

Alkaline Substances—Mix 25 cc. with 25 cc. of water and add 1 drop of methyl red indicator solution. If the solution becomes yellow it should not require more than 0.1 cc. of 0.1 *N* acid to produce a pink color.

Aldehyde—To 10 cc. of the sample add 5 cc. of ammoniacal silver nitrate solution (U. S. P. Test Solution) and allow to stand protected from the

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[1] Presented in connection with the report of the Committee on Guaranteed Reagents at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

[2] This Journal, 17, 756 (1925).

light at about 50° C. for 15 minutes. No brown color or precipitate of silver should develop.

Substances Reducing Permanganate—Add 0.05 cc. of 0.1 *N* potassium permanganate to 10 cc. of the sample and allow to stand 15 minutes at 25° C. The pink color should not be entirely discharged.

Acid, Acetic, Glacial

Requirements

Assay—Not less than 99.5 per cent CH_3COOH.
Dilution Test—To pass test.
Nonvolatile Matter—Not more than 0.001 per cent.
Chloride (Cl)—Not more than 0.0002 per cent.
Sulfate (SO_4)—Not more than 0.0003 per cent.
Substances Reducing Permanganate—To pass test.
Heavy Metals—To pass test (limit about 0.0005 per cent lead, about 0.0002 per cent iron).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble material would interfere.

Assay—The freezing point should not be below 15.7° C.

Dilution Test—Dilute 1 volume of acid with 3 volumes of water. No turbidity should be observed within 1 hour.

Nonvolatile Matter—Evaporate 100 cc. on the steam bath and dry at 105° to 110° C. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dilute 10 cc. with 35 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.02 mg. of chloride ion in the same volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Sulfate—To 50 cc. of the sample add 0.01 gram of sodium carbonate and evaporate to dryness on the steam bath. Take up in water, filter, and make up to 10 cc. in a test tube. Add 1 cc. of hydrochloric acid (1 volume strong acid in 20) and 1 cc. of 10 per cent barium chloride solution. The turbidity after 10 minutes should not be greater than is obtained in an equal volume of distilled water containing 0.01 gram of sodium carbonate neutralized with hydrochloric acid, 0.15 mg. of sulfate (SO_4), and the quantities of hydrochloric acid and barium chloride used with the sample.

Substances Reducing Permanganate—Dilute 2 cc. of the sample with 10 cc. of water and add 0.1 cc. of 0.1 *N* potassium permanganate. The pink color should not be entirely discharged at the end of 2 hours.

Heavy Metals—Dissolve 5 cc. in 45 cc. of water, pass hydrogen sulfide through the solution, and make alkaline with ammonium hydroxide. No brown color should be observed. Any green color should not be greater than is produced by 0.01 mg. of iron in alkaline solution to which ammonium sulfide is added.

Acid Hydrofluoric

Requirements

Assay—Not less than 46 per cent HF.
Fluosilicic Acid (H_2SiF_6)—Not more than 0.25 per cent.
Nonvolatile Matter—Not more than 0.003 per cent.
Chloride (Cl)—Not more than 0.003 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Sulfite (SO_3)—To pass test (limit about 0.01 per cent).
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.0005 per cent).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Assay and Fluosilicic Acid—Weigh a suitable quantity of the acid into a stoppered platinum crucible or weighing bottle tared with 5 cc. of water. Pour about 10 cc. of a saturated solution of potassium nitrate into a platinum dish, add somewhat less than the necessary amount of *N* sodium hydroxide (preferably about 50 cc.) and 3 drops of phenolphthalein indicator. Cool the solution to 0° C. and cautiously add the weighed sample of the acid. (Rapid addition may cause loss of the acid.) Titrate with the alkali till the pink color persists for 15 seconds while the temperature of the solution is near 0° C. *A*, the number of cubic centimeters of alkali used in the titration, is equivalent to all the hydrofluoric acid and one-third of the fluosilicic acid. Heat the solution to about 80° C. and continue the titration to a permanent pink. *B*, the number of cubic centimeters of additional alkali used to complete the titration, corresponds to two-thirds of the fluosilicic acid.

If *W* is the weight in grams of the sample, the percentages of hydrofluoric acid and of fluosilicic acid are calculated by the following formulas:

$$\text{Percentage of hydrofluoric acid (HF)} = \frac{2.001\,(A-0.5B)}{W}$$

$$\text{Percentage of fluosilicic acid } (H_2SiF_6) = \frac{3.602\ B}{W}$$

Acid which passes the tests for hydrochloric, sulfuric, and sulfurous acids will not contain enough of these acids to affect the titrations and calculations described above.

Nonvolatile Matter—Evaporate 30 cc. in a platinum dish on a steam bath. Add a few drops of sulfuric acid and ignite. The residue should not weigh more than 0.0010 gram.

Chloride (Cl)—Mix in a beaker 45 cc. of water, 2 cc. of nitric acid, and 0.5 cc. of approximately 0.1 *N* silver nitrate; add 3 cc. of the sample. The turbidity should not be greater than is produced by 0.01 mg. of chloride ion in 45 cc. of water by the addition of the quantities of nitric acid and silver nitrate used in the test.

Sulfate (SO_4)—Add about 0.01 gram of sodium carbonate to 20 cc. of the acid in a platinum dish and evaporate to dryness on the steam bath. Moisten the residue with 1 cc. of dilute hydrochloric acid (1 volume strong acid in 20), add 5 cc. of water, filter if necessary, wash or dilute to 10 cc., and add 1 cc. of 10 per cent barium chloride solution. The turbidity after 10 minutes should not be greater than is produced by 0.01 mg. of sulfate (SO_4) in 9 cc. of water upon the addition of the quantities of hydrochloric acid and barium chloride used with the sample.

Sulfite—Dilute 10 cc. with 40 cc. of water and add 1 drop of 0.1 *N* iodine. The solution should show a distinct yellow color.

Heavy Metals, Iron—Mix in a beaker 30 cc. of water and 15 cc. of hydrogen sulfide water, add 5 cc. of the sample, and render alkaline with ammonium hydroxide. No brown color should be produced (lead). Any green color should not be greater than is produced by 0.025 mg. of iron in an equal volume of solution containing the quantities of hydrogen sulfide water and ammonia used in the test.

Acid, Perchloric

Requirements

Assay—Not less than 20 per cent $HClO_4$.
Nonvolatile Matter—Not more than 0.015 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrogen Compounds (as N)—Not more than 0.004 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Ammonia (NH_3)—Not more than 0.001 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead, about 0.0001 per cent iron).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble material would interfere.

Assay—Titrate a weighed portion of the acid, after suitable dilution, with standard alkali hydroxide solution, using phenolphthalein as indicator.

Nonvolatile Matter—Evaporate 9 cc. of the acid and ignite gently. The residue should not weigh more than 0.0015 gram.

Chloride—Dilute 5 cc. with 40 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.05 mg. of chloride ion in the same volume of a solution containing the quantities of nitric acid and silver nitrate used in the test.

Nitrogen Compounds—Dilute 1 cc. of the sample in a flask with 10 cc. of ammonia-free water, add 10 cc. of 10 per cent sodium hydroxide solution and about 0.5 gram of aluminum wire in small pieces, and allow to stand for 3 hours protected from loss or absorption of ammonia. Dilute to 50 cc., decant from any insoluble matter, and add 2 cc. of Nessler's reagent. The color should not be greater than is produced by 0.04 mg. of N as NH_3 in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Sulfate—Dilute 10 cc. of the acid with 35 cc. of water and neutralize with ammonium hydroxide, using litmus paper as indicator. Add 0.5 cc. of dilute hydrochloric acid (1 part strong acid in 10) and 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Any precipitate of barium sulfate should not weigh more than 0.0012 gram.

Ammonia—Dilute 2 cc. of the sample with 40 cc. of ammonia-free water, add 10 cc. of 10 per cent sodium hydroxide solution and 2 cc. of Nessler's reagent. Any yellow color produced should not be greater than is given by 0.02 mg. of NH_3 in the same volume of a solution containing the quantities of sodium hydroxide and Nessler's reagent used in the test.

Heavy Metals—Dilute 5 cc. with 40 cc. of water, add 5 cc. of hydrogen sulfide water, and make alkaline with ammonium hydroxide. No brown color should be observed. Any green color should not be greater than is produced by 0.005 mg. of iron in alkaline solution to which ammonium sulfide is added.

Aluminum and Potassium Sulfate

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.0005 per cent.

Ammonia (NH_3)—Not more than 0.005 per cent.
Arsenic (As)—Not more than 0.0002 per cent.
Heavy Metals—To pass test (limit about 0.001 per cent lead).
Iron (Fe)—Not more than 0.001 per cent.

TESTS

Blank Tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Insoluble Matter—Dissolve 10 grams in 100 cc. of hot water, filter through asbestos in a Gooch crucible, wash with hot water, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Chloride—Dissolve 2 grams in 20 cc. of warm water, add 1 cc. of nitric acid and 0.5 cc. of approximately 0.1 *N* silver nitrate. The turbidity should not be greater than that produced by 0.01 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Ammonia—Dissolve 1 gram in 20 cc. of water, add sodium hydroxide solution to redissolve the precipitate first formed, and then add 2 cc. of Nessler's solution. The color should not be more than is produced by a quantity of an ammonium salt corresponding to 0.05 mg. of NH_3 in an equal volume of solution containing the quantities of sodium hydroxide and Nessler's solution used in the test.

Arsenic—Test 2 grams by the modified Gutzeit method. Special care in making blank tests is necessary in this determination.

Heavy Metals—Dissolve 2 grams in 25 cc. of water and pass hydrogen sulfide through the solution. The solution should not be darkened.

Iron—Dissolve 5 grams in 90 cc. of water and add 5 cc. of hydrochloric acid and 2 cc. of nitric acid. Boil for a few minutes, cool, make up to 100 cc., and add 5 cc. of 10 per cent ammonium thiocyanate solution. If a pink color is produced, it should not be greater than is produced by 0.05 mg. of iron in a ferric salt in an equal volume containing the quantities of the acids and thiocyanate used in the test.

Ammonium Acetate

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Nonvolatile Matter—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.0005 per cent.
Nitrate (NO_3)—To pass test (limit about 0.001 per cent).
Sulfate (SO_4)—Not more than 0.001 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.0005 per cent).

TESTS

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Insoluble Matter—Dissolve 10 grams in 50 cc. of water, filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Nonvolatile Matter—Gently ignite 5 grams of the sample. The residue should not weigh more than 0.0005 gram.

Chloride—Dissolve 2 grams in 20 cc. of water, add 1 cc. of nitric acid and 0.5 cc. of approximately 0.1 *N* silver nitrate solution. Any turbidity produced should not be greater than that produced by 0.01 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Nitrate—Dissolve 3 grams in 10 cc. of water and add 10 cc. of sulfuric acid. To the hot solution add about 5 mg. of sodium chloride and 1 drop of indigo solution (1 in 1000). The blue color should not be entirely discharged after standing 5 minutes.

Sulfate—Dissolve 10 grams in 10 cc. of water, add 0.01 gram of sodium carbonate, evaporate to dryness, and heat at 120° C. till all the ammonium acetate is volatilized. Add to the residue 1 cc. of hydrochloric acid (1 volume of strong acid in 20) and 5 cc. of water. Filter and wash till the filtrate measures 10 cc.; add 1 cc. of 10 per cent barium chloride solution. Any turbidity produced in 10 minutes should not be greater than that produced by 0.1 mg. of SO_4 in an equal volume containing the quantities of acid and barium chloride used in the test.

Heavy Metals—Dissolve 2 grams in 40 cc. of water, add 3 cc. of hydrochloric acid, and heat to boiling. Cool, neutralize with ammonium hydroxide, add 1 cc. of *N* hydrochloric acid, dilute to 50 cc., and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Make the solution from the preceding test slightly alkaline with ammonium hydroxide. If a green color is produced, it should not be greater than is produced by 0.01 mg. of iron in an alkaline sulfide solution of equal volume prepared with the quantities of hydrochloric acid and ammonium hydroxide used in the test.

Ammonium Carbonate

REQUIREMENTS

Assay—Not less than 30 per cent NH_3.
Insoluble Matter—Not more than 0.005 per cent.
Nonvolatile Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.0005 per cent.
Sulfur Compounds (as SO_4)—Not more than 0.001 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—To pass test (limit about 0.0005 per cent).

TESTS

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Assay—Titrate a weighed portion with standard acid, using methyl orange indicator.

Insoluble Matter—Dissolve 10 grams in 50 cc. of hot water. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram. Reserve filtrate for test for sulfur compounds.

Nonvolatile Matter—Volatilize 10 grams in a weighed dish on the steam bath and dry at 105° to 110° C. The residue should not weigh more than 0.0005 gram. Reserve the residue for the test for heavy metals.

Chloride—Dissolve 2 grams in 25 cc. of hot water, add 0.01 gram of sodium carbonate, and evaporate to dryness on the steam bath. Dissolve the residue in 10 cc. of water, filter if necessary, and add 0.5 cc. of nitric acid and 0.5 cc. of 0.1 *N* silver nitrate solution. The turbidity produced should not be greater than is produced by 0.01 mg. of chloride ion in the same volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Sulfur Compounds—To the filtrate obtained in the test for insoluble matter add 0.01 gram of sodium carbonate, evaporate to about 5 cc., add a few drops of bromine water (or sufficient to impart a slight color to the solution), and evaporate to dryness. Take up the residue with a few cubic centimeters of water and 1 cc. of dilute hydrochloric acid (1 volume of acid to 20 volumes of water), filter if necessary, make up to 10 cc., and add 1 cc. of 10 per cent barium chloride solution. The turbidity produced in 10 minutes should not be greater than that produced by 0.1 mg. of sulfate radical (SO_4) in an equal volume of solution containing the quantities of reagents used in the test.

Heavy Metals—Moisten the residue from the determination of nonvolatile matter with 5 drops of hydrochloric acid and dilute to 25 cc. Dilute 5 cc. of this solution to 25 cc. and pass hydrogen sulfide through the diluted solution. No brown color should be produced.

Iron—Add ammonium hydroxide to make slightly alkaline the solution which has been tested for heavy metals. If a green color is produced, it should not be greater than is produced by 0.01 mg. of iron in an equal volume of a slightly alkaline sulfide solution.

Ammonium Chloride

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Nonvolatile Matter—Not more than 0.015 per cent.
Free Acid—To pass test.
Phosphate (PO_4)—Not more than 0.0003 per cent.
Sulfate (SO_4)—To pass test (limit about 0.002 per cent).
Calcium and Magnesium Precipitate—Not more than 0.002 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.0005 per cent).

TESTS

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Insoluble Matter—Dissolve 20 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0010 gram.

Nonvolatile Matter—To 20 grams of the sample add 2 cc. of sulfuric acid, heat at a low temperature, and then ignite gently. The residue should not weigh more than 0.0030 gram.

Free Acid—Dissolve 5 grams in 50 cc. of freshly boiled and cooled water and add 1 drop of methyl red indicator. No red color should be produced.

Phosphate—Decompose 10 grams with 15 cc. of nitric acid by taking to dryness on the steam bath. Take up with 10 cc. of nitric acid, dilute with 50 cc. of water, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake the solution (at about 40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should be less than is produced when a quantity of an alkaline phosphate containing 0.03 mg. of phosphate (PO_4) is treated according to the above procedure. The ammonium molybdate solution is prepared as directed under the test for phosphate in acetic anhydride.

Sulfate—Dissolve 5 grams in 100 cc. of water, add 1 cc. of dilute hydrochloric acid (1 volume of strong acid in 4), heat to boiling, add 5 cc. of barium chloride, and allow to stand overnight. No precipitate or turbidity should be produced.

Calcium and Magnesium Precipitate—Warm the residue obtained in the determination of nonvolatile matter with 1 cc. of hydrochloric acid and 3 cc. of water. Add 2 cc. of ammonium hydroxide, filter, and add to the filtrate 2 cc. of 4 per cent ammonium oxalate solution and 2 cc. of 10 per cent ammonium phosphate. Allow to stand overnight. If any precipitate is formed, filter, wash with a solution containing 2.5 per cent of ammonia. The weight of the ignited precipitate should not be more than 0.0004 gram.

Heavy Metals, Iron—Dissolve 5 grams in 50 cc. of water, pass hydrogen sulfide through the solution, and add 1 cc. of ammonium hydroxide. No brown color should be produced (lead). Any green color should not be greater than is produced by 0.025 mg. of iron in an equal volume of solution containing the quantities of ammonium hydroxide and sulfide used in the test.

Ammonium Persulfate

Requirements

Assay—Not less than 85 per cent $(NH_4)_2S_2O_8$.
Insoluble Matter—Not more than 0.040 per cent.
Nonvolatile Matter—Not more than 0.25 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Manganese (Mn)—Not more than 0.0001 per cent.
Heavy Metals—Not more than 0.030 per cent as oxides.

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Assay—Add 0.3 gram to 25 cc. of a 10 per cent solution of potassium iodide. Then add 10 cc. of 10 per cent sulfuric acid, allow to stand one-half hour, and titrate the liberated iodine with 0.1 *N* sodium thiosulfate. Make a blank test with the quantities of reagents used with the sample and apply a correction if necessary.

Insoluble Matter—Dissolve 5 grams in 100 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0020 gram.

Nonvolatile Matter—Gently ignite 2 grams in a weighed dish. The residue should not weigh more than 0.0050 gram.

Chloride—Dissolve 2 grams in 10 cc. of water and add 0.5 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced in one minute should not be greater than that produced by 0.02 mg. of chloride ion in the same volume of distilled water slightly acidified with nitric acid and containing 0.5 cc. of 0.1 *N* silver nitrate.

Manganese—To the residue obtained from the volatilization of 9 grams of the sample add 10 drops of hydrochloric acid and evaporate to dryness on the water bath. Add 2 cc. of sulfuric acid and heat until fumes of sulfur trioxide are evolved. Cool, cautiously dilute with 20 cc. of water in a small flask, add 1.5 cc. of 0.1 *N* silver nitrate, heat to between 80° and 85° C., immediately add 1 gram of ammonium persulfate, and maintain at this temperature for 1 minute. Cool quickly and if not clear filter through a small pledget of glass wool. If the filtrate is pink, match the color in a blank (omitting hydrochloric acid) by the addition of dilute standard potassium permanganate solution. The quantity of permanganate required to match the color should correspond to not more than 0.01 mg. of manganese (Mn).

Heavy Metals—To the residue obtained in the test for nonvolatile matter add 2 cc. of hydrochloric acid and a few drops of nitric acid and evaporate to dryness on the water bath. Take up the residue with a few drops of hydrochloric acid and 10 cc. of water, filter, and wash with a small amount of hot water. Pass hydrogen sulfide through the filtrate and render the filtrate slightly alkaline with ammonium hydroxide. Heat on the steam bath to coagulate the sulfides, filter (without washing), dry, ignite, and weigh. The weight should not exceed 0.0006 gram.

Ammonium Sulfate

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Nonvolatile Matter—Not more than 0.010 per cent.
Free Acid—To pass test.
Chloride (Cl)—Not more than 0.0005 per cent.
Nitrate (NO_3)—To pass test (limit about 0.001 per cent).
Phosphate (PO_4)—Not more than 0.0005 per cent.
Arsenic (As)—Not more than 0.0005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—To pass test (limit about 0.0005 per cent).

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities. Solutions of the sample must be filtered for tests in which insoluble matter would interfere.

Insoluble Matter—Dissolve 10 grams in 50 cc. of water, filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Nonvolatile Matter—Heat 10 grams gently in a weighed dish till the salt is volatilized, and ignite at cherry redness for 5 minutes. The weight of the residue should not be more than 0.0010 gram.

Free Acid—Dissolve 5 grams in 50 cc. of carbon dioxide-free water and add 1 drop of methyl red indicator solution. No red color should be produced.

Chloride—Dissolve 2 grams in 20 cc. of water, add 1 cc. of nitric acid and 0.5 cc. of 0.1 *N* silver nitrate solution. The turbidity should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume of solution with the quantities of reagents used in the test.

Nitrate—Dissolve 3 grams in 10 cc. of water and add 10 cc. of sulfuric acid. To the hot solution add about 5 mg. of sodium chloride and 1 drop of indigo solution (1 in 1000). The blue color should not be entirely discharged after standing 5 minutes.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, nearly neutralize with ammonium hydroxide, add 50 cc. of ammonium molybdate solution, shake for 5 minutes at about 40° C., and allow to stand for 1 hour. Any precipitate produced should not be greater than is produced from a quantity of an alkaline phosphate containing 0.025 mg. of PO_4 which has been treated like the sample.

Arsenic—Test 1 gram by the modified Gutzeit method. The quantity of arsenic found should not be more than 0.005 mg. Special care in making blank tests is necessary in this determination.

Heavy Metals—Dissolve 2 grams in 50 cc. of water, add 0.5 cc. of glacial acetic acid, and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Render the solution obtained in the heavy metals test alkaline with ammonium hydroxide. If any greenish color is produced it should not be greater than is produced by 0.01 mg. of iron in an equal volume of alkaline sulfide solution.

Amyl Alcohol (Isoamyl Alcohol)

Requirements

Nonvolatile Matter—Not more than 0.003 per cent.
Boiling Range—From 128° to 132° C.
Acids and Esters (as amyl acetate)—Not more than 0.060 per cent.
Aldehydes—To pass test.
Substances Darkened by Sulfuric Acid—To pass test.

Tests

Blank tests must be made on water and all reagents used in the methods unless the directions provide for elimination of errors due to impurities.

Nonvolatile Matter—Evaporate 25 cc. on the steam bath and dry at 105° to 110° C. The weight of the residue should not exceed 0.0006 gram.

Boiling Range—Follow the directions for this test in the U. S. Pharmacopeia X, using 50 cc. of the sample.

Acids and Esters—Dilute 20 cc. with 20 cc. of ethyl alcohol, add 5 cc. of 0.1 *N* sodium hydroxide solution, and heat gently under a reflux condenser for 10 minutes. Cool, add 3 drops of phenolphthalein indicator solution, and titrate the excess of sodium hydroxide with 0.1 *N* hydrochloric acid. Not more than 0.75 cc. of the 0.1 *N* sodium hydroxide should have been consumed, correction being made for the amount consumed in a blank test.

Aldehydes—Shake 5 cc. with 5 cc. of 30 per cent potassium hydroxide solution for 5 minutes in a glass-stoppered cylinder and allow to separate. No color should develop in either layer.

Substances Darkened by Sulfuric Acid—Agitate 10 cc. with an equal volume of sulfuric acid in a glass-stoppered cylinder for 5 minutes. The liquid should be colorless or have not more than a pale yellow color.

(To be continued in the next issue)

Report of A. C. S. Committee on Guaranteed Reagents

During the year 1925–26 the committee prepared tentative specifications for twenty-three reagents, and has considered thirteen additional specifications, several of which are nearly completed.

The recommended specifications[1] do not appear to be strikingly different from others that have been published. Careful comparison, however, will show that they are more definite in the description of tests and more accurate as regards the limits represented by the tests.

[1] Beginning page 636, this issue.

W. D. Collins, *Chairman*

CHANDLER LECTURE

On April 23rd Prof. Samuel W. Parr, professor of applied chemistry at the University of Illinois, delivered the Chandler Lecture for 1926 and was presented with the eighth Chandler gold medal for achievement in chemistry. Professor Parr's principal contributions have been his fundamental work on coal, researches on coking of Illinois coals, the development of a noncorrosive alloy, and the design and perfection of the calorimeters that bear his name.

In 1910 friends of Professor Chandler presented to the trustees of Columbia University a sum of money which constitutes the Charles Frederick Chandler Foundation. The income from this fund is used to provide a lecture by an eminent chemist and also a medal to be presented to this lecturer in further recognition of his achievements in the chemical field. Under the provisions of this fund the trustees designate from time to time one who has made contributions of notable value and invite him to be the Chandler Lecturer and Medalist.

The previous lecturers, with the titles of their lectures, are as follows:

1914	L. H. Baekeland	Some Aspects of Industrial Chemistry [Vol. 6, 769 (1914)]
1916	W. F. Hillebrand	Our Analytical Chemistry and Its Future [Vol. 9, 170 (1917)]
1920	W. R. Whitney	The Littlest Things in Chemistry [Vol. 12, 599 (1920)]
1921	F. G. Hopkins	Newer Aspects of the Nutrition Problem [Vol. 14, 64 (1922)]
1922	E. F. Smith	Samuel Latham Mitchill—A Father in American Chemistry [Vol. 14, 556 (1922)]
1923	R. E. Swain	Atmospheric Pollution by Industrial Wastes [Vol. 15, 296 (1923)]
1925	E. C. Kendall	Influence of the Thyroid Gland on Oxidation in the Animal Organism [Vol. 17, 525 (1925)]

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The Constitution of Coal

Having Special Reference to Problems of Carbonization

By S. W. Parr

University of Illinois, Urbana, Ill.

S. W. Parr

THE topic of fuel is a live one at any time, but during the current year circumstances have had something of a cumulative effect in commanding the attention and interest of a wide circle, from the householder and the housewife who eye with different shades of dismay the coal bin and the window curtains, to the technologist or student of fuel problems who finds himself overwhelmed by present-day complexities and rapid changes in the entire realm of fuel requirements and possibilities. If it is true that commerce follows the flag, it is quite as obvious that the industries create commerce. Since commerce and the industries are so closely interwoven as to be substantially one and the same thing, we may properly conclude that civilization follows, or is dependent upon, fuel.

But what fuel? That is a question of far-reaching significance. It has animated and permeated almost every phase of the work of the investigator of fuel problems. It is, nowadays, made a subject of special inquiry with reference to the days ahead, and the question may be made to read: "What fuel in the future?" But just at the present time the past has a bit of interest which may help at least to a better appreciation of present-day developments in the realm of fuel research.

Fuel Research One Hundred Years Ago

There has recently come into my hands a paper which I believe to be the first published report of investigational work on fuels undertaken in this country. Under the heading of "Preliminary Remarks" as an introduction to the text, the opening paragraph reads:

The annexed paper was read before the American Philosophical Society, April 7, 1826, and was published by them in May.

Silliman's Journal, under date of May 11, 1826, Vol. 11, page 98, has a notation by Professor Silliman which reads:

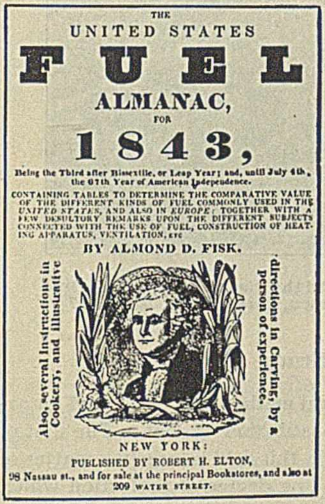
> I have been just favored with a copy of a memoir by Mr. Marcus Bull, read before the American Philosophical Society of Philadelphia, April 7, 1826, entitled, "Experiments to determine the comparative quantities of Heat, evolved in the combustion of the principal varieties of wood and coal, used in the United States, for Fuel; and also to determine the comparative quantities of Heat lost by the ordinary apparatus made use of for their combustion."

Any one who wishes to be excessively exacting about anniversary dates, and who will take the trouble to figure out the median moment between the reading of the paper on April 7th and the date of its first published reference on May 11th, will find that it falls so near the 23rd of April, 1826, that we may be reasonably safe in claiming that this present date of April 23, 1926, is the correct time for celebrating the one hundredth anniversary of the publication of the first investigational work on fuels in America.

It will occur to you at once that this seems to be a centennial year, and with a sesquicentennial and a semicentennial both scheduled for Philadelphia, there may possibly be an added reason why we may wish to have a mild celebration on the side or, let us say, lead the procession with an even centennial occasion of our own. In any event, this coincidence as to dates relating to fuel research, while purely accidental, is none the less interesting and indeed valuable as furnishing an occasion for taking account of stock or making out a trial balance whereby we may in some measure acquire an appreciation of the road over which we have traveled and at the same time some vision, more or less prophetic or venturesome as the case may be, concerning the way before us.

In making a brief résumé, therefore, of the paper of Mr. Marcus Bull, we shall expect to find our interest centering not so much in the results which he sets forth as in the attending circumstances and those incidental bits of information which give an insight into the conditions and the environmental activities of the time.

Turning again to Professor Silliman, in commenting upon this manuscript of Mr. Bull, he says:



THE
UNITED STATES
FUEL
ALMANAC,
FOR
1843,
Being the Third after Bissextile, or Leap Year; and, until July 4th, the 67th Year of American Independence.
CONTAINING TABLES TO DETERMINE THE COMPARATIVE VALUE OF THE DIFFERENT KINDS OF FUEL COMMONLY USED IN THE *UNITED STATES*, AND ALSO IN *EUROPE*; TOGETHER WITH A FEW DESULTORY REMARKS UPON THE DIFFERENT SUBJECTS CONNECTED WITH THE USE OF FUEL, CONSTRUCTION OF HEATING APPARATUS, VENTILATION, etc
BY ALMOND D. FISK.
Also, several Instructions in Cookery, and illustrative directions in Carving, by a person of experience.
NEW YORK:
PUBLISHED BY ROBERT H. ELTON,
98 Nassau st., and for sale at the principal Bookstores, and also at 209 WATER STREET.

Figure 1

> It is replete with interesting information and is to be regarded as one of the most important contributions of science to the arts and to domestic economy which has been made for a long time in this country. It is worthy of being carefully studied, both by scientific and practical men, and for the sake of the latter class it might be well if any analysis of this elaborate and detailed paper, presenting in a lucid and concise form the practical important results which have been obtained by Mr. Bull*** were prepared for extensive circulation.

That this suggestion of Professor Silliman was taken seriously and a method employed for carrying it out may be inferred from a different publication, in which all of the original tables are reproduced, and which incidentally illustrates the meager channels for disseminating wisdom at the time, in a manner well set forth in the title page as shown in Figure 1.

The tables referred to are taken from the original paper as prepared by Mr. Bull. They were still live matter, seventeen years after their first appearance, at least live enough to be embodied in a family almanac. They occupy four pages of closely printed matter, giving values for fifty different sorts of fuel by percentage comparison with a single well-known standard type. Certain columns of the tables bear the heading: "*Scale of prices:* in each column of which the prices as they correspond with the standard are in the same ratio with their respective powers of emitting heat." And so, through the medium of the family almanac there was carried out the suggestion of Professor Silliman that the results of Mr. Bull's investigation be given extensive circulation.

Turning again to the paper read before the American Philosophical Society in 1826, if we scan the very elaborate title to Mr. Bull's paper as quoted by Professor Silliman, we will find that its forty-seven words can be narrowed down to two words—What fuel?—a question even more pertinent now than it was one hundred years ago.

With respect to his apparatus Mr. Bull ventured a criticism on the calorimetric methods of Count Rumford then but recently promulgated, and he proceeded to design what was in reality a calorimeter, even though it was a small insulated room in which a given weight of fuel was burned in such a manner as to maintain a fixed temperature for a measured length of time. A series of ratios was thus obtained as between an accepted standard of reference and a fuel under observation (Figure 2). After some preliminary trials and some fundamental suggestions by Robert Hare, professor of chemistry in the University of Pennsylvania, resulting in a much improved apparatus, the experiments, it must be admitted, produced at least comparative values of a reasonable degree of reliability.

Another point of interest in this connection is the standard fuel selected as a basis of reference. We are obliged to assume that such a standard would be selected primarily because of its familiarity to all fuel users, as well as for its constancy of behavior. The standard fuel thus selected by Mr. Bull was shell-bark hickory wood. In his brief survey of the fuel situation we are particularly interested in the fact that the statistical data which he assembled show that the annual consumption of fuel by the City of Philadelphia amounted to the equivalent of 173,000 tons—of which 140,000 tons were cord wood, 5000 tons charcoal, 25,000 tons anthracite, and 3000 tons soft coal. Proceeding from the basic figures thus secured, he estimates that for the 11 million inhabitants of the United States at the time approximately 11 million tons of fuel were annually consumed, representing at $4.50 per cord—or as we can more readily think of it, per ton of standard coal—a total annual cost of a little over $50,000,000.

But the ultimate object of Mr. Bull's investigation seems intended to show not only that with shell-bark hickory at 100 per cent, soft maple, chestnut, elm, and similar woods were given a rank of 56 to 58 per cent, but also that, on the score of efficiency, anthracite coal was the equal of the best wood obtainable, to quote from his introduction:

> If we look prospectively to the early period when these coals (Lehigh or Schuylkill) may be expected to be furnished at $5.00 per ton, their substitution for other kinds of fuel, in all cases where it is practical, will become a matter of general interest* * *. This portion (the Eastern part) of the United States will, it is presumed, at no very distant period of time, be principally supplied with fuel from the coal mines of Pennsylvania, and at an estimate of one-half the required quantity will consume one and one-half million tons annually: which, at $5.00 will amount to $7,500,000.

While he was here confining his estimate to the Atlantic Seaboard we may note that the total annual fuel bill in the whole United States for domestic purposes alone is now well above one billion dollars.

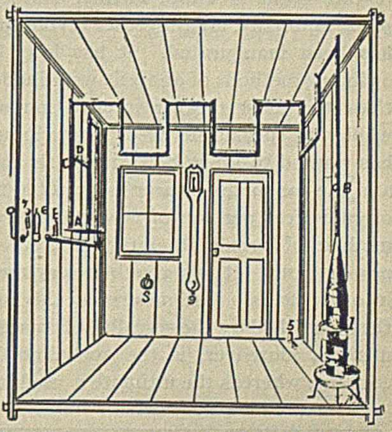


Figure 2—Apparatus Used by Mr. Bull in His Experiments on Fuel

The Fuel Situation Today

Reverting to the question of one hundred years ago, as abbreviated from the title page of the publication by Marcus Bull, we note at once both its pertinency and its persistency, for indeed it holds the foremost place in the mind of the present-day investigator of fuel problems. We may formulate it to read: "What today is the most suitable fuel and—what is the fuel of the future?"

The most striking, as it is also the most entrancing, feature of this backward glance is so appealing in its nature that we can have only sympathy for Lot's wife, who could not resist the temptation of looking back. Think of a condition or a time when less than 2 per cent of all the fuel consumed was of the smoke-producing variety. We take much satisfaction in occasionally scheduling the remarkable items of progress that have characterized the past one hundred years. Suppose we were to list those items which might be classified as retrogressions. I think the list might be very properly headed by reference to the smoke nuisance. It is not necessary to recount the distresses that attend the discharge into the atmosphere of our present-day volumes of smoke. Let us recall also that most of the difficulty originates in the house heater, so that it has been thoroughly well demonstrated that the smoke nuisance is in the main to be charged against the domestic chimneys and not to the factory stacks.

In the field of combustion the power engineer has far outdistanced the rest of us in the matter of smoke abatement. By the application of comparatively simple mechanical devices coupled with the uniform and high temperatures with which he deals, it is evident that the problem of the engineer has been relatively an easy one, and he has made very little appeal to the chemist for help.

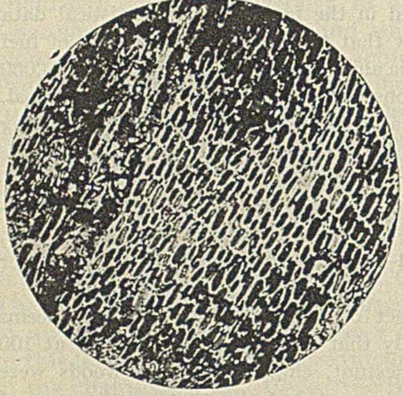


Figure 3—Microscopical Structure of Anthracites [By Turner, *Trans. Am. Inst. Mining Met. Eng.*, 71, 146 (1925)]

But investigators from the purely chemical side have not been idle. Indeed, it will be entirely correct to say that as we enter upon the second one hundred years of fuel study it is characterized by the number of workers who are studying fuel problems from the fundamental rather than the empirical standpoint.

Thus it has come about that in our new century of coal investigation the question of fuels of an improved type, with sanitary as well as economic factors—comfort, convenience, cleanliness, and efficiency—must receive consideration. The outstanding feature is the fact that in these studies, from a chemical standpoint especially, an altogether revolutionary method of procedure has been inaugurated. It has long been recognized that the ordinary methods of analysis were inadequate for supplying more than the most meager information and that confined almost wholly to specific needs of a few industries. The power plant has wanted to know how much ash and water it was paying for and the gas manufacturer has wanted to know the yield in terms of cubic feet per ton of raw material employed. The so-called method of proximate analysis grew out of the needs of the power plant. It can give but very meager information of value in other fields. But meager as this information is, it surpasses that furnished by the so-called ultimate analysis. The proximate method, moreover, is the one almost exclusively used in this country, whereas the ultimate is used in England and on the Continent. The American, therefore, feels handicapped when he is able to find no data on English coals except in terms of ultimate values, and undoubtedly the Englishman is equally disconcerted when he finds everything about American coals in terms of proximate factors only.

Figure 4—Bright and Dull Bands in Illinois Coal

These are only sample references to the many indictments that might be cited against the old investigational mechanism relating to fuels which we have inherited from the past. It has been stated, however, that really revolutionary methods of procedure have in recent years come into vogue. This fact is seen to have striking confirmation in the case of a bibliography recently compiled under the topic of the "Constitution of Coals," which lists five hundred different references to published articles in the literature.

This may be interpreted to mean that many investigators are at work in this field—which is true. It might also be interpreted to mean that we must know a lot about the subject—which is not true. It is rather an index of how little we know. It at least suggests that the subject is intricate, involved, difficult, many-sided, complex, and not solvable by the ordinary processes of simple analytical procedure—all of which is undeniably and emphatically true.

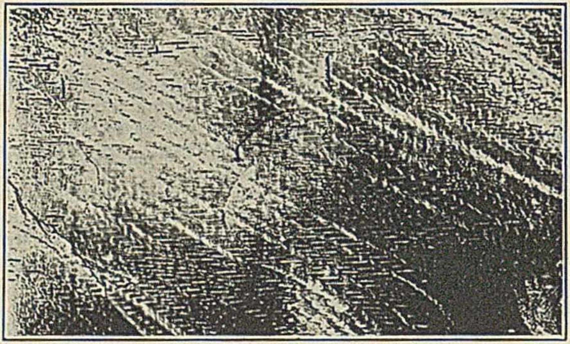


Figure 5—Cross Section of Bright Coal. Royalton Mine, Illinois. (× 200) [By Thiessen, *Bur. Mines, Bull.* 117]

Microscopical Study of Coal

At the present time three general methods are employed for arriving at a knowledge of the constitution of coal. The first of these is microscopical. Success in this field is largely a matter of technic, and it has been carried to a degree of perfection which justifies the statement that there is no particle of solid fuel in any form that cannot now be resolved by the use of the microscope into its ultimate cellular structure. It is entirely correct to state that, without exception, all the coal measures may be considered an elaborate herbarium where there have been preserved all the essential factors for determining the initial forms of the vegetable matter which entered into these fossil fuels. The technic, which has been developed to its highest stage by Professor Jeffries of Harvard and Dr. Thiessen of the U. S. Bureau of Mines, involves the securing of a section of the coal in a form so thin as to permit of the transmission of light. Professor Jeffries accomplishes this by a process of softening and the cutting of micrometer slides, and the Thiessen method involves the grinding down to a thin section. These methods, while applicable to soft coals, are not practicable for anthracites. For this latter type of coal, Professor Turner of Lehigh has developed a method of polishing and of flame-etching, somewhat similar to the preparation of metals for opaque illumination,

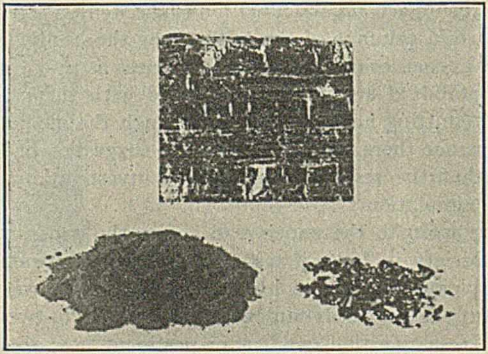


Figure 6

which has resulted in wonderfully distinct delineation of the cellular forms that enter into the composition of anthracite. (Figure 3) It is therefore seen that every conceivable form of fossil fuel is made to reveal the ultimate cellular structure which has entered into its composition. This fact has profound significance when we study the constitution of coal from the standpoint of the different layers which make up the coal mass.

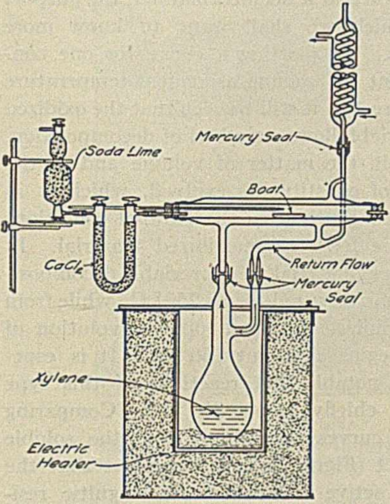


Figure 7

The midcontinental deposits lend themselves especially well to studies of this sort because of less distortion and geological deformity. Any ordinary lump of coal from Illinois, one of the greatest coal producing areas of the world, is seen to be made up of bright and dull layers (Figure 4), the bright or glanz coal being dense black in the picture and the dull coal being the light bands. The dull bands are seen to consist of streaks of bright band material with a predominating amount of mixed substance, which with higher magnification shows an assembly of twigs, spines, leaves, scales, exines, spore cases, and resins.

By contrast, the bright bands are more homogeneous, and if we take out any dense black area and subject it to higher magnification (Figure 5) we shall find that at ultimate resolution it is wholly cellular in structure and without admixture of other material, thus demonstrating that it had its origin in pure woody substance.

Solvents

A second method of study is by use of a solvent, the best adapted of which seems to be phenol. By this means we are able to separate the coal into two parts having distinctly different properties, the cell skeletons of the bright bands and the general attritus of the dull bands supplying the larger portion seen at the left in Figure 6. This is the insoluble part, made up of cell skeletons and similar material more or less closely related to lignin and designated as the lignitic residue. The other part (right, Figure 6) is the soluble portion. It is more nearly related to the resins and bitumens. It is undoubtedly a mixture of the two with the predominating material more nearly resembling the bitumens; hence the designation of "bituminic substance" is applied to the soluble extract. Subdivisions of these very complex compounds, both of the lignitic and bituminic type, have been made, but it is not our immediate purpose to follow these limits of separation into pure and identifiable compounds. This would be an almost endless task and when completed would give us none of the direct information needed which we seek—namely, a comprehension of the mechanism of carbonization. Moreover, it is not the properties of the separate compounds which will help us in this study, since they do not act as independent entities, but rather we want to know about their interactional and combined behavior, for it is these conditions with which we have to deal. Turning our attention, therefore, to the two main groups, the lignitic and the bituminic material, we find that they occur in the type of coals here studied in approximately the ratio of five or six of lignitic to one of bituminic substance. The distribution of the bituminic matter is fairly even, though the bright band has more of the soluble substance resembling the bitumens, while the dull portion, which contains more of the spore residues, seems to have an accentuation of the soluble material more nearly related to the resins, as we would expect.

Chemical Reactions

A third method of study is by means of reactivities of a chemical type which may be brought about by certain prescribed conditions intended to develop the behavior of the material as a whole, and of the subdivisions as obtained by the use of solvents. Very characteristic reactions, for example, can be employed in this type of study in noting the reaction between the coal substance or the coal components and oxygen. It has long been known that freshly mined coal has a great avidity for oxygen. If we make a systematic study, first, of the absorption of oxygen by coal and then of the absorptive capacity of the type constituents into which coal can be divided by the use of solvents, we will obtain thereby not only an insight into the characteristics of the two components, but a very definite idea as to where the action centers in the coal in its natural state.

Let us examine some of these reactions by subjecting the normal coal to oxygen at varying temperatures, first at 100°, then at 75°, and at ordinary temperatures, say 25° C. The apparatus for maintaining these conditions is illustrated in Figure 7, in which the coal sample is subjected to a temperature which may be maintained with great constancy over an indefinite period. By operating a number of such assemblies at the same time upon the same coal, with only one variable, that of temperature (Figure 8), it is interesting to note that at 100° C. there is a steady increase in the weight of the coal and at the same time a continual reaction resulting in the formation of moisture and of carbon dioxide. It is evident here that an interchange has taken place between the oxygen supplied and the components of the coal, because, having started the process at an initial stage of freedom from moisture, we still have evolved a moisture factor which at this temperature after a period of 45 days amounts

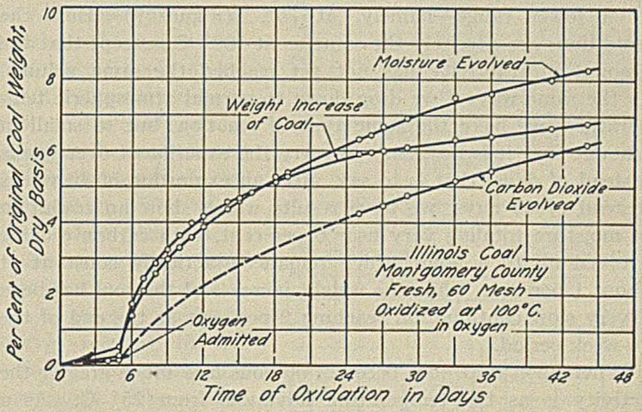


Figure 8

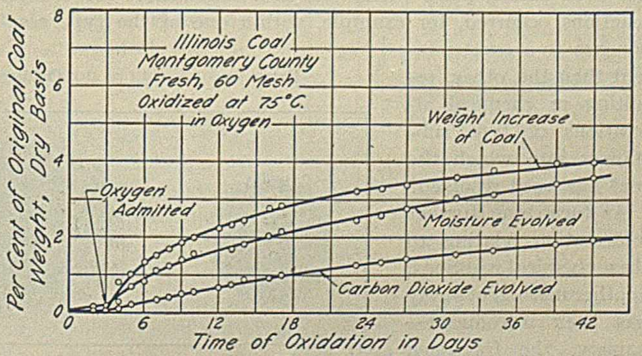


Figure 9

to very nearly 8.5 per cent of the initial weight of the coal referred to the dry basis. Similarly, the carbon dioxide evolved amounts to a little over 6 per cent of the weight of the coal while the increase in weight due to oxygen absorption is nearly 7 per cent.

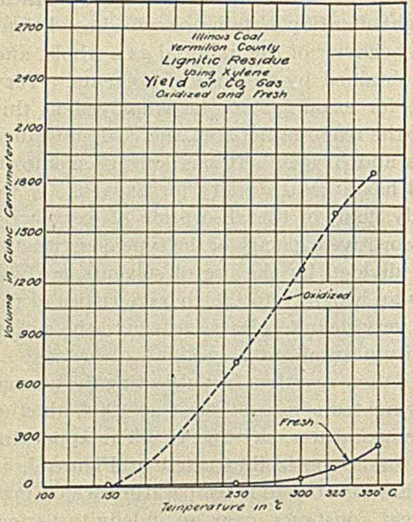


Figure 10

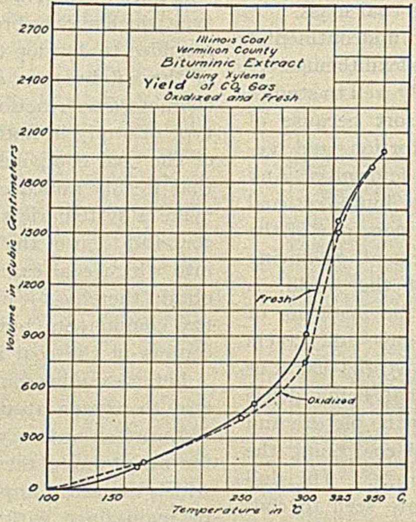


Figure 11

As these reactions may be looked upon as accentuated by the temperature employed, it will be of interest to study the reactions at a lower range—namely, at 75°. (Figure 9) Here the conditions are precisely the same as at 100° C., except that the amount of reactivity has not yet reached the same volume. In the same way, if we drop down to normal atmospheric temperatures we have the same type of reaction, but so small in amount that it is necessary to carry the experiment over weeks instead of days; that is to say, after an expiration of 46 weeks instead of 46 days, we have results which show an evolution of moisture totaling very near 6 per cent, with carbon dioxide evolved up to a point which remains practically constant at about 1 per cent, while the weight increase of the coal has been a very slow continuation reaching 2 per cent at the end of the 46-week period.

Whereupon it at once becomes obvious how much greater the activity is as the temperature advances from 25° C. As a result of these conditions the question naturally arises as to what has been taking place within the coal substance. Have these reactions occurred, for example, within one of the type components to a greater extent than the other, resulting in chemical alterations of type substances into which the coal has been resolved?

As furnishing further information relating to these chemical reactions, another method of study has been introduced—namely, the fractional distillation of coal or its subdivisions—making note of both the volume and the reaction products accompanying the various ranges of temperature employed.

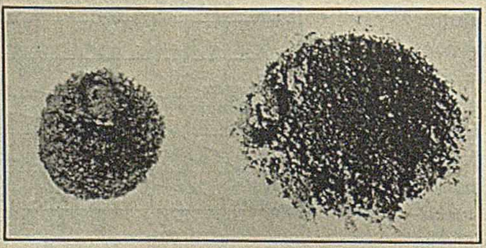


Figure 12—Coking of Illinois Coal

To show what changes have resulted in both the volume and the composition of the gas which is evolved upon heating to a temperature of 300° C., the accompanying table gives values obtained on the oxidized as compared with the fresh or unoxidized residue or lignitic substance (A). Note especially the increase in the oxides of carbon and the decrease in the hydrocarbons. In striking comparison are the results obtained by parallel procedure upon the soluble or bituminic substance (B). Here the decrease in carbon dioxide with an increase of carbon monoxide, together with a corresponding reduction in hydrogen and the hydrocarbons, suggests that reactions have been set up in the bituminic substance in a decided manner, the purport of which we shall want to know more about. By plotting a curve for one constituent by volume as against temperature (Figure 10), it will be seen that the oxidized material follows a method of decomposition, both in the matter of volume and in the type of constituents evolved, which is in marked contrast to the parallel conditions for the fresh or unoxidized material. In the fresh material no appreciable decomposition has occurred below 250° C., while from the oxidized sample a copious evolution of gas begins at about 150° C. It is especially notable that reactions of this type occur chiefly below 350° C. Comparing these curves with those from the soluble extract (Figure 11), it is evident that the most active material is the lignitic residue.

Composition of Gases Evolved up to 300° C.
(Cc. per 100 grams)

	A—Coal Residue Insoluble in Xylene		B—Xylene Extract from Coal	
	Fresh	Oxidized	Fresh	Oxidized
CO_2	153.2	1423.0	462.5	244.0
Illuminants	5.2	2.4	3.0	6.0
O_2	7.6	2.7	...	...
CO	48.5	191.2	29.5	42.6
H_2	10.5	3.1	48.5	23.2
CH_4	13.2	2.4	29.0	6.6
C_2H_6	5.1	0.0	12.0	0.0
Total volume	243.3	1624.8	584.5	322.4

These fractional decomposition studies, therefore, indicate the lively reactivity of the lignitic matter with relatively small difference in the type of change in the bituminic matter as a result of oxidation. The bituminic matter, however, is evidently very susceptible to the reactions set up by the lignitic residue. These reactions affect the bitumens below the softening temperature, from about 250° to 350° C., and since at those temperatures there is a marked evolution of carbon dioxide from the oxidized cellulosic matter and a decided evolution of the same gas from the bituminic substance, it follows that, so far as possible, there must be an avoidance of deterioration on this score before the softening stage is reached.

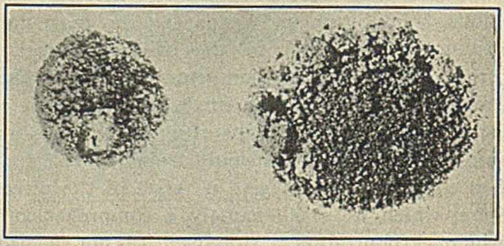


Figure 13—Recombined Lignitic and Bituminic Substances

The importance of the information thus far developed will be at once apparent when we note the effect of oxygen absorption upon the coking property of the coal. This is readily shown by the ordinary test for volatile matter determination wherein a 1-gram sample of the coal is subjected to destructive distillation within the crucible. The resulting material gives a good indication as to the coking property of the sample. There is here shown the results upon the same coal in parallel, one from the fresh unoxidized sample and the other from the same material after a long period of oxidation. The fresh coal gives a good coherent coke while the oxidized sample shows no coherence whatever. (Figure 12)

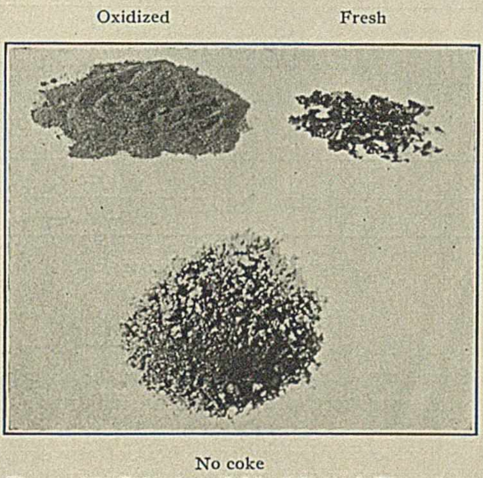


Figure 14—Behavior of Lignitic and Bituminic Substances

We will be interested now to apply this same test by recombining the two types of constituents shown in Figure 6, the cellulosic with the bituminic material, first having both in the fresh and then both in the oxidized state. In Figure 13 the coking effect on the sample at the left, both substances fresh, is the same as in the normal coal and is not at all impaired. On the contrary, in the sample at the right, where we mix the oxidized lignitic substance with the oxidized bituminic material, the coking effect is absent. Here, then, is a suggestion of an intertype reaction which we will want to verify still further by mixing an oxidized lignitic with a fresh bituminic substance as in Figure 14. Here the coking property of the bituminic substance has been completely destroyed, and obviously as a result of some interaction to be charged against the oxidized lignitic material.

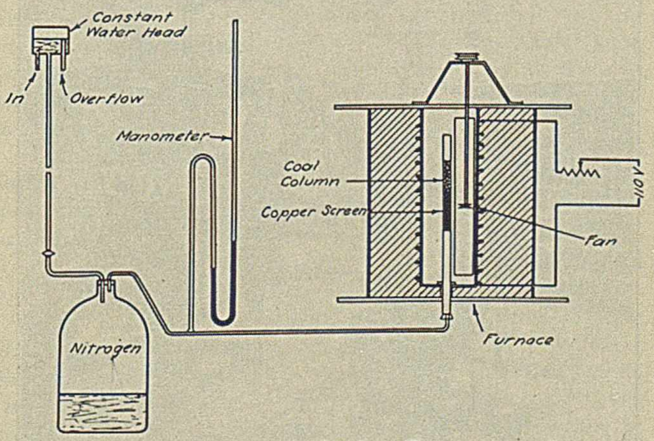


Figure 15—Melting and Solidification Temperature Apparatus [Layng and Hathorne, *This Journal*, 17, 165 (1925)]

Melting Point Determination

Some help in our attempt to understand these interactions may be gained from the study of an entirely different set of phenomena.

It can be readily understood that any substance which passes from a granular to a coherent mass as a result of the action of heat must have passed through a molten or at least a pasty stage. This is especially true of organic material, with this fact to be given emphasis—that organic substances, if they have a melting point, acquire that condition before any substantial decomposition has taken place. It is obvious, therefore, that in the case of coals, if any portion of the coal substance has this property of melting or assuming the pasty condition, it must be augmented or at least conserved in every possible way. But in applying any methods we must have basic knowledge as to the factors which may destroy or promote this all-important feature of softening or acquiring the molten phase.

We will more readily comprehend the results if we make brief reference to an apparatus (Figure 15) for measuring the fact of the melting point, the temperature at which melting occurs, and something of the speed or extent of time over which it makes itself manifest in passing over to the solid phase. Here by inflowing water at the left a slow current of nitrogen or other gas is driven past a manometer (center) and through a 10-gram sample of coal (right) held in a tube open at the top and heated by an electric resistance furnace under exact temperature control. The softening effect in the coal creates a back pressure on the manometer. The readings, when plotted in millimeters of pressure against temperatures, give very significant curves relating to the softening and solidifying properties. The results obtained on a single coal (Figure 16) will illustrate the character of the curve and the information which it may convey.

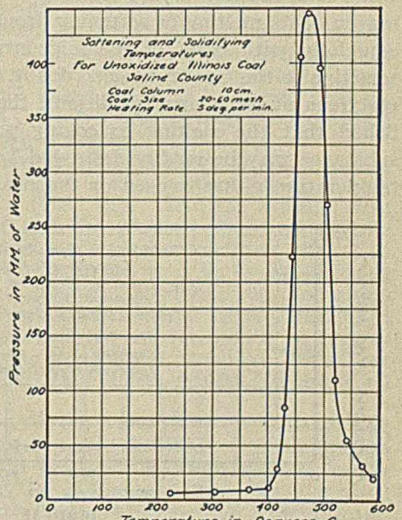


Figure 16

When this softening point determination is made on different coals, the characteristic differences in the shape of the curves suggest a feature that may be of great aid and importance in diagnosing the behavior of any single coal and may also lead to a better understanding of the reason why a better coke structure may be secured by blending coals having widely different curves than can be attained with any one of the coals alone. Here is suggested further a method for determining what reactions may have the effect of lowering or destroying the property of softening or melting. For example, Figure 17 gives curves for the same coal which after oxidation are modified in a striking manner, showing a change in composition from a substance having a positive melting point to one without any, by subjecting the coal to oxidizing conditions by maintaining it at a temperature of 110° C. in air for 100, 200, 400 minutes, respectively,

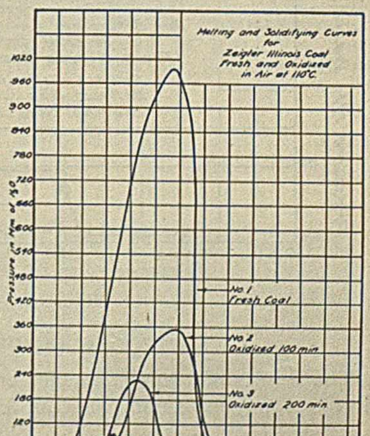


Figure 17

in the last case all of its melting, or coking, property being destroyed.

If we apply the same method to the parts separated by means of a solvent, it is apparent that:

(*a*) The lignitic residue is altogether without softening property. (Figure 18)
(*b*) The bituminic substance assumes a completely liquid condition, the maximum and minimum pressure effects being substantially what we would expect from a liquid or viscous mass. (Figure 19)
(*c*) By saturating the insoluble residue (*a*) with oxygen and combining in normal proportions with (*b*) the molten condition is destroyed. (Figure 20)

These results seem to prove that (*b*), the bituminic material, while it is the key to the entire problem of coke formation by reason of its melting or softening property, is at the same time, especially with coals of the midcontinental type, exceedingly sensitive to the treatment accorded it. By accentuating certain reactions under known conditions, the fact seems to be established that the melting or coking property of the bituminic substance may be readily destroyed by liberating at the coking temperature either oxygen or the oxides of carbon.

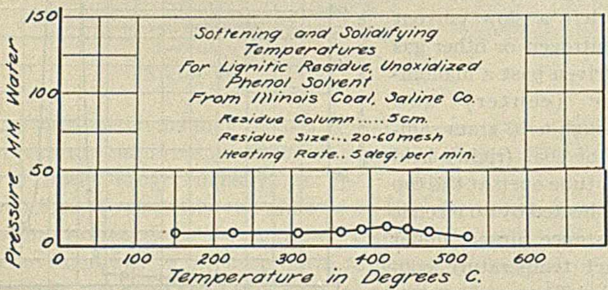


Figure 18

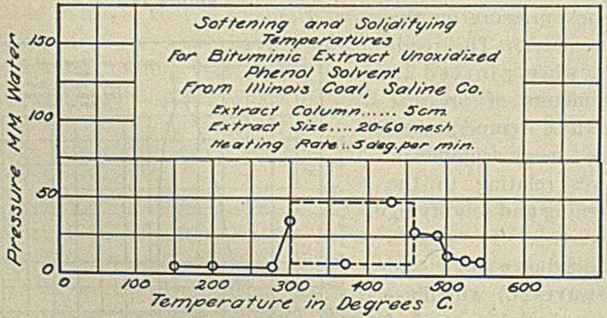


Figure 19

Summary of Reaction Studies

The results of reaction studies on the coals and their subdivisions may be summarized as follows:

(1) Coal is a very active absorbent for oxygen. This absorption begins even at the face of the vein before the coal is broken out from the seam, and proceeds with greater acceleration as the coal mass is broken into finer particles by blasting, screening, and transportation.
(2) The most active portion chemically is the lignitic constituent of the coal.
(3) The bituminic substance possesses the softening or melting property and is the fundamental substance responsible for producing a coherent coke structure as a result of heat continued through the decomposing stage.
(4) The bituminic substance softens or melts at temperatures usually below 400° and above 300° C., and below this range is very susceptible to chemical changes which tend to cause a reversion to a composition more nearly related to the lignitic substance, especially in regard to its melting property which is greatly decreased or destroyed altogether. Naturally, the time element is a factor in producing this change, a long exposure to these conditions producing a more complete effect while the reversion is minimized if the preliminary stage of high susceptibility is shortened with respect to time.

A Carbonization Theory

We may now formulate a procedure for meeting the conditions thus indicated for conserving the bituminic material and correcting such alterations in the cellulosic substance as may have stored up potential detriment, which if not disposed of will weaken the melting and bonding property of the bituminic material. The following methods seem to be indicated:

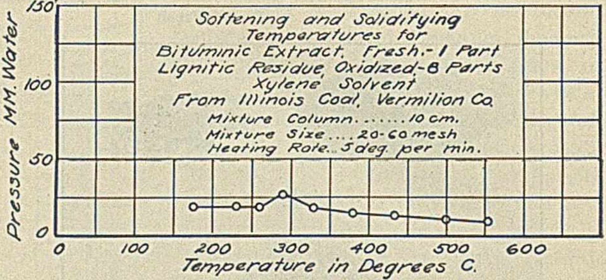


Figure 20

(1) The discharging by moderate heat of any accumulation of oxygen or oxygen compounds of carbon resulting from the absorption of that element, due to exposure to the air.
(2) The discharge and ready removal of any product of decomposition, particularly oxygen, carbon monoxide, and carbon dioxide, evolved during the rise in temperature of the bituminic material before it reaches the plastic stage. This implies that not only should there be a ready discharge or removal from the zone of activity of such gases, but the time for contact with such reacting gases must be reduced to a minimum, thereby diminishing the opportunity for deleterious chemical interactions.
(3) The time is greatly conserved by evaporating the free moisture, 10 to 15 per cent of the weight of the coal, separately and below 100° C. so that the raising of the mass through the remaining range up to 300° C. may be accelerated; thus securing a condition whereby the additional 100° C. above 300° C., required to produce the pasty condition, can be quickly distributed throughout the mass.

This last feature is the critical factor, and just in proportion as the time is long extended will the resulting coke structure be weak or noncoherent, and in proportion as the pasty stage throughout is quickly attained will the coherent and very characteristic uniform structure be attained. A striking illustration of the opposite procedure is afforded by the standard methods of coal carbonization.

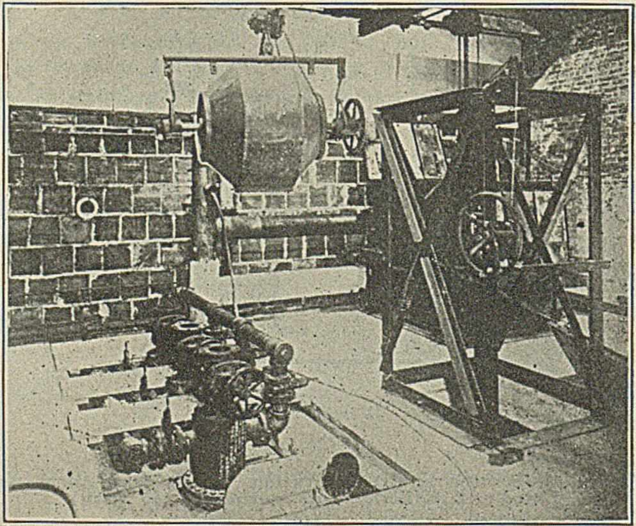


Figure 21—Apparatus for Preheating Coal

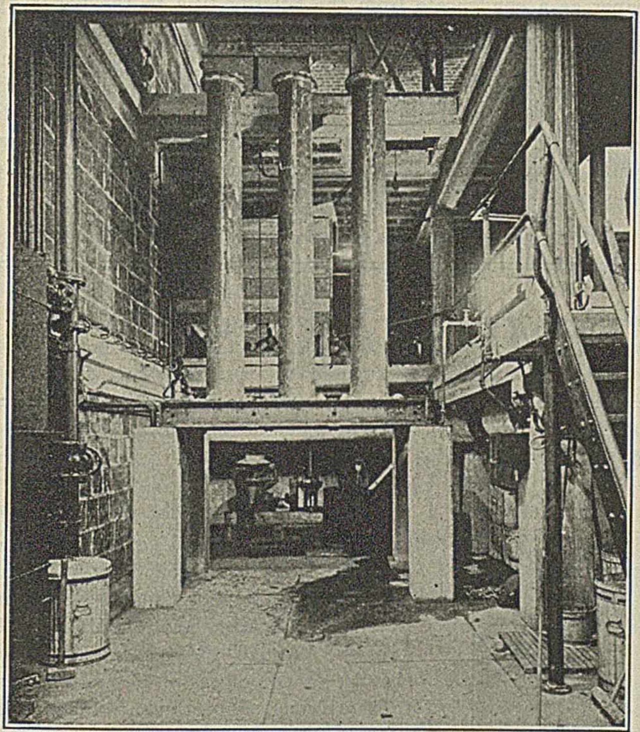


Figure 22—Metal Retorts for Coal Carbonization

A cross section of an ordinary by-product oven into which raw coal is discharged starts the carbonization process at once in the area adjacent to the hot walls. As this coke layer travels inward it is slowly preceded by a pasty zone or tar screen which, together with the exterior coke layer, builds up a very effective insulating wall against the transmission of heat to the interior of the mass. This necessitates maintaining a high heat head, (about 1200° C.) at the retort surface in order to drive the heat inward. The time factor under the best conditions is excessive, at the rate of about 0.5 inch inward per hour, under which circumstances the very undesirable condition of exposure of the sensitive bituminic substance to deleterious reactions is enormously prolonged. With coals of the so-called coking type the evil effect of this procedure is not so apparent, but with the younger coals, though they are of the true bituminous type, these conditions are harmful, if not absolutely destructive, for attaining the desired strength and coherence of the final product.

On the other hand, by maintaining the proper conditions as indicated above, it should be possible to bring the entire mass quickly into the pasty stage, and then the decomposition process proceeds without deleterious effect, requiring only the maintenance of the temperature or increasing the same, depending on the amount of volatile matter desired in the finished product.

One more point should be noted—that the quick distribution of heat throughout the mass from and above approximately 300° C. is facilitated by those decomposition reactions, which are exothermic in character. Measurements of this effect have been made and, even at an increase of 0.5 per cent of the calorific value of the fuel as obtained by direct experiment, this heat increment would represent about 65 B. t. u. per pound, or about 36 calories. Assuming a specific heat for the material of 0.40, this would represent an internal generation of heat sufficient to raise the temperature of the mass 90° C. Obviously the addition of 90° C. to the raw coal at the initial stage would be of no appreciable value, being quite wasted in doing such common work as evaporating water and raising the general temperature. But 90° C. rise from and at the initial point for entering the pasty stage has a well-nigh incalculable value in accomplishing the rapid attainment of the molten condition throughout the mass. It is of equal interest to note that in the range where this small increment of heat is most needed it is most freely generated.

From the behavior of the coal constituents as thus set forth it will be evident that with coals of the younger type especially, and as a matter of fact with all coals where low-temperature carbonization conditions are to be maintained, the following procedure is indicated:

> The coal is first preheated out of contact with the air, nearly but not into the pasty stage. This must be accomplished evenly in a closed chamber, externally heated and rotary in type, to insure an equal dissemination of the heat throughout the mass. In Figure 21, at the right is housed a rotary drum, heated by waste gases from the flues with accessory gas burners for supplemental heat. By this means the temperature is under ready control and may be arrested at any stage without detriment, since the gases resulting from the heating are automatically discharged from the system and the preliminary reactions are at substantially a standstill unless the heat is carried into the plastic stage (around 350° C.). No hydrocarbon decomposition occurs until the pasty stage is reached.
>
> After this preliminary treatment, the material still granular and in no part plastic is poured into a vertical retort already heated to the desired stage (750° C.). Here the external heat plus the reactional heat quickly advance the temperature throughout the mass, well into the plastic condition (400° C.). The metal retorts are shown in Figure 22 without the inclosing brickwork and flues. From this temperature the decomposition may be carried to completion. In the work as we have developed it, having in view the amount of gas and the quality or type of tar desired, the temperature is advanced to about 700° C. at the center of the retort, and this is accomplished in from 2.5 to 4 hours.
>
> The retorts are 14 inches in cross section at the bottom and 12 inches at the top. Moreover, this quick thermal penetration is accomplished with a heat head at the walls—that is, in the flues—of only 750° to 800° C. If this heat head only were used and the retort charged with fresh coal at normal temperatures, the coke structure would never form, as may be readily understood, because it would require 24 hours or more to attain a temperature even approaching the pasty stage (350° C.), and under such conditions, by reason of the deleterious reactions already described, the softening property would be lost. The mechanical appliances for meeting the conditions are thus seen to be comparatively simple.

Space will not permit of more than mere reference to the results (Figure 23). The main objective throughout the many years of experimentation has been to produce a fuel especially adapted to domestic use The product is entirely smokeless in combustion, kindles readily, retains its fire indefinitely, responds

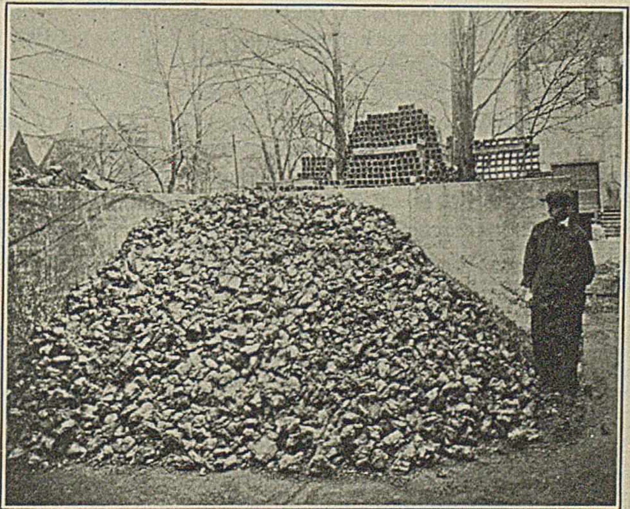


Figure 23—Semicommercial Production of Low Temperature Coke from Illinois Coal

quickly to draft regulations, and has a strength and density which meet in excellent manner the commercial requirements of handling, shipping, and storage. There is no loss from the production of fines and the amount of breeze produced is negligible. A peculiar property of the product in the matter of reactivity toward oxygen is an exceedingly interesting feature. The carbonized product formed at the temperatures indicated—namely, 700° to 750° C.—has certain combustion characteristics, especially in the matter of retention of fire, and quick response to the opening and closing of dampers which is in marked contrast to that of raw coal. Wide fluctuations in temperature are thus avoided and under conditions which preclude the possibility of producing smoke.

Conclusion

These studies, which up to the present time have been carried on from the purely theoretical standpoint, may help in arriving at an answer to the question proposed at the outset of this paper as a condensate from the lengthy title to the paper by Marcus Bull—namely, "What fuel?" What fuel will most effectively meet the ideals of convenience, of comfort, of conservation, cleanliness and health? Obviously, *gas*—and this we shall doubtless attain long before the year 2026. Meanwhile in this current time, already one hundred years late, any fuel which in a measurable degree accomplishes these same desirable ends would doubtless be a welcome substitute.

AMERICAN CONTEMPORARIES

Henry Leffmann, A.M., M.D., Ph.D.

Henry Leffmann

If THERE is any branch of scientific work with which Dr. Henry Leffmann is not familiar and upon which he cannot discourse entertainingly and to the edification of his hearers, it has not yet been discovered. In these days of hyperspecialism it is refreshing to find one who is not only learned in his own sphere of work and has made notable contributions to its advancement, but who has a breadth of knowledge and sympathy of understanding with all human learning. Art, music, literature, history, science, religion, and ethics—all are familiar topics, and concerning most of them he has written with illumination and a freedom from pedantry and bookishness.

For an outline of achievements and honors connected with an individual, one usually consults "Who's Who," but in the latest edition of that work the imposing list of accomplishments and attainments of this man is condensed into twenty lines, and fails to give any idea whatever of the lovable personality and compelling characteristics of a remarkable man.

When asked to submit a few of the outstanding facts which should form the basis of such a character sketch as this, he replied, with his characteristic humor and a twinkle of merriment in his eye—for he is an inimitable teller of tales, always welcomed as a dinner guest or at a gathering of what in these days is sometimes called "the intelligentsia"—"I would like my biography to begin as follows: 'Henry Leffmann was born on September 9, 1847, in Philadelphia. His ancestry on his father's side is partly Russian Jewish; on his mother's side, partly Welsh Quaker. He was educated in the public schools, completing the course of B. A. at Central High School, Philadelphia, and subsequently receiving the degree of M. A. *honoris causa*.' " He then added: "In these days of genetics and eugenics it is worth while to show that a mongrel may have some merit."

This might be called unassuming pride, but it is characteristic of the man who has taught more physicians and teachers, compiled more reference books and textbooks, and written more original articles and reviews than any chemist in America today.

A practicing analyst for more than fifty years, he has run the gamut of every kind of experience and position, from laboratory helper in the laboratory of a famous Philadelphia chemist of a half century ago, Dr. Charles M. Cresson, through the responsibilities of chemist to the offices of coroner and district attorney, respectively, and chemist to the Dairy and Food Commission of Pennsylvania, to one of the most noted analytical consultants of his community.

Graduating in medicine in 1869, he taught chemistry in Jefferson Medical College and in the Central High School; also toxicology in Jefferson College for several years. Subsequently he became professor of chemistry in the Pennsylvania College of Dental Surgery, in Wagner Free Institute of Science, and in the Woman's Medical College of Pennsylvania, occupying the last position for thirty years.

He was port physician in Philadelphia from 1884 to 1887, and again in 1891 to 1892, and was active in the work of the Philadelphia County Medical Society for many years, holding the offices of secretary and of president in that important organization. He was long active in the work of the Engineers' Club of Philadelphia, and was president of this body for one term. This is not only a social organization, as its name might indicate, but is one of the leading engineering societies of the country.

For many years he has been actively identified with the work of the Franklin Institute and has been of great assistance in the development of its valuable journal, to which he has contributed many valuable book reviews. At the time of the recent centenary of that famous society, he contributed largely to its success by collecting the material for the souvenir book of the occasion.

He has been actively connected with the Wagner Free Institute of Science for more than fifty years and is at present the chairman of the board of trustees, and is arranging to edit and publish a quarterly bulletin for this unique organization which has attracted so many noted scientists to its lecturing staff and has stimulated so much popular interest in scientific subjects.

For the past six years he has been lecturer on research in the

Philadelphia College of Pharmacy and Science and special contributor of editorials and book reviews to the *American Journal of Pharmacy*, which has been published for over a century by the College.

During his association with food control work in Pennsylvania, Dr. Leffmann and his associate, Dr. William Beam, later of the Burroughs Wellcome research staff at Khartoum developed the glycerol-soda process for determining the volatile fat acids of butter and other fats. For some incomprehensible reason this valuable method was at first condemned and then ignored by American official analysts. It was first officially adopted in Germany and later adopted in the United States. Dr. Leffmann was accustomed to refer humorously to this episode as a "conspiracy of silence," and it would seem as though it had been required to bear the stamp "Made in Germany" before it gained American approval.

Dr. Leffmann's contributions to chemical literature have been extensive, comprising papers on various subjects, mostly analytical, and textbooks on chemistry and manuals of analysis. Among the latter his "Water Analysis" and "Milk Analysis" have gone through a number of editions. "Select Methods in Food Analysis," written in association with Dr. Beam, was very favorably received and widely used. Several of the volumes of different editions of "Allen's Commercial Organic Analysis" were issued under his editorial supervision.

Outside of strictly scientific subjects he has written on New Testament topics; also a booklet "The States-Rights Fetish" and another entitled "About Dickens," being essays on themes suggested by the novels of that author. This work is now out of print and is being sought for by collectors of Dickensiana, at prices much above the original price of publication.

As a chemico-legal and medico-legal expert he is a shining exemplar of all that a scientific expert should be in the matter of impartial testimony of facts and opinions deduced therefrom. Newspaper editors and reporters eagerly seek his opinion upon scientific topics of popular interest, for he has a simplicity of style and a clarity of diction which are especially desirable in news articles.

In his seventy-ninth year, he is active and alert mentally and physically, and spends much of his time experimenting with color and photomicrography, which are his especial hobbies. He carries on extensive correspondence with scientists in other lands, particularly botanists, with whom he exchanges herbarium specimens. As a lecturer or talker, either to visible or invisible audiences, he is much in demand. His encyclopedic memory and apt use of quotations make him a brilliant conversationalist.

Dr. Leffmann has a liking for young men, especially those with a scientific bent, and has several times taken a young chemist into his laboratory with him, helping him, giving him the prestige of association with him, until the young man was able to stand alone, then relinquishing the business to him, as was the case with the writer of this sketch and as is now being done with another young man.

The respect and admiration of his friends and associates continue to increase as he grows older, and it is counted a rare privilege to know him and be associated with him. For some unaccountable reason he has never connected himself actively with association affairs, although he is a member of many scientific organizations of America and Europe.

Notwithstanding this lifelong tendency to hold himself aloof from his fellow workers outside of his own community, few men have labored more zealously to give chemistry a professional standing, or with greater success, than has Henry Leffmann, the Nestor of Philadelphia physicians and chemists.

Charles H. LaWall

NOTES AND CORRESPONDENCE

Decolorizing Carbons

Editor of Industrial and Engineering Chemistry:

With very great interest we have read the article on "Decolorizing Carbons," by Blowski and Bon, in your January, 1926, issue. The painstaking and systematic collection of data on the chemical and physical characteristics of vegetable carbons and their comparison with bone char form a valuable addition to the literature of the subject. Moreover, to any one familiar with the better known carbons the various samples used in the investigation are easily recognizable, and it is naturally gratifying to us that our own product should have made so favorable a showing. We cannot, however, refrain from expressing our surprise at the lack of familiarity shown by the authors with the recent accomplishments of vegetable activated carbons in the sugar industry. Because of this unfamiliarity much of what they have written is inaccurate, and many of the "probabilities" which loom so large in the latter part of the article are no longer open questions, but entered long ago the category of known facts.

We ask your indulgence to permit us to correct some of the statements made, because we feel that the authors have unintentionally created many misleading impressions in connection with a real advance in one of the largest industries in the world, in the development of which members of the American Chemical Society have had no small share.

We believe that the practical value of the results obtained by the authors in their series of tests is slightly lessened by the fact that they very thoroughly washed the carbons, first with hot tap water and then with hot distilled water, before testing. It would obviously be impossible to subject a carbon to this drastic washing in the refinery, and since the article indicates clearly that the authors had in view the accumulation of information of practical rather than purely scientific value, we believe they would better have attained their ends had they used the carbons as shipped by the manufacturers and as they would have to be used on a practical scale. However, we do not believe the washing of the carbons made any radical difference in the comparative values obtained.

It is with the conclusions drawn by the authors that we find ourselves so widely at variance. It seems to us that any unprejudiced reader would find the various tests made and described by them a striking testimonial to the efficiency of vegetable carbons for treating sugar solutions. The main conclusions, however, are not based on their experiments, but are, for the most part, expressions of personal opinion and suppositions without experimental basis. One of the chief criticisms of vegetable carbons, repeatedly either made or implied, is that they do not absorb nonsugars. One searches the article in vain for any experimental basis for such a statement. On the contrary, there is overwhelming evidence that the carbons *do* absorb nonsugars. In test after test it is shown that the carbons absorbed from 40 to 99 per cent of the color present in sugar solutions of various kinds. What was this color? It is impossible to believe that the authors assume that this "color" was some imponderable matter, a sort of phlogiston or ectoplasm—"color" in the abstract. The matter absorbed by the carbons was, of course, impurities in the sugar—in other words, nonsugars. The removal of color was merely incidental to the removal of these impurities—an indication of their removal. The authors could very easily have satisfied themselves on this point, either by analyzing the liquors after treatment or, even more simply, by weighing the carbons after use. In the latter case they would have found that the "color," so far from being imponderable, had increased the weight of the carbon from 25 to 50 per cent.

Much of the argument in Section IV we do not find entirely clear, but unless we have misread the article, the authors' argument might be summed up as follows: Vegetable carbons absorb little, if any, nonsugars. This leads to a smaller recovery of sucrose and an increased production of molasses. It also throws an increased burden on the remelt pans amounting to 140 per cent increase.

Can the authors point to any experimental or factory results which justify such a conclusion? If not, are not the statements at the top of column 1, page 41, too sweeping to find a rightful place in an article of a scientific character? On the other hand, if there is any evidence on which to base such startling conclusions, would it not have been in order to refer their readers to that evidence?

The facts are that the liquors produced from the ordinary refinery melt by our activated carbon are of such high purity and degree of decolorization that they can be boiled to five strikes of standard refined sugar before being sent to the remelt pans. We believe it will be admitted that no more can be said for the average bone-char liquor. Because of this fact, and because of the lower inversion losses due to the shorter time in process and the elimination of loss involved in washing bone char, the recovery of sucrose in the Suchar process is slightly higher than in the bone-char process. These facts are readily available, and we can at any time refer the authors to authorities of unquestioned standing and ability who will confirm our statement. In July, 1924, C. C. Krumbhaar, associate manager of the estate of H. C. Minor, wrote:[1]

> The melt, mixed with 1 per cent carbon on solids, using Suchar*** was kept hot while being pumped through filters***. The liquor is boiled to white sugar***. With Suchar we were enabled on account of the almost perfectly decolorized liquors and high purities to boil many times for granulated sugars.

Blowski and Bon also assume that the melt liquors are subjected to a triple filtration with activated carbons. On page 39 they state: "This laboratory test approximates the three-stage decolorization process to which the melt liquor would be subjected in actual operation," and on the following page: "The authors have never been able to produce anything approaching a refinery granulated liquor with less than a three-stage process."

This is indeed surprising. With our own carbon a three-stage filtration has never been used and, as far as we are aware, the same holds true for all other carbons. A two-stage filtration is common, but if a three-stage filtration has ever been used the conditions must have been most unusual, and under no possible interpretation of the facts could such a procedure be considered standard practice. Further, it is very difficult to reconcile the authors' second statement, quoted above, with the results which they report in their paper. At the top of page 40 they state that a 98.2 per cent decolorization gives a "satisfactory granulated liquor," and we believe that any one familiar with sugarhouse practice will agree that such a liquor would be very satisfactory. Yet we find on page 37, Plate VI, that with a single filtration the authors succeeded in removing over 99 per cent of the color from a washed sugar liquor. Still more striking results are shown in Plate VIII, as in these experiments, with a single filtration and using only 4 per cent carbon, the authors succeeded in removing 99 per cent of the total color, in spite of the fact that the purity of the washed sugar was only 98.8, instead of over 99, which they state to be the purity commonly used in bone-char refineries. Finally, in Plate IX, using apparently a melt of the same sugar, but using new bone char in place of the decolorizing carbons, they succeeded in removing only 96.5 per cent of the color, even with 100 per cent of the bone char. In view of these experimental results, the statement quoted above requires further explanation.

In a report by one of the leading sugar chemists in this country, connected for many years with one of the large bone-char refineries in the East, the following sentences occur:

> The prefiltration with once used Suchar reduced this (the color) to about 2.5, and the second filtration with freshly revivified Suchar reduced it further to about 1.2, giving a liquor of a better color than is frequently the case with first liquor from bone black. The liquor was always very brilliant, after even the first filtration, and proved quite satisfactory for boiling to granulated sugar.

Lest it should be said that such results can only be obtained with Louisiana sugars, it may be stated that at the time this report was made the refinery was operating on Cuban raws. Three weeks later the same investigator wrote:

> The color of the liquor and its purity compared favorably with that obtained in bone-black refineries and gave no trouble in working. Five strikes of granulated sugar were boiled from these liquors and this is better than is often done in bone-black refineries.

On page 39 the authors state: "The carbon process***has not been so much concerned with high quality," and on the following page, middle of second column: "It would probably develop that in order to insure absolute clarity a final filtration of decolorized liquors with a standard filter aid would be necessary."

We invite you to purchase on the market a sample of any standard granulated sugar made by any refiner using the bone-char process and to compare it as regards color, appearance, and purity with the Suchar. No filter aid of any kind was used either before or after the carbon treatment. Sugar of this quality has been on the market since the fall of 1923 competing successfully with sugars made by the bone-char process. This information also was readily available to the authors.

It is regrettable that the authors paid such small attention to the question of revivification of the used carbon. Any one familiar with the history of activated carbons, both in this country and in Europe, knows that the problem of revivification has proved to be the most difficult of any to solve—in some cases so difficult that the entire carbon process has been pronounced a failure because of the lack of success in this one particular. The assumption on page 38, therefore, that the carbons "A" and "D" "presumably can be as economically regenerated as the other carbons" is a rather hasty dismissal of an exceedingly important point. One page 40 we have an unsupported statement that "carbon used on unfiltered liquors suffers a gradual reduction in filtration efficiency." That statement we believe to be true of one of the carbons examined by the authors. It certainly is not true of all carbons. At the time the authors presented their paper, many hundreds of cycles of Suchar revivification had been carried through successfully, and we could have referred them to those who, we are sure, would gladly have testified that the filtration properties of revivified Suchar are fully equal to those of virgin Suchar.

The authors have apparently made no tests of any kind on the revivification of any of the carbons which they examined, and again we feel that an unqualified statement based on hearsay is out of place in a scientific paper.

There are many other points which we should like to discuss, but we believe enough has been said to show that the whole case built up by the authors against vegetable carbons falls to the ground in the light of the facts.

LEONARD WICKENDEN

SUCHAR PROCESS CORP.
50 BROAD ST., NEW YORK, N. Y.
January 14, 1926

. . . .

Editor of Industrial and Engineering Chemistry:

Mr. Wickenden's letter was very interesting to read, as it is always both interesting and instructive to learn the views of others whether they are favorable or otherwise. We do feel, however, that Mr. Wickenden has mistaken the purpose of our study—for it was not, as he believes, to build up a case against decolorizing carbons. As might be expected in an industrial laboratory, the investigation was originally started with the object of determining, for this company's uses, what advantage might be gained from recent developments in the field of decolorizing carbons. In fact, publication was not even thought of at the time. If it can be said that a case was built up, it was not done deliberately, but rather it built itself up as the investigation progressed. As a matter of fact, our paper presented so many favorable aspects of decolorizing carbons that publication would have been withheld had we desired to build up a case against carbons.

However, Mr. Wickenden brings up a number of points which, in all fairness, should be discussed. Separating these points as well as can be done, they are discussed as briefly as possible, as follows:

1—He believes it incorrect in principle to wash the decolorizing carbons before studying their properties.

Most carbons, as purchased, contain soluble salts which would greatly reduce their value if put directly into sugar liquors, and

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[1] *Louisiana Planter*, **73**, 58 (1924).

some have a very acid reaction, which would render them destructive of sugar if used in the original form. As washing would greatly improve many of these, and would be inexpensive, it would be the logical course to follow in actual practice, and also in making comparative tests. Distilled water was used, of course, merely to be assured of identical conditions in all tests.

Also, in practice a carbon would be used ten to twenty times, its life depending on losses in regeneration. Between cycles, with each regeneration, it would be washed. If a carbon lasted for twenty cycles, then it would be washed before nineteen of these cycles, regardless of whether or not it had been washed when purchased. Obviously, in comparing properties, it would be unfair to consider the first cycle only and forget the others.

2—In referring to our paper, Mr. Wickenden says, "One of the chief criticisms of vegetable carbons repeatedly either made or implied, is that they do not absorb nonsugars," and he goes to considerable length of argument to prove that such a view is wrong.

It would appear that Mr. Wickenden has not read our article completely, for his statement is incorrect. On page 37 we devote almost an entire column to showing that decolorizing carbons have a very definite power of adsorbing mineral salts—even showing that in some cases this exceeds that of bone char for the same conditions.

However, we do state that the methods of refining with decolorizing carbons are so different from those used with bone char that the actual elimination of nonsugars (in weight) would be negligible with carbons. This was briefly explained in our paper, but for the benefit of those who are unfamiliar with refinery practice it will be explained here in more detail:

In all methods of sugar refining the raw sugar is first washed, thus separating it into two constituents—a washed sugar containing about 90 per cent of the sucrose and about 10 per cent of the nonsugars of the raw product, and an affination (or wash sirup) containing the remaining 10 per cent of the sucrose and about 90 per cent of the nonsugars. In both bone-char practice and decolorizing carbon methods the washed sugar is then dissolved in water, but from that point the two methods of refining differ.

In modern bone-char refining the melted washed sugar (raw liquor) and the affination sirup are first cloth-filtered and then filtered over bone char—the amount of revivified char used each day for this filtration being about equal to the weight of raw sugar melted daily. The common practice is to put the raw liquor over the char filters first, and then follow this up with low-grade products (affination sirup itself or products derived from it by previous char filtration). In particular, three points in connection with bone-char refining should be noted:

(*a*) As both the raw liquor and affination sirup are char-filtered, *all* of the nonsugars are passed over the char (in fact, most of them are filtered repeatedly), giving the char the fullest possible opportunity to use its adsorbing power.

(*b*) A weight of char about equal to the raw sugar melted is used, this providing high adsorptive capacity.

(*c*) The char filters are finished off with low-purity products having a high concentration of nonsugars. This, of course, tends to give a high adsorption of nonsugars by the char.

As a result of this intensive char filtration with bone char, there is a large adsorption of salts and other nonsugars by the char, with a complete elimination of a considerable portion of them by means of the subsequent washing and kilning of the char. In this manner about 50 per cent of the nonsugars entering the process is eliminated. As these nonsugars have the power of preventing the crystallization of sugar, this elimination results in an increased recovery of crystallizable sugar.

In the case of refining with decolorizing carbons, the systems proposed by the carbon manufacturers, and actually in use, provide for the filtration of the melted washed sugar and high-purity remelt sugar only—the affination sirup, which contains the bulk of the nonsugars, being boiled to remelt sugars without carbon filtration. Carbon filtration of the affination sirup is not even proposed by carbon manufacturers, presumably because, to obtain appreciable benefit, such large quantities of carbon would be required and such an extensive multiple-stage filter-press station would be necessary that the system would be far from economical. For this reason the following points should be noted:

(*a*) As the raw-liquor and high-purity remelts which are filtered contain only about 10 to 15 per cent of the nonsugars in the raw product, fully 85 per cent of the nonsugars never even come in contact with the adsorption medium. Manifestly, there is no opportunity for the carbon to adsorb the 50 per cent of nonsugars that is eliminated with bone char.

(*b*) Only about 2 per cent of decolorizing carbon (on raws melted) is used. As this is only about one-fiftieth as much adsorbing medium as is used in the bone-char process (with about the same ash-removal power per unit weight), it will be seen that the adsorbing capacity provided is very trifling. It is evident that, of the small quantity of nonsugars filtered, only a relatively small portion can be adsorbed.

(*c*) As only high-purity products are filtered, the concentration of nonsugars in contact with the adsorbing medium is very low. This, of course (according to well-known laws of adsorption), will result in a relatively small adsorption of nonsugars.

Any one of these conditions alone is sufficient to reduce the elimination of nonsugars to only a fraction of that obtained with char. With all three conditions working together, it is evident that the elimination will be reduced to a negligible quantity.

Mr. Wickenden points to the removal of color as a removal of matter. That is true, but every refiner knows that the weight of this coloring matter is so extremely small that sugar solutions often have the great bulk of their coloring matter removed without showing any change in composition, by analysis.

3—Mr. Wickenden takes exception to the statement that, with the use of decolorizing carbons, it would be necessary to boil 140 per cent more remelts than with the use of bone char.

The calculation of this, which is based directly on refinery results, is very simple—all the essentials being given in our paper at the top of page 41. This calculation will probably be made clearer when it is explained that all of the nonsugars in the raws (except those eliminated by adsorption and those diverted to soft sugar) must be boiled to remelts in order to be eliminated as molasses. The amount of these remelts that it is necessary to boil, therefore, is proportional to the quantity of these nonsugars.

A brief description of the mechanism by which the use of bone char reduces the amount of remelts it is necessary to boil will be clearer than the calculation:

In any sugar refinery the main original source of material for remelts is the affination sirup (raw wash sirup), this commonly amounting to about 12 per cent of the raws handled. In refining with decolorizing carbons the accepted procedure is to boil all of this material to remelt sugars (the remelted sugar to be later reboiled for granulated).

In modern bone-char practice, however, the customary procedure is to filter this material over bone char, eliminate about 50 per cent of the nonsugars, and so improve the material that it can be boiled directly to white granulated sugar. The sirup spun off of this white granulated sugar (about one-half of the original volume of affination sirup) then becomes the starting point for the remelt system. At one sweep, therefore, this system of char filtering and boiling directly to white granulated sugar cuts the main source of remelts in half.

(The above outline is merely for the purpose of illustrating the mechanics of the bone-char process in reducing the amount of remelts. Any exact calculation must be based on the quantity of nonsugars handled, as was done on page 41 of the original paper.)

4—Mr. Wickenden states that a three-stage process for decolorizing washed sugar liquor is unnecessary, basing his statement upon two premises:

(*a*) That commercial sugars are actually produced by a two-stage process.

This means nothing unless the degree of washing and subsequent reboiling is known. Our conclusion was based upon the necessity for securing a granulated liquor equal in quality to that used by bone-char refiners. The standard of color for white granulated sugar liquors set forth in our paper is actually reached in refinery practice, and is believed to be necessary for the highest quality of output. From the standpoint of a refiner considering the adoption of a new process, a lowering of standards could not be considered.

In order to satisfy ourselves of the necessity of a three-stage decolorization process, we examined commercial sugars made by the two-stage carbon process. These, while passable in some markets, were decidedly inferior to the average bone-char granulated sugar, and could not safely be handled by large refiners who must be in a position to compete in all markets.

(*b*) That he believes our tests to be inconsistent among themselves because of the following facts which we brought out in our paper:

(1) A 98.2 per cent decolorization of raw liquor produces a satisfactory granulated liquor.

(2) In our "efficiency tests" we obtained 99 per cent decolorization with single filtrations with carbons.

(3) In similar efficiency tests with char we obtained only 96.5 per cent decolorization.

We would call attention to the following facts which Mr. Wickenden has apparently overlooked:

(1) Where he states that we obtained 99 per cent decolorization with single-stage filtration with carbons (in one case the exact figure is 98.5 per cent), this was accomplished with 4 per cent carbon in one case and 8 per cent in the other, while 2 per cent is all that is recommended by carbon manufacturers and all that can be considered economical in practice.

(2) These tests were made for comparative efficiency studies only, and were therefore conducted under test conditions of 47.5° Brix, at which point the decolorizing efficiency of carbons is about 20 per cent higher than at 60° Brix, which would be used in actual practice and which was used in the three-stage experimental "run."

(3) Even if we disregard these test conditions, a two-stage process using 2 per cent carbon is not the same as a single-stage process using 4 per cent, for in the former case one filtration is with a partly exhausted carbon.

(4) It should be brought out that these "efficiency tests" referred to by Mr. Wickenden, while closely resembling the manner in which decolorizing carbons would be applied, bear no resemblance to the actual use of bone char. Bone-char filtration, from its nature, is essentially a multiple-stage filtration. At the surface of the char in the filter the liquor is in equilibrium with the char soon after filtration begins, but as the liquor goes through the 20-foot column of char it passes through innumerable strata of increasingly fresh material until it comes in contact with practically fresh char as it emerges from the bottom of the filter. For this reason the actual decolorization with bone char in practice is far greater than indicated by the 96.5 per cent result shown in the laboratory "efficiency test." Relative decolorizing power of various agents as shown by efficiency tests should not be confused with actual results obtained in practice, where the manner of application may be entirely different with the different materials.

5—Mr. Wickenden comments upon the lack of data upon revivification and, because of this, questions some of our statements.

It is true that the study of revivification has not been included in our experimental work, as we lacked the facilities for this work. However, in estimating costs for our final conclusions we accepted the figures as actually advertised by carbon manufacturers. It is conceivable that these are too low, but it is doubtful if they are too high.

With regard to the statement that carbons decrease in filtration efficiency with continued use, the authorities for this statement are Horne[1] and Sauer.[2] Accepting the results of such widely known investigators cannot fairly be construed as basing our statements on "hearsay." According to Sauer, this decrease in the filtration efficiency of carbons is due chiefly to the accumulation of impurities—mineral substances and also fine carbon derived from the organic matter filtered and adsorbed out of the liquors. If Mr. Wickenden has found a way to overcome this, then he has made a decided and startling improvement in the industry. However, as there have been no published data available to show that such an improvement has been developed, we believe that a refiner is justified in relying on the previous widespread knowledge regarding this point until such a time as this improvement has been clearly demonstrated.

If Mr. Wickenden will reread our paper and also read the foregoing comments, we think he will find that our conclusions are all based on carefully conducted experimental work, on accurate refinery results or upon statements by authorities of unquestioned standing. Any differences of opinion appear to be due chiefly to points overlooked in the reading of the article or to points with which refiners only are familiar.

It is quite natural that the viewpoint of a manufacturer of carbon should be different from that of a sugar refiner. As refiners of sugar, it has been our object, from the purely selfish standpoint of our own information, to determine both the advantages and disadvantages of decolorizing carbons, and we have endeavored to point these out impartially as we found them. However, it is felt that those actually engaged in the refining of sugar, knowing its problems well, are in a particularly advantageous position to determine the weaknesses of such new developments, and if the manufacturers of decolorizing carbons will take advantage of such criticisms to develop their product still more, it will probably secure a much more widespread use than it has at present.

A. A. Blowski
J. H. Bon

California & Hawaiian Sugar
Refining Corp.
Crockett, Calif.
February 13, 1926

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[1] This Journal, **12**, 1015 (1920).

[2] *Intern. Sugar J.*, **25**, 485 (1923); **26**, 27, (1924).

Natural Indigo Industry Still Exists

Editor of Industrial and Engineering Chemistry:

I am impelled by the penultimate paragraph of the interesting article "Is Commercial Synthetic Rubber Probable?" which appears in your April issue, to ask space in your columns for brief comment. My object is twofold—to correct what I find is a widely held misapprehension, and simultaneously to stress the moral which the writer of the article draws.

The natural indigo industry is by no means dead. I have no recent returns at hand, but I should be surprised to find that the average annual production of the last five years was much less than that of the decade immediately preceding the war. Moreover, the industry is not, nor has it ever been, "entirely in the hands of the uneducated native." It is true that in former years a large amount of inferior indigo was produced by native manufacturers in southern India and, so far as export trade is concerned, this section is practically extinct. The greater portion and the better quality natural indigo is, however, and always has been, produced by the planters of northern Bihar and Orissa. These planters are not only British born, but in most cases are members of families which have owned large indigo properties and had representatives in the country engaged in the industry for several generations. Considerable fortunes were derived from it by these families in the past.

It is largely due to the enterprise of the present-day planters, or their immediate predecessors, in securing scientific aid at the time of the introduction of synthetic indigo and since, that the industry still survives. In 1898, when that event occurred, a leading representative of the Badische Anilin und Soda Fabrik expressed the opinion publicly that in five years natural indigo would be a thing of the past. As a result, however, of scientific work undertaken by the planters, with government assistance, a number of improvements were introduced into the methods of manufacture and agriculture, which have resulted in the continued existence of the industry. How far the survival will be permanent remains to be seen. The fortunes of the planters are, of course, no longer those of the days of their monopoly, but the fact that the natural product can still compete with the synthetic, even on a limited scale, twenty-eight years after the introduction of the latter indicates that the argument from the story of indigo to the probability of the rapid extermination of plantation rubber, if the synthetic article can be perfected, rests on a somewhat insecure foundation. Particularly is this so when regard is had to the much greater interests vested in plantation rubber than ever were in natural indigo.

C. Berkeley

The Biological Station
Nanaimo, B. C.
April 13, 1926

Rayon Conference

A group of rayon manufacturers and representatives of various textile associations, the members of which are using this fiber in the manufacture of their product, conferred with representatives of the Bureau of Standards recently for the purpose of outlining the research program on rayon.

The following projects were discussed: the effects of moisture on the physical and chemical properties; standard moisture regain; kind and percentage of oils to be used in manufacturing and its effect on the physical and chemical properties; uniformity and stability of the fiber, and such problems as effect of cleaning, ironing, perspiration, light, etc.

The conference agreed that studies of the effect of moisture on the properties of rayon and the stability or resistance to aging were of most immediate importance. It was stressed particularly that the proposed project should be planned to study not only what occurs but why it occurs, so that possible remedies may be found.

Laboratory Safety

Editor of Industrial and Engineering Chemistry:

Your editorial on this subject in the April issue attracted our attention favorably, and it has since occurred to us that our own experience might be of interest to those in the profession.

When the decision was handed down in the New York State courts in the case of Cornell University some five years ago, we seriously undertook to prevent such an occurrence here. In consultation with legal authorities we arrived at the use of the following system:

On registering for any course in chemistry the student makes a deposit with the department for materials consumed and broken in the course—there is no fee for laboratory courses. At this time an agreement is executed in duplicate whereby the student promises not to use certain specified dangerous chemicals without written permission.

When in the course of the work it becomes necessary for a student to use any of these chemicals, he is required to prove his ability to use them properly and to avoid the dangers incident to their misuse. When we are convinced of this a permit is issued, and every transaction at the stock room is indorsed with date and quantity on the permit. As a rule no first-year student receives a permit, experiments involving such reactions with these chemicals as are necessary are incorporated in the lecture demonstration work, and the precautions are emphasized. Thus a serious respect for the chemicals is stressed.

If a student should show carelessness in the use of any dangerous chemical, the permit for the use of that chemical is immediately revoked *permanently*. Only one incident of this nature has occurred and that not serious enough to receive more than passing notice in many laboratories. It may be worth noting that the student who made the error just mentioned was working in his third year with sodium, and was the same student who caused a hydrogen generator to explode in his first year, also the only such happening in this time.

We are attaching blank copies of the agreement and permit exactly as executed. We have found that the labor incident to the use of the system is more than compensated by the confidence that such precautions are for the safety of all working in the laboratories.

R. K. STRONG

REED COLLEGE
PORTLAND, OREGON
April 26, 1926

AGREEMENT

The undersigned, a student of Reed College in the Department of Chemistry, in consideration of permission to avail himself of apparatus and chemicals (other than the chemicals named below) of Reed College Chemical Laboratory, hereby agrees not to use in the said chemical laboratory any of the following chemicals without written permission of the Head of the said Department of Chemistry:

Bromine
Carbon disulfide
Ether
Hydrofluoric acid
Phosphorus, yellow or red
Potassium chlorate
Potassium or sodium cyanide
Sodium, metal

Receipt of a duplicate of this agreement is hereby acknowledged.

..................192.. ....
Signature of Student

PERMIT FOR USE OF DANGEROUS CHEMICALS

To..........................

You are hereby granted special permission for the period of.... months from the date hereof to use in the Chemical Laboratory of Reed College the following chemicals:

Bromine
Carbon disulfide
Ether
Hydrofluoric acid
Phosphorus, yellow, red
Potassium chlorate
Potassium and sodium cyanides
Sodium, metal

This permission is granted upon your representation that you are familiar with the characteristics of the chemicals above named and with the dangers incident to the use thereof.

This permission shall only be operative on your signing a duplicate hereof and thereby assuming all risks incident to the use of said chemicals.

Date..................192.. ....
Professor of Chemistry

I hereby agree, in consideration of the foregoing permission, to assume all risks of injury thereunder.

Date..................192.. ....
Signature of Student

Calendar of Meetings

American Leather Chemists' Association—23rd Annual Convention, Traymore Hotel, Atlantic City, June 2 to 4, 1926.

National Lime Association—8th Annual Convention, French Lick Springs, Ind., June 8 to 11, 1926.

American Institute of Chemical Engineers—Berlin, N. H., June 21 to 23, 1926.

American Society for Testing Materials—Atlantic City, N. J., June 21 to 25, 1926.

Fourth Annual Colloid Symposium—Massachusetts Institute of Technology, Cambridge, Mass., June 23 to 25, 1926.

American Chemical Society—72nd Meeting, Philadelphia, Pa., September 6 to 11, 1926. 73rd Meeting, Richmond, Va., April 12 to 16, 1927.

American Electrochemical Society—Fall Meeting, Washington, D. C., October 7 to 9, 1926.

Lettering on Drawings

More satisfactory cuts can be made from drawings if authors will bear in mind that the lettering should be plain and at least *1 mm. high* when the drawing is reduced to the size suitable for our pages. This size depends on the shape of the drawing and the amount of detail that it contains. Usually $3^1/_4$ inches in width is the most convenient, but sometimes it looks best at 2 inches or, less frequently, at $6^3/_4$ inches. Most figures can be advantageously drawn for a linear reduction to one-half or one-fourth.

Report of A. C. S. Committee Advisory to the Bureau of Standards—Correction

In this report, THIS JOURNAL, **18**, 542 (1926), the statement in regard to the examination of pure zinc should read "a zinc of a high degree of purity," instead of "spectroscopically pure." This zinc showed an analysis of 99.993 per cent zinc, but did contain impurities detectable by the spectroscope. The spectroscopically pure zinc of the New Jersey Zinc Company shows only zinc lines when given a long exposure on a large quartz spectrograph, and is truly spectroscopically pure zinc, with an analysis of at least 99.9999X per cent zinc.

BOOK REVIEWS

International Critical Tables of Numerical Data, Physics, Chemistry, and Technology—Vol. I. Edward W. Washburn, Editor-in-Chief. Prepared under the auspices of the International Research Council and National Academy of Sciences, by the National Research Council. 415 pages. McGraw-Hill Book Co., Inc., New York, London, 1926. To be published in 5 volumes. Price, $60 per set on orders for sets only; payable at the rate of $12 per volume as issued.

Any few lines of description will, of necessity, fail to serve as a satisfactory review of a book which is itself full of reviews, and reviews about everything in physics, chemistry, and technology. But one may still call attention to a truly wonderful undertaking. This first volume of critical tables is devoted to fundamental constants of nature, systems of measurement, and laboratory technic of many kinds. It includes an enormous amount of data on the chemical and physical properties of elements and compounds, and covers also X-rays, radioactivity, and astronomical, geodetic, and aerodynamic data.

It is nothing like an engineer's handbook, nor like a dictionary or an encyclopedia. For example, "noon" is not described as "midday," but careful definitions distinguish between local time noon and mean noon. A mere atomic weight table here becomes eight large pages, which include the atomic weights of all the elements as officially determined since 1882, together with Aston's list of isotopes, with the mass numbers, a modern periodic chart, and Soddy's decay chart of radioactive elements. There has been introduced here complete discussion of atomic structure, including the modern table showing arrangements of electronic orbits of all elements. Thus, also, many other subjects are treated by good descriptive matter in addition to the numerical data. Thermometry and optical pyrometry, maintaining constant low temperatures, constant humidities, etc., are descriptively handled by experts. Thus the Tables become highly instructive, pure scientific reading matter, with some emphasis on the "pure." The old story of indicators becomes a whole chapter in which buffer solutions, pH values, and hundreds of new indicators are described. An interesting and valuable chapter of psychological data on observational errors, including curves of eye and ear sensitivity, shows how far beyond a mere list of critical data the volume really goes.

The reference tables proper cover most of the properties of matter and are surprisingly complete. There are over 3300 inorganic compounds for which melting point, density, etc., are given. There are thousands of refractive indices. Over 6000 organic compounds are listed as to chemical formula, name, molecular weight, melting point, boiling point (where known), etc. There are also additional index tables ingeniously arranged so that one may quickly find, in the major tables, such things as compounds which melt, boil, or freeze at some particular temperature. In my first hour I wanted to know the latest gravity determination of pollucite, a rather rare mineral, and I also sought a group of salts which might melt at about 300° C. Finding these data in the Tables, I was naturally favorably impressed. There are 5 pages of liquid-crystal substances with melting point and transition temperatures, and 14 pages of data on crystallography of organic compounds. The X-ray crystal structures with unit cell dimensions cover organic and inorganic compounds, metals and alloys, and fill 16 pages. Moreover, there are 400 literature references accompanying this subject alone.

Remarkable new matter, including explanatory notes, has found its way into these Tables. For example, data on dispersoidology, relative sweetening powers, odoriferous materials, and odorimetry are all qualitatively treated. Radioactivity is fully discussed, and about 20 pages cover all parts of the topic. This naturally leads to tables of ages of minerals calculated from the "lead ratios." Stars and nebulae come in for 8 very instructive and readable pages. Gravity data, with the latitude and longitude of many selected world stations, are given, and a chapter on aerodynamics gives much information on wind pressures, on various shapes of obstruction, propellers, surfaces, etc.

If the volumes that are to follow fulfil the promise of this first one, the Critical Tables will be a unique collection of scientific data indispensable to every working scientist. It is very evident, from the care with which the Tables have been made and the interest embedded in the short descriptive articles which introduce so many of the subjects, that research men from all parts of the world have exerted themselves to make the work a success.

W. R. Whitney

The Enrichment of Coal Gas by the Injection of Oil into the Retort during Carbonizing. Department of Scientific and Industrial Research, Fuel Research Board, *Technical Paper* **14.** 61 pages. Published under the authority of H. M. Stationery Office, London. Price, 1 s. 9 d. net.

This report covers work done by the Fuel Research Board in studying methods for the operation of continuous vertical retorts in order to permit greater flexibility in operation. In order to develop a method for enriching the gas that would be made with a high input of steam, experiments have been carried on in which oil was introduced through a water-cooled tube into the coal during the carbonizing period, and this report is a summary of these experiments.

It appears probable from the gas analyses that the oil vapors may come into contact with the walls of the retort, which are at a temperature of about 1050° C., and this temperature is probably too high for the most efficient treatment, as is evidenced by the considerable increase in hydrogen and the rather low thermal efficiency secured from the oil. The fact that the "unaccounted for" in both the heat and weight balances is considerably less than 2 per cent gives evidence of the very great care that has been used in performing the experimental work.

The use of the volatile determination in nitrogen at 925° C. will not appeal to those who follow our American practice.

A very good case for the more general use of the assay test for comparison of different shipments of coal is presented.

From a thermal standpoint, the American gas manufacturers would probably not be very enthusiastic about a method of operation in which some 27.8 therms are expended in increasing the output of the apparatus by 13.7 therms. In the United States, where carbureted water gas apparatus is generally available, it would seem highly probable that this same increase in thermal capacity could be secured at very much higher efficiency.

The gas industry as a whole is greatly indebted to the work of the Fuel Research Board for the detailed and careful study they are making of the operations of the various processes used in the manufacture of gas.

W. H. Fulweiler

Recipes for the Colour, Paint, Varnish, Oil, Soap and Drysaltery Trades. Compiled by an Analytical Chemist. 3rd revised edition. 358 pages. Scott, Greenwood & Son, London; D. Van Nostrand Co., New York, 1926. Price, $5.00.

These recipes have been compiled by an analytical chemist of Great Britain who remains the anonymous author of this volume. This is another addition to the several books of recipes now available, but devotes by far the greatest space to the specialties above indicated. There are recipes for pigments or colors for paints, lithographic and letter press printing inks, for mixed paints, paint removers, and other preparations for paint-making, whitewashing, and paper hanging. Varnishes form the subject of another chapter, as do soaps, perfumes, and lubricants. Adhesives are given considerable space. There is a section on writing, marking, and stencil inks, on waxes, and similar office sundries, and another section on preparations for the laundry, kitchen, and general household use. Attention is also given to disinfectant preparations and insecticides and a number of recipes pertaining to oils, varnishes, dressings, greases, etc., for leather. An interesting section is the one on miscellaneous preparations, which treats methods of silvering glass, coloring metals, preparation of crayons, and the usual handy formulas for the jack-of-all-trades.

The volume is well indexed and, although we have had neither the time nor the opportunity to test the value of a single formula, we have no hesitation, based upon experience with other books of recipes, in recommending this collection to those who find such compilations of value.

Chemistry in Agriculture. Joseph S. Chamberlain, Editor; C. A. Browne, Advisory Editor. 384 pages. Published by The Chemical Foundation, Inc., New York, 1926. Price, $1.00.

This is "a coöperative work intended to give examples of the contributions made to agriculture by chemistry." The book is written in popular style, easily understood by the general reader as well as the student. At the same time, it is accurate and scientific. It is one of a series produced on a nonprofit basis for use in the Prize Essay Contest of the American Chemical Society.

It is a symposium of sixteen chapters each prepared by an outstanding specialist. While each subject is approached from the chemical standpoint, it is undoubtedly the clearest way to give a connected and logical understanding of the great basic problems of agriculture and food production and use. Dr. Chamberlain puts it in a few words in the preface—"The farmer tills the soil that plants may grow that man may live."

It is a book that will interest all intelligent people and open up a new world to many. It will be especially valuable to students, farmers, and business men interested in agriculture. It should help the public generally to get a clearer vision of how such sciences as chemistry minister to the general welfare.

The general subjects covered are: I—Crops and the Soil; II—The World's Food Factory, or the Plant in Air and Light; III—Soil Life; IV—Where the Nitrogen Comes from; V—Maintaining Soil Fertility; VI—Cereals; VII—Sugar and Sugar Crops; VIII—Fruit and Vegetables; IX—Fermentations on the Farm; X—Chemical Warfare to Save the Crops; XI—Agriculture and the Evolution of Our Diet; XII—Vitamins in Human and Animal Nutrition; XIII—Meat in Its Relation to Human Nutrition and Agriculture; XIV—Chemistry as a Guide in Animal Production; XV—The Chemistry of Milk and Its Products; and XVI—The Chemist as Detective and Policeman, or Fertilizer, Feed, and Insecticide Control.

The book is beautifully printed and illustrated and a credit to the authors and to the Chemical Foundation.

A. F. Woods

Centrifugal Dryers and Separators. By Eustace A. Alliott. Chemical Engineering Library. Second Series. 151 pages. Ernest Benn, Ltd., London, 1926. Price, 6 s. D. Van Nostrand Co., New York. Price, $2.00.

Mr. Alliott is the first to collect the scanty information scattered through transactions and periodicals and make it available and useful to the designer and operator of centrifugal apparatus. It is, therefore, doubly welcome and in the tiny compass of 150 small pages a great deal of ground is covered. This is doubtless the reason for many omissions and for the scanty treatment of important subjects.

The descriptions of the construction, operating features, and service results are excellent and show the author to have carefully observed and adequately described the actual performance of centrifugals, particularly those of the large size, perforated-basket type. The descriptions of the two-liquid types of separators are not nearly so good and operating results are lacking for cream separators and oil purifiers, which have come into extremely widespread use all over the world. It is not clear why the odd name of "plate type" should be foisted upon the centrifugal bowls with cone-shaped separating disks, which have universally been called "disk bowls" ever since they were first developed.

The mathematical theory is poorly arranged and scattered with no logical order throughout the book and omits many important parts. Furthermore, critical selection would have avoided quoting an equation for clean skimming of milk (page 90) from Richmond's "Dairy Chemistry," showing a butter-fat loss in skim milk proportional to the square root of the cube of the throughput and following this with the statement that others have proposed functions of the linear value of the throughput and of the square root of the throughput. Careful tests on this point have shown that butter-fat loss in skim milk is directly proportional to the throughput.

It is also not clear why Stokes' law for the free fall of a sphere through a viscous medium is quoted and then, without further application, dropped in favor of the partial pressure gas law as published by Ayres. Neither is it clear how formula 7 (page 15) is derived, or why the pressure on the supporting basket rim from packed solids should differ from that due to liquids. Moreover, on the very next page the author recommends using the formula for liquids.

The statement on page 25 that fine swarf holds less oil after centrifuging than coarser chips is not in accord with the reviewer's experience. Contrary to the statement on page 43, brakes can be applied to self-balancing bowls.

In discussing, on page 87, the balance between two separated liquids of different specific gravities, the treatment should have dealt in the first instance with the respective net heads measured from the "balance" circle, rather than from the outer radius of the separating disk.

It is a pleasure to read the clear, brief, and pointed description of the phenomena and effects of critical speed, balance, and stability of self-balancing bowls given on pages 112 to 141.

A. E. Flowers

Industrial Water Supplies of Ohio. With chapters on Impurities in Water, Methods of Analysis and the Statement of Results, and Their Interpretation, the Behaviour of Water in Use, and the Industrial Purification of Water. By C. W. Foulk. Geological Survey of Ohio, 4th Series, *Bulletin* 29, 1925. 385 pages. 20 tables and index. Published by The Kelly-Springfield Printing Co., Springfield, Ohio, under the supervision of the State Geologist. Price, $1.00.

Although this publication is primarily for the chemists of Ohio who have to consider waters in their industrial relations, it is of great interest to other classes of readers, particularly to water-supply engineers and to others who may be attracted by the lore of water.

The first 159 pages contain much general information regarding impurities in water, water analysis methods, and their interpretation, the characteristics of water such as hardness, H-ion concentration, gas content, and mineral content, and in general those which interfere with the detergent action of soap, cause corrosion of metals, scale formation, foaming, and priming in steam boilers. The book also discusses in general terms methods of purification, particularly from the chemist's standpoint.

All the chapters are clearly written, the treatment is scholarly and modern, and while some of the chapters, such as the one on corrosion, are rather technical for the general reader, the reviewer knows of no publication of its kind which is so good or so generally useful.

The chapter on water softening is excellent, although probably more could have been written regarding the various zeolite processes and the usefulness of waters of zero hardness in certain industries.

The second part of the book contains the results of chemical analysis of the surface waters of Ohio, and the third part similar data regarding the ground waters.

The results are given in ionic form, and are expressed both as p. p. m. and grains per gallon. Throughout the whole work, particularly regarding methods of expressing results of analysis, the author shows commendable wisdom in applying to practice chemical theory without losing sight of the necessities of those readers whose understandings are tied to old ideas. Because of its breadth of treatment, the book will interest a wide circle of readers, many of them beyond the limits of Ohio. Its subject matter cannot be too widespread.

Robert Spurr Weston

Shipping Containers. By Bronson L. Huestis. No. 37 of Ronograph Series. 133 pages. The Ronald Press Co., New York. Price, $1.25.

The publisher's foreword describes this book as "a careful, authoritative presentation of the essentials of designing and utilizing shipping containers prepared to assist shippers in obtaining the full benefits of all possible economies."

Most of the subject matter has been collected from reliable sources. Under the heading "What a Shipping Container Should Do," the requirements of a container in domestic transportation are well outlined. In another place some additional requirements of a container for export shipment are presented. Nailed wooden boxes and crates are discussed at some length. Quality and defects of lumber, fastenings, and methods of reenforcing are considered. The advantages of the "three-way" corner and diagonal braces in crate construction and of metal strapping for boxes are shown. Fiberboard and corrugated strawboard boxes receive a rather extended general treatment. Barrels, drums, and cans are discussed in some detail, and a number of tables showing recommended features of the design of wooden and metal barrels are included. A chapter on packing dangerous articles is of interest and value. The final chapter is devoted to brief discussion of various methods of testing shipping containers and container parts.

The range of the book is thus seen to be quite complete in its field. As in any new treatise on a new subject, however, some inaccuracies and an occasional lack of clarity are to be found. "Wirebound" boxes are dismissed with a statement that they are "properly designed to begin with" (page 58), a conception which is wide of the mark in many instances. A chart which is properly used as a guide in the design of factory-made "wirebound" boxes appears, from its position in the book on page 104, to apply to the selection of wires for the reënforcement of nailed wooden boxes—a very different matter. Prominence is also given to certain factors which are generally conceded to be comparatively unimportant, and questionable statements are made of the relative merits of different types of containers.

In spite of occasional inaccuracies, Mr. Huestis' little manual presents good general information on shipping containers. It should create a desire on the reader's part to make a thorough study of his packing problems, and it will suggest to him sources from which additional information may be obtained.

IRA B. LANPHIER

Potter's Compend of Materia Medica, Therapeutics, and Prescription Writing, with Special Reference to the Physiological Action of Drugs. BY A. D. BUSH. 262 pages. P. Blakiston's Son & Co., Philadelphia, 1926. Price, $2.00.

The brief résumé of materia medica is based on the Tenth Revision of the United States Pharmacopeia, and in this respect is quite up to date. All the drugs official in the Pharmacopeia are listed under various pharmaco therapeutic classifications, followed by a short discussion of the actions and uses. Unlike most "Materia Medicas," however, the chemical description is lacking. While many useless and discarded remedies are mentioned, there is a conspicuous absence of the newer worthwhile additions to materia medica, particularly those developed by the coöperation of American chemists.

For those who desire a "pocket dictionary" type of reference book on drugs, it may be found very serviceable, but for critical discussions the more comprehensive works on pharmacology should be consulted.

PAUL NICHOLAS LEECH

Metallurgy. BY E. L. RHEAD. New edition. 403 pages. Longmans, Green & Co., London, New York, 1924. Price, $2.50.

This very condensed textbook in general metallurgy has passed through several editions, the first of which appeared in 1895, with 282 pages. The great progress of thirty years is therefore compressed into 121 pages of new matter, and of course the treatment of this material is necessarily very sketchy.

Tribute has been paid to the changed viewpoint in the study of metallurgy by considerable additions to sections dealing with fundamental principles and theories. The importance of the study of structure of metals in relation to treatment and properties has been recognized and several pages of metallographic information are included, together with characteristic photomicrographs. The large increase in the knowledge of the properties of metals has been discussed and some of the more modern mechanical methods of testing have been included. The section dealing with ore-dressing practice is somewhat enlarged and brief mention is made of some of the improved methods, although buddles and Frue Vanners are still included as modern equipment.

The discussion of fuels is considerably improved and fairly adequate treatment of fuel testing is given. The discussion of coking is not at all up to date, however, and much of the description is practically obsolete. Gaseous fuels are treated briefly and with no very modern viewpoint.

In the metallurgy of the various metals there is a great deal described which is entirely obsolete from the standpoint of American practice. The improved methods which are given are seldom up to date. There is practically no attempt to discuss the application of physical chemistry to metallurgical processes, either in its general aspects or in its relation to specific operations.

The section on copper smelting has been given somewhat better revision than other portions of nonferrous metallurgy, and the large development of reverberatory copper smelting and of copper converting, especially the operation of basic-lined converters, is discussed, as well as some of the improvements in the refining of copper. Hydrometallurgy of copper is very poorly treated, and there is no discussion of modern processes and plants that are in actual operation, such as those at Chuiquicamata, Chile, and at the New Cornelia Copper Company. The treatment of lead smelting is particularly antiquated. The same is true of the metallurgy of silver, where much space is given to obsolete amalgamation and wet processes. The very extensive developments in the cyanide process for gold are only briefly mentioned and almost no attention is paid to the wonderful development of mechanical appliances for effective cyanide treatment.

Similar criticism might be made of the sections devoted to zinc and the minor metals, but enough has been given to indicate that in general the revision is inadequate to meet modern metallurgical conditions and that the book is hardly satisfactory as a textbook from a modern viewpoint. Incidentally, this fact emphasizes the lack of an up-to-date textbook on general metallurgy, treating in not too extended form the more important phases of modern metallurgical theory and practice and adapted especially to the use of students of chemistry and other courses not specializing in metallurgy.

D. F. MCFARLAND

Staub Explosionen. BY PAUL BEYERSDORFER. 125 pages. Theodore Steinkopff, Dresden and Leipzig, 1925. Price, 7 marks.

The author of this book has followed quite closely the general arrangement and treatment of the subject adopted by American and English authors of similar publications. He has had access, however, to sources of information not readily available to American and English writers, and in addition has drawn upon his own experiences and reported the results of his many valuable investigations of the phenomena of dust explosions.

Reference is first made to the frequency and variety of dust explosions and the conditions necessary to produce an explosion. These conditions are then discussed separately with special attention to the explosion limits and the various possible sources of ignition. The prevention of dust explosions by controlling the dust cloud, controlling the source of ignition, or controlling the presence of oxygen, is discussed quite fully, and the possibility of limiting the extent of an explosion by means of special construction or arrangement of the mill plant is also mentioned. Reference is made to the value of educating employees to the dangers of dust explosions. The discussion of the relation between pure dust explosions and mixed dust-gas explosions and the author's views on the theory of electrostatic ignitions are especially interesting. The reference to a dust explosion in a flour mill in Italy, December 14, 1785, which the author assumes, after examining notes of the Turin Academy of Sciences, to be the first dust explosion recognized as such, and the references to the explosions which have occurred in Germany are interesting additions to the information available on the history of dust explosions.

At the end of each chapter there are many references to the literature on particular phases of the subject, and important parts of reports not readily accessible are given in detail or quoted literally in the text. The book is a valuable addition to the literature on dust explosions.

HYLTON R. BROWN

Die Glasfabrikation. Band I. Compiled by ROBERT DRALLE. 766 pages. R. Oldenbourg Verlag, München and Berlin, 1926. Price, paper 60 marks; cloth, 64 marks.

The second edition of this book is a rearrangement and amplification of the first edition. It consists of nine sections by several authors, as follows: (1) Physical and Chemical Properties of Glass, including considerable theory (Keppeler); (2) Raw Materials (Keppeler and Muhlert); (3) "Processes" during Melting and Cooling (Keppeler); (4) and (5) Fuels (Keppeler and Wolff); (6) Pyrometry and Furnace Control (Maurach); (7) Refractories (Keppeler); (8) Furnaces (Keppeler and Wolff); (9) Machines (Wendler).

The text is well illustrated, numerous cross references are given, but references to publications are not always so numerous as could be desired.

The volume comprises a general summary of available information relating to the theory and practice of glass-making and will be helpful to those desiring such information. As a text for American glass-makers it will be somewhat disappointing, for several reasons: information regarding batch compositions is very meager; the data on fuels are based on foreign material and will serve only as a basis for comparison; pyrometric instruments described are of foreign design and yet in principles of construction and operation are very similar to American instruments; refractories, one of the most important problems in the glass industry, are not adequately treated (only

40 pages) and the treatment is apparently largely based on the opinion of the author.

Machines are discussed at greater length (226 pages) than any other subject and are quite comprehensively and thoroughly treated.

The volume is not indexed, but the author states that the second volume, which will be available this year, will contain a complete index. Furthermore, the second volume will, according to the author, contain considerations of specific phases of the industry, as distinguished from the generalities in the first volume.

A. N. Finn

Lehrbuch der Chemischen Technologie. By H. Ost. 15th edition. 828 pages. Max Jänecke, Leipzig, 1926. Price, paper, 15 rentenmarks; cloth, 16.80 rentenmarks.

A textbook of chemical technology that is the accepted leader in that field in Germany must have fundamental merit. The fifteenth edition of this book is but a slightly modified reprint of the fourteenth edition (1924). A few illustrations have been replaced by more modern ones, and a brief description has been added of some recent developments—e. g., synthetic acetic acid from calcium carbide (page 427), synthetic methanol (page 430), reduction of acetaldehyde to ethyl alcohol (page 610), etc.

Professor Ost possesses the faculty of selecting the truly salient points of his topics and of presenting them in an interesting manner. In the 828 pages of his book he has found space for some historical development of the important subjects; for statistical data indicating the relative commercial value of certain products or processes; for a theoretical discussion of the fundamentals involved where such are directly applicable; as well as for many plans, drawings, and illustrations. And all this without apparent crowding of the body of descriptive matter and general information pertinent to chemical technology.

The one criticism that might justly be made by the American reader is the failure in some instances adequately to present American practice. It is most unfortunate that there exists no comparable work of the same compass in America, although many books undoubtedly owe more than "inspiration" to H. Ost's "Lehrbuch der Chemischen Technologie."

Chemical Engineering Department
University of Cincinnati

La Fabrikation de l'Acide Sulfurique par le Procédé de Contact. By Henri Braidy. 302 pages. Editions of *L'Industrie Chimique.* H. Mownier, Paris, 1925. Price, 15 francs.

This book is an assembly of a series of articles that appeared from February, 1922, to November, 1924, in *L'Industrie Chimique,* under the same title. The author states in his preface that there is no practical treatise on this subject. Since the manuscript was not revised after the material had been prepared for its publication serially, there is perhaps an excuse for the failure to mention the new book on contact sulfuric acid, of the Lunge-Cumming series, by Miles, published in 1925. There is not, however, the same excuse for ignoring the existence of "American Sulfuric Acid Practice (1921)," by de Wolf and Larison, which contains five chapters devoted to the contact process; the British book "Technical Records of Explosives Supply, No. 5 (1921)," containing much practical detailed information on English practice; and the U. S. Bureau of Mines *Bulletin* **184** (1920), by Wells and Fogg, which contains authoritative information on the contact sulfuric acid process, especially from the standpoint of American practice.

The book is divided into three parts, the first of which contains four chapters on the theory of the contact process. The second part takes up the raw materials, the methods and equipment for roasting pyrites, the purification of the roasting gases, the absorption of sulfur trioxide, and the auxiliary equipment of a contact plant. The third part of the book consists of a summary of the physical and chemical properties of sulfur trioxide and of sulfuric acids of various strengths.

The printing is very good and the paper has a very good surface; but there seems to be little excuse for the several different shades of paper. The illustrations in general are good, although a few might have been clearer.

Among the several items in this book that may be commended are the information on the production and treatment of pyrites, the absorption of sulfur trioxide, the preparation and regeneration of platinum contact masses, the comparison of the different processes and the merits of each (although the writer seems to have had personal experience with only one), and the method for the comparison of the activities of different contact masses.

It is hoped that the author will make any subsequent edition of this book more cosmopolitan in character by revising and correcting the present work so as to contain current practice in the principal countries of the world outside of France. An index would also be very useful.

J. H. Perry

Die Beseitigung des überschussigen belebten Schlammes bei der Abwasserreinigung. By F. Sierp. 27 pages. 9 figures. Verlag Wasser, Berlin-Dahlem, 1925. Price, paper, 1.80 marks.

Of various methods used for biological purification of sewage, the activated sludge process is most efficient. It has the disadvantage of having a large excess of sludge containing 98 to 99 per cent moisture. The methods proposed for drying the sludge in Europe and America are not entirely satisfactory, though the product when dried makes a good fertilizer.

The adoption of the activated sludge process in Germany depends on a satisfactory method for the disposal of excess sludge. Experiments on a small scale show that the return of excess sludge to the fresh sewage at the entrance to Imhoff tanks gives a satisfactory solution to the problem. The moisture of the sludge is reduced 80 per cent. The amount of gas obtained is increased from 8 to 16 liters per capita per day. The amount obtained depends on the amount of organic matter present. A disadvantage is that the mixture of excess activated sludge with decomposed sludge in the Imhoff tanks reduces the amount of nitrogen in the dried sludge. The amount of sludge from the Imhoff tanks is increased from 0.2 to 0.36 liter per capita per day, and the sludge chamber must be increased.

The proposed method for sludge disposal is worth considering, as the value of the gas obtained and the easier method for sludge disposal may compensate for loss of nitrogen and the increased size of sludge digestion chambers required.

Edward Bartow

Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren (Introduction to the Detection, Separation, and Determination of the Monosaccharoses and Aldehyde Acids). By A. W. van der Haar. vii + 345 pages. 14 figures, 10 tables. 16.5 × 25 cm. Gebruder Borntraeger, Berlin, 1920.

In this monograph the author has assembled and tested experimentally the methods used in detecting, separating, and determining eight monosaccharoses and three aldehyde acids that occur frequently as products of the hydrolysis of plant gums and glucosides. The substances discussed are: *l*-arabinose, *d*-xylose, *l*-rhamnose, fucose, *d*-glucose, *d*-mannose, *d*-galactose, *d*-fructose, *d*-glucuronic acid, *d*-galacturonic acid, and aldehyde mucic acid.

The first eight chapters deal with the properties of the substances in question and the separation of mixtures. The ninth chapter describes the analysis of glucosides. The tenth chapter gives the complete separation and determination of the products of hydrolysis of apricot gum, chestnut saponin, and gum tragacanth. The monograph is very valuable to investigators in this special field.

Ernest Anderson

Die Holzverkohlung und Ihre Erzeugnisse. By Günther Bugge. 140 pages. 40 figures. 10.5 × 16 cm. Walter De Gruyter & Co., Berlin and Leipzig, 1925. Price, 1.25 rentenmarks.

This booklet on wood distillation and its products is one of the "Sammlung Göschen," a convenient pocket edition of tabloid texts on various branches of technology.

The subject is introduced with a brief review of the chemistry and physics of wood. Then follow condensed yet comprehensive chapters on the theory of wood carbonization; technology of commercial processes; properties, methods of analyzing, and uses of distillation products; and synthetic processes for the manufacture of acetic acid, acetone, methanol, and formaldehyde.

The subject matter is presented in a simple and direct style. The sentences are unusually short, making it easy to read. The booklet should commend itself to the busy chemical engineer or teacher of chemical engineering who wishes to obtain a scientific birdseye view of the subject while riding on street cars or in other odd moments.

A. C. Fieldner

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 Foreign and Domestic Commerce

British Rayon Industry Continues to Expand. Based on reports of C. G. Isaacs and K. A. H. Egerton. Reprint from *Commerce Reports* for March 22, 1926. 3 pp.

Opportunity for the Sale of Chemicals and Allied Products in France. *Circular* 132, Chemical Division. 3 pp. Issued May 15, 1926.

Bureau of Mines

Abrasive Materials in 1924. F. J. Katz. *Mineral Resources of the United States, 1924.* Part II, pp. 241–52.

Asbestos in 1924. B. H. Stoddard. *Mineral Resources of the United States, 1924.* Part II, pp. 305–9. Published April 2, 1926. Paper, 5 cents.

Barytes and Barium Products in 1924. C. E. Siebenthal and A. Stoll. *Mineral Resources of the United States, 1924.* Part II, pp. 311–19. Published April 3, 1926. Paper, 5 cents.

Consumption of Explosives in March, 1926. W. W. Adams. *Reports of Investigations* 2748. 8 pp. Issued April, 1926.

Flotation of Limestone from Siliceous Gangue. Oscar Lee. *Reports of Investigations* 2744. 3 pp. Issued April, 1926.

Gold, Silver, Copper, and Lead in Arizona in 1924. Mine Report. V. C. Heikes. *Mineral Resources of the United States, 1924.* Part I, pp. 165–97. Issued April 2, 1926. Paper, 10 cents.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1924. Mine Report. J. M. Hill. *Mineral Resources of the United States, 1924.* Part I, pp. 199–234. Published April 12, 1926. Price, 5 cents.

Natural Gas in 1924. G. B. Richardson and H. Backus. *Mineral Resources of the United States, 1924.* Part II, pp. 321–9. Published April 3, 1926.

Progress in Use of 1-Inch Steel in the Tri-State Lead and Zinc District. C. R. Forbes. *Circular* 6002. 2 pp.

Record of the Pittsburgh Testing Station Standard Dynamite. S. P. Howell. *Circular* 6004. 4 pp. Issued April, 1926.

Study of the Reactions in an Iron Blast Furnace. S. P. Kinney, P. H. Royster, and T. L. Joseph. *Reports of Investigations* 2747. 11 pp. Issued April, 1926.

Tests and Characteristics of Dust Respirators. S. H. Katz, G. W. Smith, and E. G. Meiter. *Reports of Investigations* 2745. 8 pp. Issued April, 1926.

Thirteenth Semi-Annual Motor Gasoline Survey. E. C. Lane, H. M. Thorne, and John Devine. *Reports of Investigations* 2740. 3 pp.

Bureau of Standards

A Study of Case-Lining Papers for the Purpose of Developing Standard Specifications. B. W. Scribner and F. T. Carson. *Technologic Paper* 312. 10 pp. Paper, 5 cents.

Nonflammable Liquids for Cryostats. C. W. Kanolt. *Scientific Paper* 520. 15 pp. Paper, 10 cents.

Bureau of the Census

Classification by Industries. *Census of Manufactures, 1925.* 69 pp.

Congress

Acids. Hearing, 69th Congress, 1st Session, on H. R. 8305, to safeguard distribution and sale of certain dangerous caustic or corrosive acids, alkalies, and other substances in interstate and foreign commerce. March 4, 1926. 43 pp. Paper, 5 cents.

Corn Sugar. Hearing, 69th Congress, 1st session, on H. R. 39, to amend section 8 of the 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, approved June 30, 1906, amended August 23, 1912, March 3, 1913, and July 24, 1919 (relative to the use of corn sugar for preserving or sweetening). March 2 and 3, 1926. 150 pp. Paper, 15 cents.

Poisons. Hearing 69th Congress, 1st session, on S. 2320, to safeguard the distribution and sale of certain dangerous caustic or corrosive acids, alkalies, and other substances in interstate and foreign commerce. March 5, 1926. 26 pp. Paper, 5 cents.

Same. Report to accompany S. 2320. Submitted by Mr. Watson, March 11, 1926. 2 pp. *S. Rept.* 357. Paper, 5 cents.

Potash. Mining of potash on public domain, report to accompany H. R. 5243, Submitted by Mr. Sinnott, March 11, 1926. *H. Rept.* 508. 2 pp. Paper, 5 cents.

Same. Report to accompany S. 1821 authorizing joint investigations by the Geological Survey and Bureau of Soils to determine the location and extent of potash deposits or occurrence in the United States and improved methods of recovering potash therefrom. Submitted by Mr. Mayfield, March 9, 1926. *S. Rept.* 318. 3 pp. Paper, 5 cents.

Raw Materials. Preliminary report on crude rubber, coffee, etc., pursuant to H. Res. 59. Submitted by Mr. Newton of Minnesota, March 13, 1926. *H. Rept.* 555. 23 pp. Paper, 5 cents.

Sulfur. Production of sulfur on the public domain, report to accompany S. 3186. Submitted by Mr. Oddie, March 20, 1926. *S. Rept.* 418. 1 p. Paper, 5 cents.

Tariff Commission. Hearings, 69th Congress, 1st session, pursuant to S. Res. 162, authorizing and directing investigation of manner in which flexible provisions of tariff act of 1922 have been or are being administered. March 23 and 24, 1926. Part I, 75 pp. Paper, 10 cents.

Department of Agriculture

Airplane Dusting in the Control of Malaria Mosquitoes. W. V. King and G. H. Bradley. *Department Circular* 367. 16 pp. Paper, 5 cents.

Calcium and Phosphorus Metabolism in Dairy Cows. E. D. Meigs, W. A. Turner, T. S. Harding, A. M. Hartman, and F. M. Grant. *Journal of Agricultural Research,* 32 (May 1, 1926), 833–60.

Carbon Disulfide as an Insecticide. W. E. Hinds. *Farmers' Bulletin* 799. 13 pp.

Washing and Sterilizing Farm Milk Utensils. R. J. Posson. *Farmers' Bulletin* 1473. 6 pp.

Department of Labor

Effects of Applied Research upon the Employment Opportunities of American Women. *Bulletin* 50, Women's Bureau. 54 pp. Paper, 10 cents.

Geological Survey

Guides to Ore in the Leadville District, Colorado. G. F. Loughlin. *Bulletin* 779. 37 pp. Paper, 35 cents.

Mineral Industry of Alaska in 1924 and Administrative Report. P. S. Smith. *Bulletin* 783-A. *Mineral Resources of Alaska, 1924-A.* 39 pp.

Surface Water Supply of the United States, 1923. Part II—South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. Grover, A. H. Horton, W. E. Hall, and W. R. King. *Water-Supply Paper* 562. 86 pp. Paper, 15 cents.

Public Health Service

The Influence of Vitamin Deficiencies on Susceptibility to Certain Poisons. M. I. Smith, W. T. McClosky, and E. G. Hendrick. *Public Health Reports,* 41 (April 23, 1926), 767–79.

New Books

All about Pollopas, A New Synthetic Colloid. Fritz Pollak and Kurt Ripper. 28 pp. Reprinted from *Chemiker-Zeitung,* August, 1924. Dr. Fritz Pollak, Mollardgasse No. 85a, Vienna.

Argiles Réfractaires. Matières Premières et leur Emploi dans l'Industrie des Produits Réfractaires. Carl Bischof. 4th edition revised by K. Jacob and E. Weber. Translated by A. Schubert. 416 pp. Illustrated. Dunod, Paris. Price, 6 francs 30.

Dyeing with Coal-Tar Dyestuffs. C. M. Whittaker. 2nd edition. Industrial Chemistry Series. 248 pp. Baillière, Tindall & Cox, London. Price, 10 s. 6 d. net.

Formulaire des Médicaments Nouveaux pour 1926. D. R. Weitz. 319 pp. 32nd edition. J.-B. Baillière et Fils, Paris.

Low Temperature Carbonisation: A Consideration of Processes for the Production of Free-Burning Smokeless Fuel Involving the Mechanical Compression or Briquetting of the Charge before or during Carbonisation. David Brownlie. 104 pp. South Wales Institute of Engineers, Cardiff, Wales.

Manuel du Teinturier. Gnehm. French edition, entirely rewritten by Raoul de Muralt. 400 pp. Illustrated. Dunod, Paris. Price, 6 francs 30.

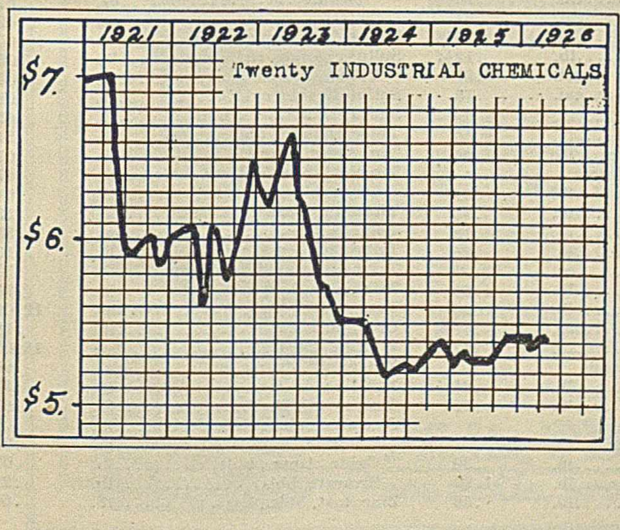
Physico-Chemical Methods. J. Reilly and T. S. Wheeler. 735 pp. Methuen & Co., Ltd., London. Price, 30 s.

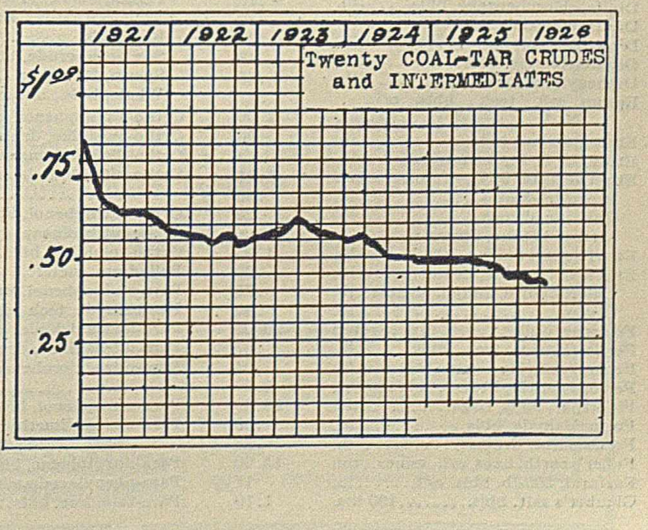
Study of the Nutritive Value of Gelatin. Thomas B. Downey. 24 pp. Reprinted from the *Journal of Metabolic Research,* Morristown, N. J.

MARKET REPORT—MAY, 1926

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON MAY 15

Acetanilide, tech., bbls.	lb.	.27
U. S. P., bbls.	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.13
Acetophenetidine, bbls.	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.24
56%, c/1. bbls.	100 lbs.	6.09
Glacial, c/1. bbls.	100 lbs.	11.47
Acetylsalicylic, bbls.	lb.	.65
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.57
Boric, bbls.	lb.	.09½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums.	lb.	.37
Chromotropic, bbls.	lb.	1.35
Cinnamic, 5-lb. cans.	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.45
Cresylic, pale, drums.	lb.	.59
Formic, 85%, cbys., N. Y.	lb.	.10
Gallic, U. S. P., bbls.	lb.	.65
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.85
H, bbls., wks.	lb.	.63
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.00
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.10
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.36
Lactic, 22%, dark, bbls.	lb.	.05½
66%, light, bbls., wks.	lb.	.26
Metanilic, bbls.	lb.	.60
Mixed, tanks, wks.	N unit	.06
	S unit	.01
Molybdic, 85%, kegs.	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Neville & Winther's, bbls.	lb.	.95
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.25
Oxalic, bbls., wks.	lb.	.10¾
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.07
Picramic, bbls.	lb.	.50
Picric, bbls. c/l.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.85
Salicylic, tech., bbls.	lb.	.27
Stearic, d. p., bbls. c/l.	lb.	.13¾
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.25
66°, tanks, wks.	ton	14.00
60°, tanks, wks.	ton	10.00
Oleum, 20%, tanks, wks.	ton	17.00
40%, tanks, wks.	ton	40.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.29½
Tobias, bbls.	lb.	.85
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.75
Amyl, 10%, Imp. drums.	gal.	1.20
Butyl, drums, wks.	lb.	.18½
Cologne Spirit, bbls.	gal.	4.85
Denatured, No. 5, Comp. denat., drs.	gal.	.32
No. 1, Spec. denat., drs.	gal.	.32
Isobutyl, ref., drums.	lb.	1.10
Isopropyl, ref., drums.	gal.	1.00
Propyl, ref., drums.	lb.	.75
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.15
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.50
Soda, bbls., wks.	100 lbs.	3.50
Aluminum, metal, N. Y.	lb.	.27
Aluminum chloride, anhyd., drums.	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.22
Aluminum sulfate, comm'l bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	2.00
Amidopyrine, boxes	lb.	4.60
Aminoazobenzene, 110-lb. kgs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.13
Ammonia water, 26°, drums, wks.	lb.	.03
Ammonium acetate, kegs.	lb.	.43
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes.	lb.	.53
Carbonate, tech., casks.	lb.	.08¾
Chloride, gray, bbls.	lb.	.06½
Lump, casks	lb.	.11½
White, bbls.	lb.	.05½
Iodide, 25-lb. jars.	lb.	5.20
Lactate, bbls.	lb.	.15
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs.	lb.	.35
Persulfate, cases.	lb.	.25
Phosphate, dibasic, tech., bbls.	lb.	.18
Tribasic, bbls.	lb.	.04
Sulfate, bulk, wks.	100 lbs.	2.70
Thiocyanate, tech., kegs.	lb.	.40
Amyl acetate, tech., drums.	lb.	1.75
Aniline oil, drums.	lb.	.16
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.95
Antimony, metal.	lb.	.11¾
Antimony chloride, anhyd., drums.	lb.	.16
Oxide, bbls.	lb.	.19
Salt, Dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.15
Vermilion, bbls.	lb.	.48
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.06½
Arsenic, metal, kegs.	lb.	.45
Red, kegs, cases.	lb.	.12
White, cases, bbls.	lb.	.03½
Asbestine, bulk, c/l.	ton	16.00
Barium carbonate, bbls., bags, wks.	ton	51.00
Chloride, bbls., bags, wks.	ton	63.00
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04½
Nitrate, casks.	lb.	.07½
Barium sulfocyanide, 400-lb. bbls.	lb.	.30
Barytes, floated, 350-lb. bbls., wks.	ton	26.00
Benzaldehyde, tech., drums.	lb.	.65
F. F. C., cbys.	lb.	2.00
U. S. P., cbys.	lb.	1.25
Benzene, pure, tanks, mills.	gal.	.25
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, carboys.	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums.	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases.	lb.	3.35
Bismuth nitrate, 25-lb. jars.	lb.	2.05
Oxychloride, boxes.	lb.	3.50
Subnitrate, U. S. P., 25-lb. jars.	lb.	2.85
Blanc fixe, dry, bbls.	ton	75.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs.	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.05

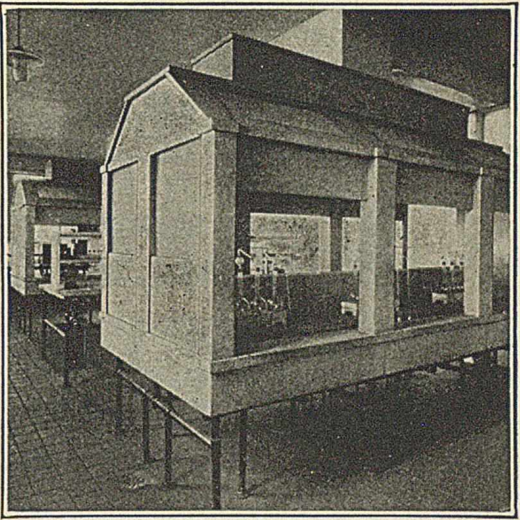




Bordeaux mixture, bbls.	lb.	.11½
British gum, com., c/l.	100 lbs.	4.27
Bromine, bot.	lb.	.47
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.57
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.40
Calcium acetate, bags	100 lbs.	3.25
Arsenate, bbls.	lb.	.06
Carbide, drums	lb.	.04¼
Chloride, drums, wks.	100 lbs.	21.00
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	52.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.10
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.84
Jap., cases	lb.	.79
Crude, cases	lb.	.54
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.15
Carbon bisulfide, drums	lb.	.06
Carbon black, cases	lb.	.13
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06½
Casein, tech., bbls.	lb.	.13
Cellulose acetate, kegs	lb.	1.45
Cerium oxalate, kegs	lb.	.35
Chalk, pptd., casks	lb.	.04¼
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bgs.	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine T., 5-lb. bot.	lb.	1.35
Chlorcosane, 5-lb. bot.	lb.	.55
Chlorine, liq. c/l., cyl.	lb.	.05½
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.28
Chlorohydrin, anhyd., drums	lb.	.75
Chromium acetate, 20° sol., bbls.	lb.	.05½
Sulfate, bbls.	lb.	.07
Cinchonidine sulfate, 100 oz.	oz.	.35
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.10
Cod-liver oil, bbls.	bbl.	27.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	lb.	.13⅞
Copper carbonate, bbls.	lb.	.16¾
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, c/l., bbls.	100 lb.	4.65
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.21
Cyanamide, bulk, N. Y.	Ammon. unit	1.90
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.25
Dichlorobenzene, drums	lb.	.06
Diethylaniline, drums	lb.	.55
Diethylphthalate, drums	lb.	.35
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.32
Diphenylamine, bbls.	lb.	.48
Diphenylguanidine, bbls.	lb.	.85
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	2.00
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.14
Ethyl acetate, 99%, drums	gal.	1.05
Bromide, drums	lb.	.50
Chloride, drums	lb.	.26
Methyl ketone, drums	lb.	Nom.
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums	lb.	.75
Glycol	lb.	.30
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07½
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.09
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. bbls. c/1	lb.	.17½
Glauber's salt, bbls.	100 lbs.	1.10

Glucose, 70°, bags, dry	100 lbs.	3.24
Glycerol, C. P., drums	lb.	.24½
G salt, bbls.	lb.	.50
Hexamethylenetetramine, U. S. P. drums	lb.	.60
Hydrogen peroxide, 25 vol., bbls.	lb.	.07
Hydroquinone, kegs	lb.	1.40
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	260.00
Kieselguhr, bags	ton	60.00
Lead, metal	lb.	.07¾
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.10½
Red, bbls.	lb.	.11
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.10¾
Sulfate, bbls.	lb.	.10
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.45
Lithopone, bbls.	lb.	.06⅛
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	34.00
Fluosilicate, cryst., bbls.	lb.	.11
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.31
Mercury, flasks, 75 lbs.	flask	92.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.85
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, 97%, tanks	gal.	.57
Methyl acetone, drums	gal.	.70
Salicylate, cases	lb.	.37
Methyl chloride, cylinders	lb.	.60
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.05¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.07½
Double, bbls.	lb.	.08
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.09½
Oil, castor, No. 1	lb.	.13½
China wood, bbls.	lb.	.11½
Coconut, Ceylon, tanks	lb.	.10
Cod, N. F., tanks	gal.	.57
Corn, crude, tanks, mills	lb.	.11¼
Cottonseed, crude, tanks	lb.	.12
Lard, edible, bbls.	lb.	.17¼
Linseed, bbls.	lb.	.108
Menhaden, crude, tanks	gal.	Nom.
Neat's-foot, pure, bbls.	lb.	.16¼
Oleo, No. 1, bbls.	lb.	.13
Olive oil, denat., bbls.	gal.	1.15
Foots, bbls.	lb.	.08½
Palm, Lagos, bbls.	lb.	.08½
Peanut, crude, tanks	lb.	.10
Perilla, bbls.	lb.	.13½
Rapeseed, bbls., English	gal.	.94
Red, bbls.	lb.	.10½
Soy bean, crude, bbls.	lb.	.12¼
Sperm, 38°, bbls.	gal.	.87
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.13
Ortho-toluidine, bbls.	lb.	.25
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.10
Paraldehyde, tech., drums	lb.	.30
Para-formaldehyde, cases	lb.	.42½
Para-nitroaniline, drums	lb.	.47
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.30
Para-phenylenediamine, bbls.	lb.	1.20
Para-toluidine, bbls.	lb.	.50

Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums	lb.	.22
Phenolphthalein, drums	lb.	1.30
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.68
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	105.00
Potash, caustic, drums	lb.	.07½
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.85
Carbonate, 80–85%, calc., casks	lb.	.05½
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.52
Meta-bisulfite, bbls.	lb.	.10
Permanganate, drums	lb.	.14½
Prussiate, red, casks	lb.	.37
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums	gal.	4.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.35
Rochelle salt, bbls., U. S. P.	lb.	.19
R salt, bbls.	lb.	.48
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06¼
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.44¾
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.10
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.48
Carbonate, sal soda, bbls.	100 lbs.	1.30
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.09
Hyposulfite, reg., crys., bbls.	lb.	.02½
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.63
Nitrite, bbls.	lb.	.08⅞
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod.	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.10
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04½
Stannate, drums	lb.	.42½
Sulfate, anhyd., bbls.	lb.	.02
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.04
Sulfocyanide, bbls.	lb.	.40
Tungstate, kegs	lb.	.85
Strontium carbonate, bbls.	lb.	.07
Nitrate, bbls.	lb.	.07½
Strychnine alkaloid, 100 oz., powd.	oz.	.61
Sulfate, powder	oz.	.42
Sulfur, bulk, mines, wks.	ton	19.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, cyl.	lb.	.08
Sulfuryl chloride, drums	lb.	.65
Thiocarbanilid, bbls.	lb.	.24
Tin, Amer., stand.	lb.	.61⅜
Tin bichloride, 50% sol., bbls.	lb.	.17¾
Oxide, bbls.	lb.	.64
Titanium oxide, bbls., wks.	lb.	.13
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.70
Triphenyl phosphate, bbls.	lb.	.75
Tungsten	WO_3 unit	12.00
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.60
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	lb.	.07¼
Zinc ammonium chloride, bbls.	lb.	.06¼
Chloride, granulated, drums	lb.	.06¾
Oxide, Amer., bbls.	lb.	.07⅜
Stearate, bbls.	lb.	.21½
Zinc dust, bbls., kegs, c/l	lb.	.09

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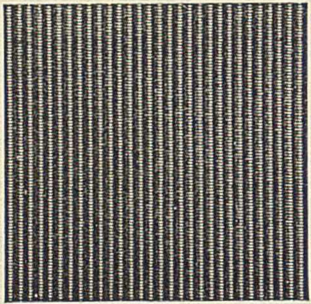

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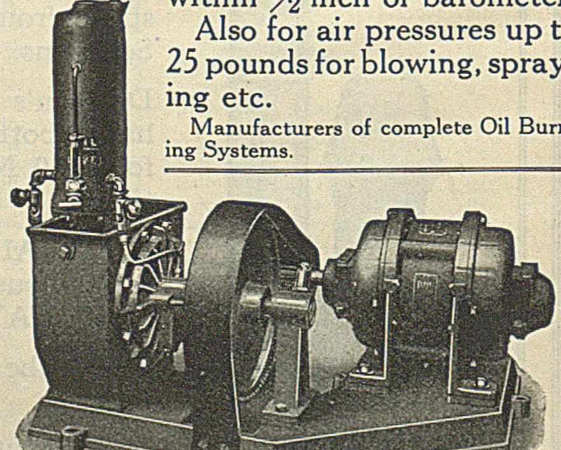

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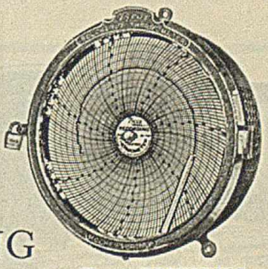

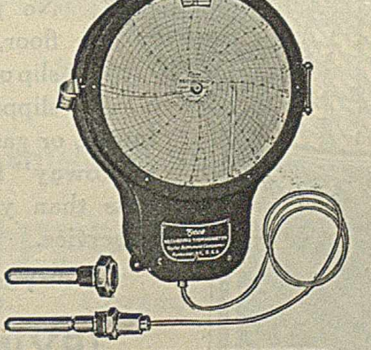

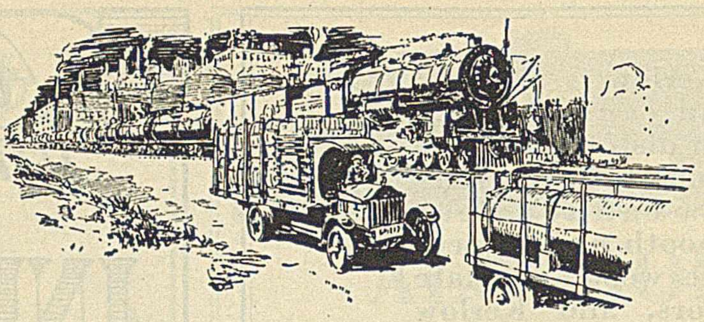

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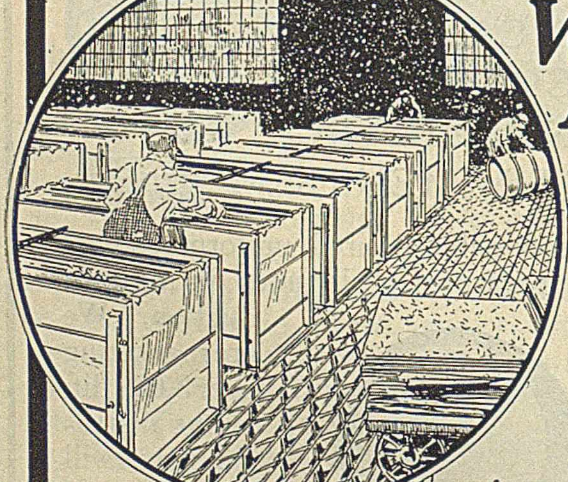

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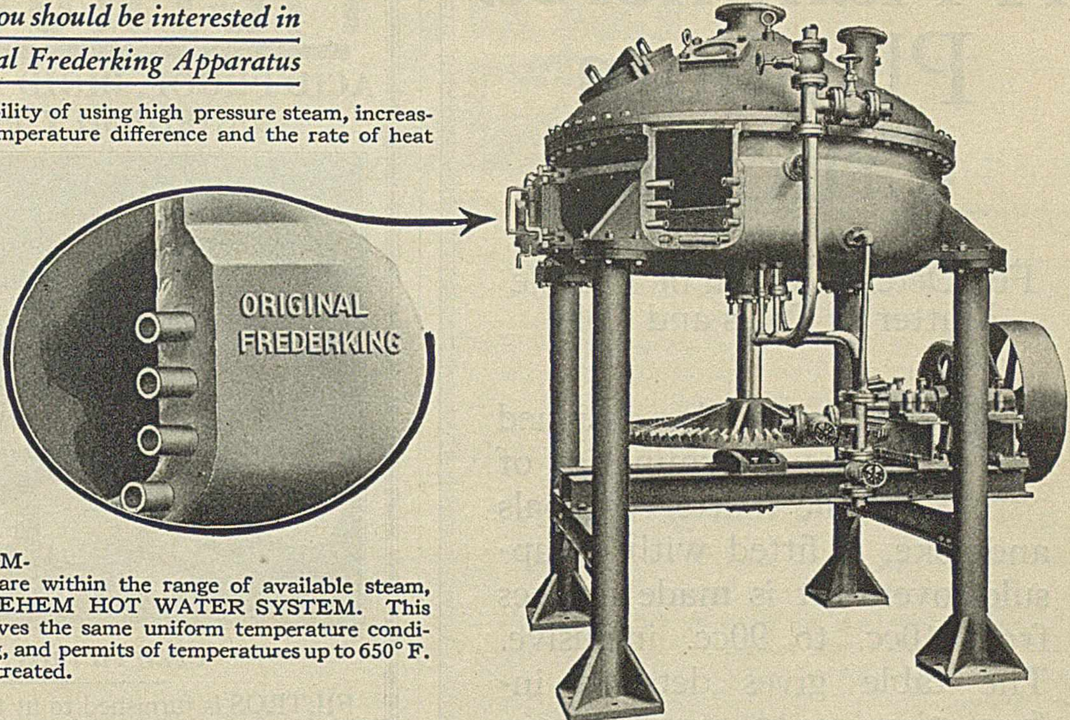

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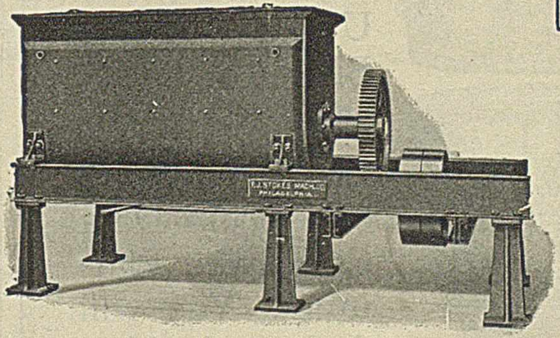

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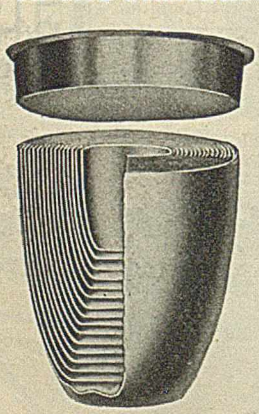

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8	10	2.2	50	55	4.4
10	12	2.5	60	67	4.7
15	17	3.0	70	71	5.0
20	23	3.3	80	74	5.3
25	28	3.5	90	76	5.4
30	34	4.0	100	87	5.6
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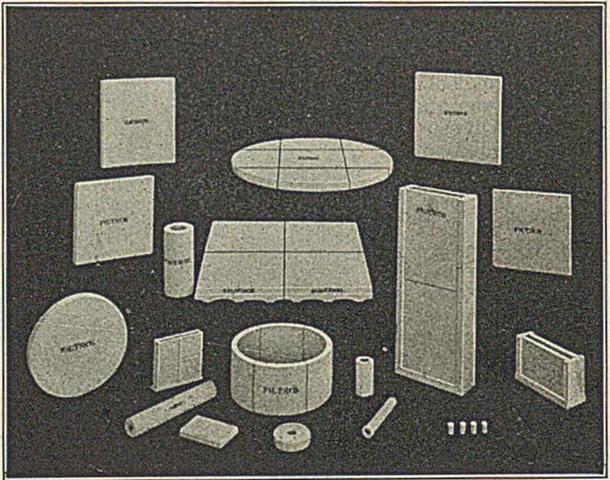

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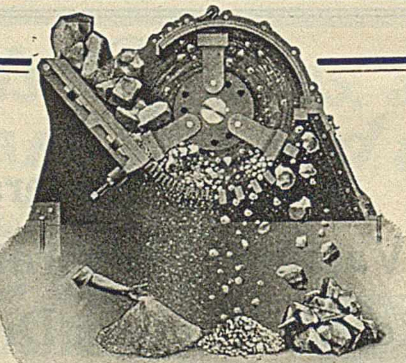

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