INDUSTRIAL & ENGINEERING CHEMISTRY

Published by the American Chemical Society

EDITORIAL OFFICE:
Room 706, Mills Building
Washington, D. C.
TELEPHONE: Main 848
CABLE ADDRESS: Jiechem (Washington)

NEWS EDITION:
Managing Editor: Robert P. Fischelis

ADVERTISING DEPARTMENT:
19 East 24th St.
New York City
TELEPHONE: Madison Square 5940

Volume 17 MAY 1, 1925 No. 5

CONTENTS

Subscription to non-members, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage $1.00 except to countries accepting mail at American domestic rates and to Canada. Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Secretary, 1709 G St., N. W., Washington, D. C. Member of Audit Bureau of Circulations.

EDITORIALS

Unity in Chemistry

WHEN the New Jersey Chemical Society, after months of investigation and discussion, decided by letter ballot to become the Northern New Jersey Section of the AMERICAN CHEMICAL SOCIETY, a progressive step was taken. Several of our strongest sections began as local chemical societies, but if our information is correct, this is the first state society to cast its lot with the national organization and become one of its local sections. This has been done without loss of identity and, we believe, without the sacrifice of any advantages which it possessed as a state society. It has become a part of a great national organization which will assist it in its local work and which it, in turn, can help in matters of national importance.

Today we have several examples of ways in which specialties in chemistry may be developed. In the judgment of certain groups, their objects can best be accomplished by creating separate societies with all that involves in the way of financial support, publications, meetings, the time required of officers, and the like. No one would belittle what has been accomplished, for example, by the American Electrochemical Society, the American Ceramic Society, the American Institute of Chemical Engineers, the American Leather Chemists Association, and other special groups.

An equal or perhaps larger number of examples may be drawn from those who find in the divisions of the AMERICAN CHEMICAL SOCIETY opportunities to advance their specialty in a way that could not be done in a separate organization. We doubt whether the present excellent conditions in the field of rubber chemistry could have been brought about in any other way. Those who attended the first meeting of the Rubber Section in 1910, when a handful of cautious chemists came together, each instructed by his employer to keep quiet and listen to the other fellow, would not have believed that it would be possible within fifteen years to hold such a crowded meeting as that at Baltimore. The fruitful discussion of but three of the papers on the program occupied a full half day, and interest was maintained at high pitch throughout the meeting. Members of this division attend the sessions of such general divisions as Organic and Physical and Inorganic Chemistry and attract to their discussions the leaders in these other fields. They become personally acquainted with many men who work on problems more or less closely related to their own.

The Petroleum Division and the Sections of Gas and Fuel and of Paint and Varnish Chemistry are newer groups to attain marked success and to attract large numbers to their earnest discussions.

A study of the experience of the eighteen divisions and sections of the SOCIETY would indicate that, whatever the work in American chemistry, it can be accomplished to the best advantage through the AMERICAN CHEMICAL SOCIETY, and that the chemists of America should carefully preserve for themselves the advantages which unquestionably come from unity within a profession, a craft, an occupation, or a business. This point is continually stressed by the prominent chemists who visit us from all over the world, and in *Chemistry and Industry* for March 13 we find on page 271:

> Indeed the outstanding impression is inevitably the extent to which all the American chemists know one another personally, the enthusiastic manner in which they work together in every thing likely to advance the cause of chemistry. The fact that the very active American Chemical Society represents them all and that they therefore all speak with one voice counts for much, both in regard to economy and efficiency in organization, and influence with the public. The specialist societies are few and their very useful work is done in coöperation rather than in competition with the A. C. S. The American chemist is entirely convinced of the value and necessity of getting together.

Unity of American chemists has contributed much to the success of chemistry in America. From a further consolidation of American chemists strength and inspiration for new achievements will be derived.

The Meeting at Baltimore

ANY doubt as to the success of the Baltimore meeting can be dispelled by reference to the extensive and creditable notice given the meeting in the daily press. Even if this were our only measure we could say that the Baltimore meeting has made the high record. But it is not our only way of evaluating the Sixty-ninth Meeting of the AMERICAN CHEMICAL SOCIETY.

The interest in all sections and divisions was indeed encouraging. Not only were the rooms filled to overflowing, but several groups continued their discussion at dinner and far into the evening, and unquestionably there were others who would have sacrificed the excursions to gain more time for their papers and the discussion. Several industries sent representatives to hear special papers and participate in their discussion, and whereas not long ago division chairmen and secretaries were planning for more leisure, there now has developed a desire for more time for work.

The progress of our science in America is to be measured to some extent by the programs which are compiled each six months in addition to the many papers presented before local sections. The character of our programs and the number of people attracted by them have made the semiannual meetings of the AMERICAN CHEMICAL SOCIETY events of national importance.

"And Some Fell into Good Ground"

VARIATION of interest in the purposes of the Prize Essay Contest is to be expected, but we are nevertheless impressed by the extremes.

In the contest just closed, the island possessions of the United States evidenced a keen interest on the part of teacher as well as of pupil. Hawaii, the Philippine Islands, and Porto Rico submitted more than sixty essays, some of which arrived by air mail to be sure that the time limits were respected, and some came approved not only by teachers of English and chemistry, but by the principal of the school and the superintendent of the province as well. Many of the contestants use English in the classroom only and their efforts are therefore more highly commendable.

Individuals in certain localities have been of very great assistance. In Anderson, Indiana, resides Hugh Hill, a business man who has personally offered awards to the school children of the public and parochial schools of his city. The

rules governing the awards were the same as those of our contest, and fifty dollars provided twenty for the first, ten for the second, and five each for the third, fourth, fifth, and sixth best essays. Mr. Hill personally presented the prizes to the winners and derived a deal of pleasure and satisfaction from the experience. If prominent citizens elsewhere could be induced to offer similar local prizes, our work would be greatly expedited and more progress made in better acquainting an increasing number of people with what science means to them.

Our picture is one of contrasts from high lights to deep shadows and reminds us of the parable of the sower—"But others fell into good ground, and brought forth fruit, some an hundredfold, some sixtyfold, some thirtyfold."

What Is Muscle Shoals?

WE have not forgotten that the President has appointed a commission to ascertain the facts regarding Muscle Shoals and to recommend to him what disposition should be made of the Government's investment in that geographical quarter known as Muscle Shoals, Alabama. However, we hold that if the American people could be brought to understand what it is at Muscle Shoals that has become a political football, the task of the commission would be easier and the attention of many citizens could be diverted into more profitable channels.

We have always contended that Muscle Shoals is primarily a question of power development and power utilization without reference to special industries. It is regrettable that this power development is usually described in terms of Niagara Falls and the Wilson Dam as the Niagara of the South. Statistics indicate that a dozen Muscle Shoals, as it will be when the Wilson Dam is completed, would be required to equal the present developed horsepower at Niagara Falls. The records of flow in the Tennessee River show that on the average not more than one hundred thousand and more frequently ninety thousand primary horsepower is available with the ninety-five foot head of the Wilson Dam. Notwithstanding this, eight units are now being installed or are on order, totaling two hundred and sixty thousand horsepower, and six hundred thousand is the figure most frequently occurring in the press. If six hundred thousand is the figure to be taken, it is interesting to note that in 1904 there was only enough water in the river for 9 per cent of the time and that it occurred in such periods as four days, eleven days, sixteen days, and three days, with considerable intervals between. Similar figures can be given for many other years. Engineers estimate that if anything like the power claimed for the Shoals is to be developed, further expenditures in dams and reservoirs totaling more than one hundred million dollars will have to be made. Muscle Shoals therefore as a power site is important, but not of the transcending importance some would have the public believe. It has even been suggested that the most useful role for the six hundred thousand horsepower figure is as a divisor for the large sum expended on the development, and even this, when proper interest charges are added, gives a high development cost per horsepower.

There are two villages at Muscle Shoals, the larger at the site of Plant No. 2, and although both represent considerable investment, they are insignificant in the present picture. The plant numbered one was the experimental synthetic ammonia plant which never operated, and could not now be used for the modern synthetic ammonia process. The redesign and rebuilding might easily be less economical than the construction of a new plant. The plant numbered two is in good condition and portions operated indicate that it will produce at rated capacity, but it is based on the cyanamide process which, so far as the fixation of atmospheric nitrogen as synthetic ammonia is concerned, has been made commercially obsolete by the developments of the past few years at home and abroad. Many people believe that it might be held in readiness for a few years until our synthetic ammonia industry is further developed, but its operation for the production of fertilizers would require a frank subsidy if it is to compete with more modern processes. Data can be presented to show that the utilization of Muscle Shoals power for phosphorus might be quite as important as for fixed nitrogen, while the consensus of opinion among chemical engineers is that at the present time cheap hydrogen is far more important than hydroelectric power at any figure which the industry could pay in competition with other power-consuming interests.

As we have indicated previously, real estate operations have become a large factor in the Muscle Shoals situation. Electrochemical industries require more power per employee than the textile, boot and shoe, automobile, and many other manufacturing industries. Therefore cities such as Niagara Falls, which are dependent upon electrochemical industries, show at best a slow growth. Notoden and Rjukan in Norway, where three hundred thousand horsepower is employed, have a combined population of less than twenty thousand. So the hope of large increase in real estate values because of the location of electrochemical plants is not warranted.

It seems to us, therefore, that Muscle Shoals is simply a fair-sized water-power development in which the Government has a large sum invested and that the trend of scientific work clearly indicates the folly of committing any large proportion of its power for an indefinite period to any particular industry. It is to be hoped that the Muscle Shoals Commission can find a way to disregard the political influences that will be brought to bear, that it will not allow the agricultural organizations who are farming the farmer to persuade it against its own good judgment, and that it will take pains to have the public understand just what Muscle Shoals is. It is wonderful enough without being misrepresented, overrated, or used as a catchword. We repeat that when the people realize with what they are dealing, the solution of the problem becomes simple.

Steam Generation

CHEMISTS, in common with other industrialists, are vitally concerned with steam generation and the provision of apparatus more efficient in the utilization of heat.

Chemistry and Industry, the *Journal of the Society of Chemical Industry*, in the issues of February 20 and 27, publishes two papers read on this subject at a joint meeting of the Institution of Chemical Engineers and the chemical engineering group of the Society of Chemical Industry on February 11. The first, by Brunler, presents the results of many years' work by his father and himself in an effort to devise an internal combustion boiler in which a flame would burn in the water. This procedure, regarded as practically impossible by many prominent engineers and once made the subject of an article headed, "How a rich man spends his money for an idiotic idea," appears to have been accomplished not only on a laboratory but on a fairly large scale. Many data have been obtained, and the interesting fact noted that for weeks at a time an efficiency exceeding one hundred per cent of that calculated from calorimetric measurements and chemical analysis has been secured from a given fuel. The possibility of improving upon the efficiency of evaporators has also been investigated by Brunler, who has concentrated more than twenty different chemical solutions with the submerged flame without encountering difficulties.

The second is by Brownlie and discusses the apparatus known as the Benson generator used in the apparently successful attempt to generate steam under critical conditions and its utilization at very high pressures and temperatures of superheat. By this method high efficiencies have been obtained and data are presented to show that adoption of such a method would not only be economical but would materially conserve our fuel resources.

These two papers justify Brownlie's opening statement that it is "no exaggeration to state that during the past ten years there has been more progress made in the technic of steam generation and utilization for the production of power than in all the previous period right back to the days of Hero of Alexandria in 150 B. C." The perfection of the submerged flame boiler and the conversion of water on a practical scale into a dry, saturated steam under the actual critical conditions, rank high in the list of these achievements.

The Decision of the Court

EVERYONE interested in the advance of chemistry in America should read the decision handed down by the United States Circuit Court of Appeals for the Third District in the case United States of America *vs.* the Chemical Foundation, Inc. Reference was made to this decision in the April number of THIS JOURNAL, but at that time the complete decision was not at hand, and its far-reaching importance was not emphasized. The printed document of fifty-nine pages might be called a zero milestone in American chemistry, for from this opinion we are able to take new measurements of the importance of industrial chemistry. We regret that we do not have the space to print the opinion in full, but we will give a quotation or two to indicate the trend of this remarkable decision.

In the paragraphs on the relation of organic chemistry to all phases of modern life, we find: "Thus it will be seen that the chemical industry is probably the most complex industry calling for unusual qualities in the men who direct and partake of its activities." Again, "It is now realized that the striking power of the nation is in proportion to its supply of coke by-products." And again, "It is fair to assume that even if no further advances are made in chemistry the next war will begin where the last left off."

Those of us who have been interested in spreading the truth regarding chemical warfare and the relation of the dye industry to national defense read with interest, "Germany demonstrated that munition plants based on organic chemical industry can be effectively created and maintained in no other way. Having no such industry when it entered the war, the United States built the Edgewood Arsenal at a cost of $35,000,000. Though a colossal plant, it is valueless unless vast sums are annually spent not in maintaining the structure, but in producing organic chemicals and keeping chemists, workmen, foremen, and technicians constantly trained that they may know how to carry on the manufacture of munitions when the demands of war come. It was therefore evident to the officials of the National Government that a dye industry is a national bulwark in chemical warfare and that in the United States it had become an imperious necessity. The chemical industry is also one of great importance in times of peace. It is a key industry."

With this true statement a matter of record as the opinion of an unbiased court of high authority, what individual, what member of Congress, or what administration would have the temerity to sanction any step which might injure an industry that has become "an imperious necessity"?

With reference to the action of President Wilson in authorizing private sale, the court, referring to the law under which he acted, finds, "This expression of the section contemplates something more than money because by its terms it calls upon the President to regard the public interest in departing from the statute's general rule of public sale. Public interest is not limited to dollars." So much has been said regarding the circumstances surrounding the actual sale that we shall do well to hear the court on this point. Referring to Mr. Garvan as an officer of the Chemical Foundation and Alien Property Custodian, the court points out that "When later he became Alien Property Custodian and also President of the Chemical Foundation, there was present the element of two official positions, and in these positions it is true he carried out the contract previously made, but there was lacking the element of a direct or indirect interest on his part in the pecuniary profits or contracts of the Foundation, for he agreed to serve as its president without compensation and he has kept his agreement. He has not received from it any money for any purpose, even for his expenses."

The court then proceeds to discuss the relation of other gentlemen identified with the Foundation and finds "that at no time did any one of these gentlemen perform acts within the offense defined by the law. It follows that the transaction was not consummated in violation of this criminal statute and therefore it is not invalid on this ground."

Then follows a discussion of the value of the patents, from which these clauses will serve to illustrate its tenor:

> Even though he had powers of a trustee, the Custodian, "in addition," was authorized by the statute to do what he did. * * * We are not concerned in this case with their value to the Germans. * * * The value of the patents to the United States was their value in the American market. * * * Again, the thing—mechanism, product, or process—may be "useful" in the sense of invention, but not "usable" in a practical sense, and if not usable it therefore may not be valuable. * * * The disposition of German applicants for patents being to make meager and sometimes insufficient disclosures * * * because their disclosures are wholly inadequate to workers in the chemical art in America, these patents are without substantial affirmative value to American citizens. * * * By authority of the act, which means by authority of Congress, the patents were sold stripped of their characteristic of monopolies and sold on conditions that the United States should have free licenses under all of them and that its citizens should have nonexclusive licenses on equal terms. These, briefly, were the conditions. What did the United States receive? It received the $250,000; it also received licenses under the patents; and it obtained the creation of an industry which stands equipped, manned, and maintained in full operation ready to be converted at once into a line of national defense in the event of war. There is no evidence of the value of the licenses which the Government received, nor, very naturally, is there evidence of the value of the national defense in chemical warfare placed in the Government's hands. Yet, we surmise, these things have values, and, taken together, we believe they are greater than the value of the patents at the time of their sale. We are of opinion that the price paid in the circumstances was not inadequate.

And then, after reviewing the fact that in the first trial the judge admitted all evidence, so that without regard to the usual rules of procedure everything might be offered which would tend to prove or disprove every issue, and noting how the Government during the trial shifted its charge of conspiracy from the persons named in the plea to the officers of the Government, the court finds none of the charges sustained and affirms the decree of the lower court.

Notwithstanding unqualified defeat in both the original trial and the appeal of the case, the Government has appealed and in due course arguments will be presented to the Supreme Court. We may look with confidence and without fear to the future. Whatever the outcome, the decision of the Circuit Court of Appeals remains an invaluable statement from a source of high authority. Would that all officials, executives, and others in authority might catch an equally clear vision of what chemistry means to America!

Industrial Applications of Invertase[1]

By H. S. Paine, C. F. Walton, Jr., and M. S. Badollet

CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, WASHINGTON, D. C.

SUCROSE has long been the world's foremost commercial sugar. Aside from its availability in large quantities and the comparative cheapness with which it can be produced, sucrose has certain advantages over some other sugars because of its high degree of sweetness, relatively low degree of hygroscopicity, crystal form, solubility, and facility of crystallization. To these favorable properties should be added the fact that sucrose may be readily hydrolyzed with formation of invert sugar.

The ability to undergo hydrolysis with transformation into invert sugar is one of the important properties of sucrose and plays an essential part in many commercial methods of utilization of this sugar. The enzyme invertase is more suitable than an acid as a catalyst in the case of saccharine products which exhibit a pronounced buffer effect toward added acid and which possess a flavor adversely influenced by the quantity of acid required. The use of invertase as a catalyst for sucrose inversion has been successfully industrialized in the case of a number of commercial products in which sucrose is the principal saccharine constituent. Suitable procedures for invertase inversion of sucrose in golden sirup, cane and sorghum sirups, maple sirup and maple cream, and fondant types of confectionery have been devised.

Considering the large number of food products in which sucrose is an important constituent and the varying physical character of these products, the advantages of inversion of sucrose may be summarized as follows: (1) increase in solubility of total sugars due to the presence of sucrose and invert sugar in mixture, thus making it possible to increase the density of sirups containing sucrose as the essential constituent; (2) hygroscopic character due to the presence of levulose, thus retarding the drying of such products as fondant confections and icings; (3) influence of invert sugar in controlling crystallization of sucrose so as to cause the formation of small crystals, thereby improving the consistency of fondants, icings, etc.; (4) modification of flavor. These advantages are of varying degrees of importance according to the product in which sucrose is present—for instance, whether in a sirup or in fondant confections containing a large proportion of the sucrose as minute crystals.

Certain disadvantages also result from the inversion of sucrose. Among these the following are of primary importance: (1) readiness with which levulose is decomposed at elevated temperatures; (2) tendency of levulose to undergo destructive reactions at even moderate acidity or alkalinity, thus tending more narrowly to limit the permissible pH range of the product; (3) since invert sugar has practically the same degree of sweetness as sucrose, the tendency of the decomposition of levulose to decrease the sweetness of the product; (4) crystallization of dextrose in case too great a proportion of sucrose is inverted in sirups of high density. These disadvantages also vary greatly according to the nature of the product involved, in many cases being of practically no importance. On the whole, especially with proper control, the advantages of inversion are distinctly greater than the disadvantages, and the ready convertibility of sucrose into invert sugar constitutes one of the important properties which have contributed to the commercial preeminence of sucrose.

Acids and acid salts have customarily been used as inverting agents in industrial practice. These reagents are eminently satisfactory in the case of grades of sugar with relatively small ash content and buffer effect. In the case of sucrose-containing sirups, however, which exhibit a decided buffer effect, results are less satisfactory, owing to the resulting increase in the quantity of acid required and the unfavorable influence of this increased quantity of acid on the flavor and color of the product. Even with close control of time, acidity, and temperature, such as is provided by more recent procedures for acid inversion, there may be a detrimental effect on flavor and color which varies in importance with the nature of the product. The result has been that either more expensive indirect methods have been used or inversion has not been commercially feasible in the case of certain products.

Conditions Requisite for Industrial Use of Invertase

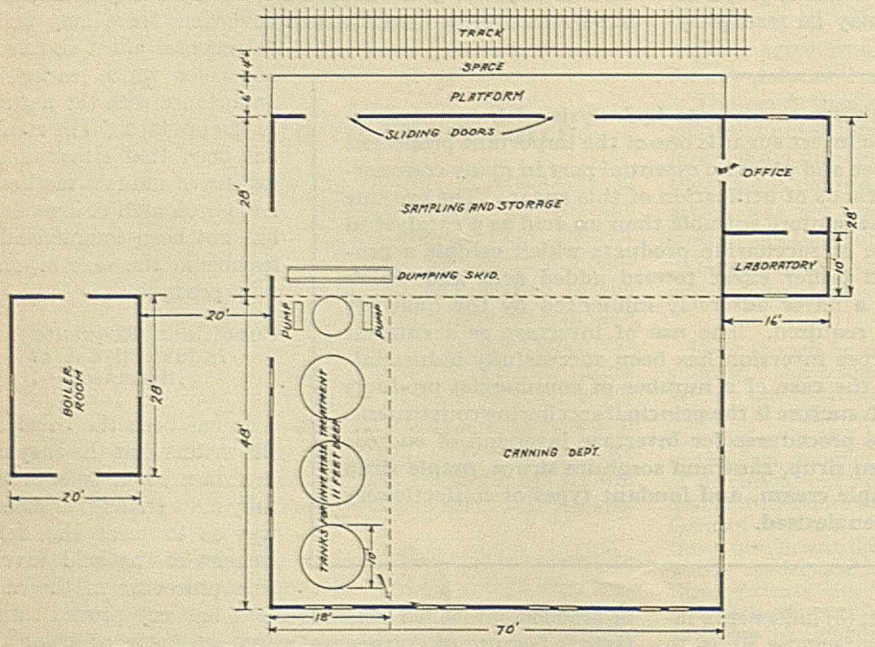
It has been the belief of the writers that the enzyme invertase could be successfully industrialized in such a way as to meet the deficiencies of the acid inversion procedure in the case of products for which acid inversion has not proved satisfactory because of detrimental effect on flavor or color or both. The determining conditions for the successful industrial use of invertase are as follows: (1) temperature requirements sufficiently low to minimize the heat inactivation and destruction of invertase; (2) a pH range of the products sufficiently restricted to minimize the danger of inactivation or destruction of invertase due to excessive alkalinity or acidity; (3) a period for inversion under optimum conditions which is not so short as to require an excessive quantity of invertase, thereby unduly increasing the cost; (4) an invertase preparation of constant activity available in commercial quantities at a reasonable price. The nonavailability of such a standardized commercial invertase preparation and the lack of data on proper operating conditions in practice have until recently presented a serious obstacle to industrial utilization of invertase. It is believed that these obstacles have now been largely removed.

The writers have determined the most economical conditions for the industrial use of invertase in the case of various typical sucrose-containing products largely unsuited to acid inversion. The salient features of these procedures, several of which have already been adopted commercially, are presented herewith.

In all the experiments a standard invertase preparation was used, its activity being arbitrarily determined in the following manner: Five grams of the invertase preparation were dissolved in water and diluted to a volume of 1 liter. Twenty cubic centimeters of this dilute solution were added to 200 cc. of a 10 per cent sucrose solution acidified with glacial acetic acid to a pH value of 4.3 to 4.6. During inversion this solution was kept at a constant temperature of 25° C.

[1] Presented before the Division of Sugar Chemistry at the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924.

Portions of the solution were removed at stated intervals. The polarization of these portions was determined by means of a saccharimeter, after they had been made slightly alkaline with sodium carbonate to complete the mutarotation of dextrose and levulose. The average value of the unimolecular reaction velocity constant, k, calculated from the inversion periods and polarizations, is 0.0022 to 0.0023 for this standard invertase preparation under the conditions given and without correcting for dilution. Since the invertase inversion reaction is not rigorously unimolecular, the writers customarily employ standard time periods in order that the calculated k values may be comparable. The word "invertase," as hereafter used, refers to such a standard invertase preparation in undiluted condition, unless otherwise indicated.



Floor Plan Central Cane Sirup Plant Employing Invertase Inversion

Invertase inversion is very flexible in the matter of possible combinations of inversion period, temperature, sucrose concentration, and proportion of invertase. Other conditions being identical, time and volume concentration of invertase are inversely proportional for a given degree of inversion; invertase cost frequently may be reduced at the expense of time. In many cases this increase in time involves no expense other than suitable increase in tank or other form of storage capacity for holding sirups and similar products during inversion. Products to be inverted should in general be adjusted to the optimum pH value (4.3 to 4.6)[2] and maintained as nearly as practicable at the optimum temperature for invertase activity during inversion. The cost of evaporating water and the possible detrimental influence of high temperature on the flavor and color of the sirup or similar product may render inversion at lower ranges of sucrose concentration inadvisable, particularly with products of very high density.

In the case of products with delicate flavor, such as high-quality maple sirup, it may be advisable to conduct inversion at a pH value higher and temperature lower than the optima. The point of departure in the adjustment of these factors has been the consideration of keeping the expense for invertase within the approximate limits of 0.5 to 1.0 cent per gallon of finished sirup, concessions from the optima of other conditions controlling the rate of inversion being made only as required for special reasons. Invertase costs have been based upon the price of one of the invertase preparations placed upon the market as a result of this investigation.

Inversion of all the sucrose present in a sirup is not only unnecessary but also undesirable, because of the danger of crystallization of dextrose. The degree of inversion of sucrose should be such as to yield a ratio of sucrose and invert sugar which will not permit crystallization of either sucrose or dextrose. The influence of nonsugar substances on the solubility equilibrium between sucrose and invert sugar is also to be considered. Furthermore, in some commercial products a marked degree of supersaturation may be maintained for fairly long periods. Owing to the difficulty of stopping inversion at even a somewhat definite invert sugar–sucrose ratio in the case of acid inversion, it is usually necessary to mix uninverted sirup with practically completely inverted sirup in suitable proportion, the required ratio being thus obtained with sufficient accuracy. In the case of invertase inversion the inversion may be stopped at the required invert sugar–sucrose ratio, thus obviating the necessity of mixing inverted and uninverted sirups.

After the required degree of inversion is reached, it is usually necessary to destroy the invertase by heating the product to about 90° C. This need not be done where the sirups are of sufficiently low density to prevent crystallization of dextrose when largely inverted, nor where the presence of an increased proportion of levulose is not objectionable because of its tendency to undergo decomposition.

If reduction of the pH of the product to 4.3–4.6 unfavorably affects the flavor, inversion may nevertheless be conducted at this optimum pH and the pH subsequently increased.

Note—pH values were determined by the Barnett-Gillespie method. In the case of cane products the colorimetric method was found to be more dependable than any electrometric method except that employing the quinhydrone electrode.

Hydrochloric acid may be added in minimal quantity, with subsequent addition of sodium carbonate to increase the pH to the desired value after inversion. Even with subsequent partial neutralization of acidity, this procedure may unfavorably modify the flavor of certain products, especially when the pH is increased to a value close to neutrality. In such cases inversion should be conducted at the natural pH or at a pH value as near to 4.3–4.6 as can be obtained without detrimental effect on flavor. It must be kept in mind that flavor is an important factor in the commercial value of sirups and that inversion should be accomplished without impairing it.

The foregoing statements represent guiding principles in the industrial use of invertase which have been impressed upon the writers as the result of many experiments. The precise details of adjustment of time, temperature, sucrose concentration, invertase proportion, and pH are, however, best determined independently for each particular product. Once they are determined the procedure is easily standardized for the product in question. The flexibility of the invertase inversion procedure is, therefore, a distinct advantage. It is desirable, whenever possible, to reduce the proportion of invertase at the expense of time. In the case of sirups it is often feasible to conduct the inversion during a period when the product would in any event be held in storage. The time element, therefore, involves no expense,

[2] Euler and Myrbäck, *Z. physiol. Chem.*, **120**, 61 (1922).

and no manipulation is required other than the mere mixing of the invertase with the product with suitable adjustment of the pH if desired. The use of invertase is particularly advantageous when inversion is to be conducted at ordinary temperatures, say 10° to 30° C. The foregoing factors are more fully discussed in connection with the specific products.

Golden Sirup and Similar Products

The term "golden sirup" has for many years been applied commercially to an article prepared by mixing bone char–filtered refiner's sirup with an invert sugar sirup prepared from granulated sugar. Since golden sirup is usually sold at a high density (ordinarily about 80 per cent solids), the admixture of invert sugar is required to increase the total sugar solubility and to prevent crystallization of sucrose. The invert sugar sirup also acts as a diluent of the color and intense saline flavor of refiner's sirup. Refiner's sirup contains on the average about 7 to 8 per cent ash and exhibits a pronounced buffer effect toward added acid.

It is possible to select an intermediate sirup in process in the refinery which, except for invert sugar content, will closely duplicate a golden sirup prepared in the usual way. If this intermediate sirup could be directly inverted to the required degree, the expense of producing a granulated sugar for the purpose of making invert sugar sirup could be avoided and the entire process simplified. As a result of the pronounced buffer action of the salts present in such intermediate sirup, the quantity of acid required to give the pH value requisite for inversion is decidedly greater than for a granulated sugar sirup of the same sucrose concentration. Owing to the influence of this large quantity of acid on the flavor of the product, the most feasible procedure in case acid inversion were employed would be to use sulfuric acid, subsequently eliminating the excess as calcium sulfate after the addition of lime. Aside from other considerations, however, an additional filtration to remove the calcium sulfate would be necessary.

The writers have found that such intermediate refinery sirups can be satisfactorily inverted by means of invertase. Various combinations of temperature, time, and proportion of invertase may be employed. In the present instance it proved advisable to employ the optimum temperature for invertase action, which was found to be 65° C., and to maintain this temperature practically constant for 24 hours. In practice it is desirable to use tanks suitably insulated and provided with steam coils or means for injecting steam. Such conditions are practicable in a sugar refinery, and little attention is required to keep the temperature between 60° and 65° C.

Table I—Inversion of a Refinery Sirup at 65° C. and Varying Degrees Brix

Apparent solids content ° Brix	Invertase Gram/cc. sirup	Apparent purity after inversion Per cent
55.5	0.000220	25.17
50.7	0.000190	25.22
45.0	0.000168	24.61
38.0	0.000148	25.35
33.0	0.000140	25.34
28.0	0.000130	25.06

Enough of the standard invertase preparation was used to reduce the apparent purity (ratio of direct normal weight polarization to degrees Brix) to approximately 25 per cent in 24 hours at 60° to 65° C. The value designated as "apparent purity" does not definitely indicate the proportion of sucrose to invert sugar. It serves rather as a convenient and readily determined criterion of relative change in invert sugar–sucrose ratio which is applicable to products of the same approximate initial composition. In the case of the intermediate refinery sirups studied, an apparent purity of 25 per cent was found to be suitable for preventing crystallization of either sucrose or dextrose from an 80° Brix golden sirup. The proportion of invertase required varied with the density to which the intermediate sirup was diluted, as shown in Table I.

Table II gives additional data on the inversion at 28.0° to 55.5° Brix of the sirup reported in Table I.

Table II—Cost of Invertase Required for Inverting a Refinery Sirup at Varying Degrees Brix

Apparent solids content at which sirup was inverted ° Brix	73.3° Brix sirup before diluting to ° Brix shown in Col. 1 Gallons	Sirup obtained after diluting to ° Brix shown in Col. 1 Gallons	Water to be evaporated to obtain 80° Brix sirup Gallons	80° Brix sirup obtained Gallons	Invertase required to reduce volume of sirup in Col. 3 to 25% apparent purity Pounds	Total cost of invertase	Cost of invertase per gallon of 80° Brix final sirup
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
55.5	697.6	1000.0	380.6	619.4	1.831	$7.32	$0.0118
50.7	697.6	1084.6	465.2	619.4	1.717	$6.87	$0.0111
45.0	697.6	1225.1	605.7	619.4	1.720	$6.88	$0.0111
38.0	697.6	1450.6	831.2	619.4	1.797	$7.19	$0.0116
33.0	697.6	1682.3	1062.9	619.4	1.973	$7.89	$0.0127
28.0	697.6	1950.1	1330.7	619.4	2.124	$8.50	$0.0137

Table III gives further data on the same sirup. The practical constancy of the values in Column 4 for the inversion constant k shows that inversion proceeded at a constant rate for the different densities indicated in Column 1. This is to be expected from the fact that the proportions of invertase were so adjusted as to reduce sirup of the various densities to practically the same apparent purity in the same length of time. Comparison of the values in Column 4 also serves to check the precision of weighing, dilution, control of temperature, etc., in the experiments.

Table III—Constant Percentage Inversion of a Refinery Sirup at Varying Degrees Brix

Apparent solids content ° Brix	Initial polarization ° V.	Polarization at conclusion of inversion ° V.	Inversion velocity constant, k	Time Minutes
(1)	(2)	(3)	(4)	(5)
55.5	47.29	13.88	0.000232	1440
50.7	43.60	12.87	0.000231	1440
45.0	38.60	11.05	0.000235	1440
38.0	32.60	9.63	0.000231	1440
33.0	28.11	8.39	0.000229	1440
28.0	24.25	7.02	0.000234	1440

Unfortunately, the actual solids contents of the sirup at the apparent solids contents shown in Table II, Column 1, were not determined, and the values in Table II, Column 3, were calculated from the initial normal weight solution polarizations in Table III, Column 2, upon the assumption that the latter, after being corrected to a constant basis of sucrose specific rotation, are accurately inversely proportional to the values required in Table II, Column 3.

Note—The average of the Tollens and Nasini-Villavecchia formulas $[\alpha]_D^{20} = 66.412 + 0.012673_p - 0.0003766_{p^2}$, was used. The direct normal weight solution polarizations were substituted for p and, while not rigorously equal thereto, the error involved is negligible.

The same sirup, when analyzed at 61.4° Brix "apparent solids," had a direct normal weight solution polarization of 50.62° and contained 50.70 per cent sucrose. Any error involved in assuming that the influence of the salts content of the sirup on the sucrose polarization is proportionately constant at the dilutions indicated may safely be regarded as immaterial. Likewise, the error due to slight variation in the values in Table I, Column 3, is relatively negligible.

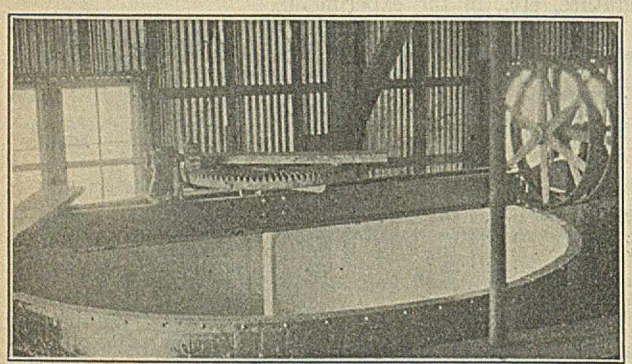
Invertase doubtless undergoes a certain degree of destruction at 65° C., especially at pH values as low as 4.3 to 4.6, regardless of the fact that this is the approximate optimum temperature under the experimental conditions. Variation in the rate of destruction because of the variation in the net protective action of sucrose at the different dilutions is a possible factor in the relation between the values in Table II, Column 6. Further investigation is required,

however, in order to explain fully the variation in invertase efficiency under the conditions indicated in Table II.

An apparent solids content of 55° Brix was selected as most suitable for subsequent experiments. The cost of invertase per gallon of 80° Brix finished sirup when inversion was effected at 55° Brix was 1.2 cents. In the experiments the results of which are recorded in Tables I, II, and III, the pH was adjusted to 5.5–5.7. With most sirups of this type, however, it is possible, by using a strong acid such as hydrochloric in minimal amounts, to adjust to pH 4.3–4.6 without appreciably affecting flavor. If the pH of the sirup is adjusted to 4.3–4.6, the cost of invertase is reduced by approximately 25 per cent—that is, to about 0.9 cent per gallon of 80° Brix finished sirup.

The quality of the golden sirup produced is determined by the quality and composition of the intermediate refinery sirup selected for inversion. Golden sirup was prepared in the foregoing manner from several intermediate sirups of varying quality. In all cases the products obtained required no treatment other than concentration in vacuum to an apparent solids content of approximately 80° Brix to produce commercially acceptable articles. The sirups were clear and the flavor was not changed by the invertase. This simple procedure may be contrasted with the indirect and more expensive methods mentioned.

This general method may also be used for producing a high-density sirup prepared from any grade of soft sugar or from beet or cane sugar-house or refinery intermediate sirups.



A 5000-Gallon Partially Insulated Tank Used for Invertase Inversion

In the case of sirups which are sometimes prepared from a mixture of soft sugar and granulated sugar, the granulated sugar, if used in sufficient quantity (as is usually the case) to furnish the invert sugar required to prevent sucrose crystallization, may be inverted in separate solution by means of acid and then mixed with the soft sugar sirup. Since the granulated sugar acts primarily as a diluent of the soft sugar, however, it would probably be cheaper, even in such cases, to use a higher grade soft sugar corresponding in quality to the mixture of granulated and soft sugar and to invert this soft sugar sirup direct with invertase. In the case of sirups prepared exclusively from soft sugar, inversion by invertase is the indicated procedure. Soft sugars in general contain approximately 0.2 to 2.5 per cent of ash. Application of invertase to sirups of the foregoing type is covered by public patent.[3]

Maple Sirup and Maple Cream

It is sometimes desirable to market maple sirup at a density higher than that which corresponds to the prevailing standard of 35 per cent maximum water content. Partially inverted maple sirup of increased density is also a desirable intermediate product in processes which are described later. The purity (ratio of sucrose to total solids) of maple sirup is usually about 90 to 95 per cent, and the amount of invert sugar present is usually so small as to have little effect in increasing total sugar solubility. Consequently, maple sirup readily undergoes crystallization if the density is increased materially above 65 per cent solids content. For sirups of moderate density a relatively small degree of inversion is sufficient to overcome this difficulty.

Crystallization of commercial sirups prepared by mixing a granulated sugar sirup and maple sirup may readily be prevented by partially inverting the granulated sugar sirup with acid, no inversion of the maple sirup being required, provided enough granulated sugar sirup to furnish sufficient invert sugar to prevent sucrose crystallization is used. In the case of a pure maple product, however, it is necessary to invert some of the sucrose of the maple sirup. The flavor of a good quality of maple sirup is very delicate and is adversely influenced by even a slight increase in acidity. The ash content of maple sap sirup is approximately 0.5 to 1.0 per cent[4] and the buffer effect toward added acid is considerable. Acid inversion of maple sirup is therefore difficult to accomplish without injuriously affecting flavor and color.

The writers found it best to invert the maple sirup at its original density, thereby restricting heating to that required for concentrating to higher density. The pH value of the maple sirups studied was 5.8 to 5.9. In the case of the highest grades of maple sirup, even the addition of concentrated acid such as hydrochloric in quantities sufficient to give a pH value of 4.3 to 4.6, the optimum for invertase action, unfavorably affected the mild, delicate flavor.

In one experiment it was desired to reduce the apparent purity of a 70° Brix maple sirup from 90 to 70, the proportion of invert sugar and sucrose corresponding thereto being amply adequate to prevent sucrose crystallization at this concentration. Invertase inversion was allowed to proceed at the natural pH value of the sirup. Also, in order to prevent any injurious effect of elevated temperature on flavor and color, inversion was conducted at atmospheric temperature (approximately 25° C.). At the same time it was desired to limit the cost for invertase to 1 cent per gallon of maple sirup. Under these conditions, 1/4 pound of invertase was required for 100 gallons of sirup and approximately 1 week was needed for the degree of inversion indicated. This inverting period, although somewhat long, becomes quite feasible when maple sirup is held in storage for a certain period, as is usually the case. The required amount of invertase may be added to the container, whether barrel or tank, and inversion may proceed during the regular storage period. If the sirup is held at a very low temperature, an increased proportion of invertase or increased period of inversion is required.

In the case of maple sirup invertase inversion is preeminently superior to acid inversion at ordinary temperature, because the increased quantity of acid required under this condition has a pronounced effect on the flavor. Although high temperatures are in general not desirable for the inversion of maple sirup on account of the effect on color and flavor, there is considerable latitude with respect to combinations of time, temperature, and proportion of invertase which may be used. With low-quality maple sirup, which is not so adversely affected by elevated temperature as high-grade sirup, the period required for a given degree of inversion with a definite amount of invertase may be decreased by increasing the temperature during inversion. Also, with sirups of this character, it is possible to reduce the natural pH somewhat, thereby approaching nearer to the optimum pH for invertase activity without adversely affecting the

[3] Walton, U. S. Patent 1,465,459 (August 21, 1923).

[4] *U. S. Dept. Agr., Bur. Chemistry, Bull.* **134**, p. 66.

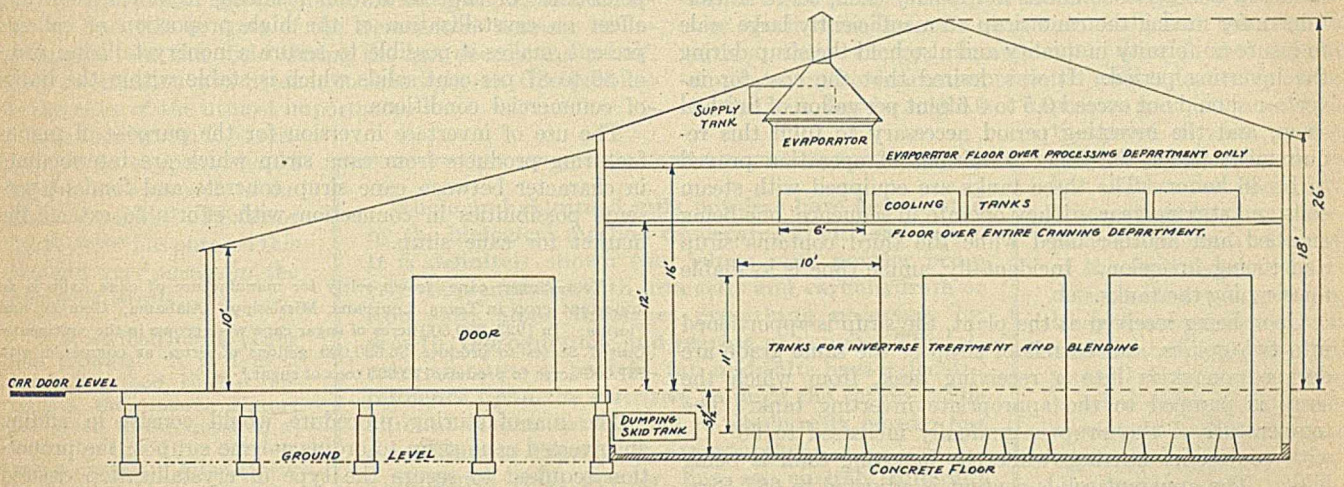
flavor of the product. Application of invertase to maple sirup is covered by public patent.[5]

Invertase inversion also lends itself admirably to the preparation of maple "cream," also termed maple "butter" and maple "icing." Maple cream is essentially a maple fondant, prepared by boiling maple sirup to a temperature of 114.4° to 116.6° C. (238° to 242° F.), cooling to approximately 32.2° C. (90° F.), and then agitating in such manner as to cause crystallization of sucrose in the form of a multitude of microscopic crystals. It should have essentially the same consistency as the ordinary fondant or "cream" used in confectionery manufacture. Owing to the large proportion of sucrose to invert sugar and nonsugar compounds in ordinary maple sirup, it is difficult in practice to control crystallization so as to secure sufficiently minute crystals of the desired degree of uniformity in size. The maple fondant thus produced is frequently granular, owing to the presence of crystals of excessive size, and the mother sirup, not being sufficiently retained in the capillary spaces between these larger crystals, exudes after a certain period, collecting on the surface of the fondant. Furthermore, this supernatant sirup frequently undergoes fermentation after the maple cream is packed, usually in friction top cans. Owing also to the difficulty of controlling crystal size, it has been customary to prepare maple fondant in small batches and to "cream" (promote crystallization) it on a slab by hand instead of using a mechanical beater.

These difficulties may be eliminated by preparing an inverted maple sirup by the use of invertase and mixing this with the regular batch in such proportion that the invert sugar may control the size of the sucrose crystals. By thus diminishing the size of the crystals so that they are impalpable to the tongue, the maple fondant not only becomes smoother in consistency but also retains the mother sirup, thereby presenting a more homogeneous and attractive appearance. The presence of invert sugar also so increases the solubility of total sugars as materially to increase the density of the mother sirup, thereby, owing to increased osmotic pressure, greatly reducing the tendency of the sirup to undergo fermentation. The inverted maple sirup may be used in the same manner as glucose in confectionery manufacture to control the size of sucrose crystals, thus making it possible to work with large batches and to use a mechanical beater to replace hand manipulation.

The inverted maple sirup required for manufacture of maple cream may be prepared essentially in the manner already described. Since the inverted maple sirup is to be used in relatively small proportion in the maple fondant, a slightly tart taste would not perceptibly affect the flavor of the final product. Therefore, it is possible to reduce the natural pH of the maple sirup somewhat and thus accelerate inversion. Each lot of maple sirup should be considered on its own merits in this respect. It is sometimes advisable to prepare stock inverted maple sirup of such high solids concentration (say 42° Baumé) that it may be kept at ordinary temperature without undergoing fermentation. A certain degree of modification of flavor (production of so-called caramelized flavor) is unavoidable when maple sirup is concentrated to such high density, although this may be reduced somewhat by concentration in a vacuum pan. If the flavor is not unduly modified, it would not be objectionable in the final product, because the inverted maple sirup is used in only moderate proportions. It is best to add the inverted maple sirup at the "break" during the beginning of "creaming" of the regular batch, or when it becomes "runny," as it is sometimes termed, and also when the batch is remelted in a steam-jacketed kettle in order to make it sufficiently fluid to pour into the package. To 100 pounds of maple sirup of usual density, 1 pound of 42° Baumé invert maple sirup may be added in the first instance and 1 pound additional in the second instance. The proportion of invert maple sirup may be increased as desired in order to produce a softer consistency or to secure higher density of mother sirup, thereby retarding fermentation. Application of invertase to production of maple fondant is covered by public patent.[6]

Inverted maple sirup may advantageously be present in relatively small proportion during the process of crystallizing maple sugar from sirup. The maple sugar thus produced is of finer texture and smaller crystals than that ordinarily obtained. In a similar manner addition of inverted maple sirup is of value in the manufacture of pure maple confections of the fondant type.



End Elevation Central Cane Sirup Plant

Cane Sirup

A more recent development[7] in the commercial use of invertase in cane sirup manufacture has been introduced in a plant designed by the writers and erected in the sugar cane district of Texas. As usually made by small producers, cane sirup varies greatly in quality. This has made it difficult for the smaller producers to furnish a sufficient volume

[5] Walton and Paine, U. S. Patent 1,467,022 (September 4, 1923).

[6] Paine and Walton, U. S. Patent 1,467,007 (September 4, 1923).

[7] The use of invertase during the course of manufacture of cane sirup for the purpose of preventing crystallization was originally proposed by Hudson and Dale, of the Bureau of Chemistry.

of sirup of uniform quality to enter directly the established channels of large-scale commercial distribution. The plant mentioned was therefore designed to provide for the inversion, blending, and canning of cane sirup manufactured by small producers in the customary manner and delivered to the plant in barrels (90 per cent by railroad). (This plan of operation is made feasible commercially by a refining-in-transit freight rate.) The plant has a capacity of 5000 gallons of sirup per 12-hour day, with a view to handling 500,000 gallons per 100-day season. Three partially insulated, covered steel tanks, of 5000 gallons effective capacity each, serve as containers for mixing the cane sirup on a sufficiently large scale to insure uniformity in quality and also hold the sirup during the inverting period. It was desired that the cost for invertase should not exceed 0.5 to 0.6 cent per gallon of finished sirup, and the inverting period necessary to fulfil this requirement under the other conditions of operation proved to be 36 hours. The three tanks are equipped with steam coils and stirring gear. They operate in sequence, one being emptied and another filled while the third contains sirup undergoing inversion. Incidentally, ample time is available for cleaning the tanks.

Upon being received at the plant, the sirup is apportioned into two grades, and barrels of sirup of the same grade are dumped on skids into a receiving tank, from which the sirup is pumped to the appropriate inverting tank. The temperature of the sirup is gradually increased to 60° C., with continuous stirring, while the inverting tank is being filled. The apparent solids content is adjusted to 68° Brix, the addition of dilute sirup resulting from cleaning the barrels with steam to dissolve crystallized sugar being largely sufficient for this purpose.

Invertase is added in the proportion of 1 pound to 700 to 800 gallons of sirup. The exact proportion may vary somewhat, depending upon the ratio of sucrose and invert sugar present as determined by the variety of sugar cane, various cultural conditions, and the degree of inversion produced during manufacture. Under the standardized conditions of operation, the apparent purity is reduced at the end of the 36-hour inverting period to 50 to 55 per cent. This apparent purity allows sufficient margin of safety to prevent sucrose crystallization at the temperature range to which the sirup is ordinarily exposed. The sirup is then pumped to an open copper evaporator, where it is quickly concentrated to standard density (approximately 74° Brix), the invertase being destroyed at the same time. From the evaporator the sirup flows to a battery of cooling tanks, where it is cooled to canning temperature and thence passes to the canning department, which is equipped in the customary manner. The technical operation of this process has proved to be eminently satisfactory in practice and is sufficiently economical to meet competitive commercial conditions.

Another use of invertase, established as a result of the work here described, is its application to the manufacture of *la cuite*. This product is made from cane juice by the process of clarification by sulfur dioxide and lime which is used in the manufacture of the so-called Louisiana type of cane sirup. *La cuite* is, however, evaporated to a much higher density (86 to 87 per cent solids) than the cane sirup. *La cuite* is highly esteemed in Louisiana, but it has had a limited market because of the great degree of sucrose crystallization which ensues shortly after manufacture. It is customarily canned hot and then cooled rapidly. In the absence of "seeding" by sucrose crystals, supersaturation may be maintained for some time, but when the can is opened initial sucrose crystals are quickly produced by film evaporation, and crystallization is so rapid that the product soon becomes almost solid.

When using invertase in the manufacture of *la cuite*, inversion is accomplished in a 45° Brix sirup at an intermediate stage of manufacture, the apparent purity being reduced to 20 to 25 per cent from an initial value of approximately 70 per cent. This intermediate sirup is then concentrated to final density in the customary manner. The solids content of the final sirup exceeds the maximum solubility of approximately 81 per cent[8] established for a mixture of sucrose and invert sugar in aqueous solution, but the influence of nonsugar compounds on solubility, together with possible persistence of supersaturation resulting from the retarding effect on crystallization of the high proportion of colloids present, makes it possible to secure a noncrystallizing sirup of 86 to 87 per cent solids which is stable within the limits of commercial conditions.

The use of invertase inversion for the purpose of manufacturing products from cane sirup which are intermediate in character between cane sirup concrete and fondant presents possibilities in connection with efforts to extend the market for cane sirup.

Note—Sugar cane grown solely for manufacture of cane sirup is an important crop in Texas, Louisiana, Mississippi, Alabama, Georgia, and Florida. In 1923 200,000 acres of sugar cane were grown in the continental United States to produce 33,620,000 gallons of sirup, as compared with 231,000 acres to produce 172,000 tons of sugar.[9]

The manufacturing procedure would consist in adding an inverted cane sirup to ordinary cane sirup in the proportion required to secure the type of crystallization desired and then concentrating to the requisite density, the crystallizing temperature and degree of agitation being adapted to the consistency to be obtained.

Miscellaneous Products

Invertase is also being used to prevent sucrose crystallization in sorghum sirup. Inversion is effected at an intermediate stage during manufacture, an overnight period being employed without delaying the process. Owing to the presence of comparatively large proportions of invert sugar and colloidal material, sorghum sirup in general shows less tendency than cane sirup to undergo crystallization. This tendency varies, however, according to the variety of sorghum and cultural conditions, and a suitable means of increasing the ratio of invert sugar to sucrose is frequently desirable.

From an ordinary commercial standpoint, the use of invertase for producing invert sugar sirup from good grades of granulated sugar is in general not advisable. Invert sugar sirup produced by invertase inversion, however, is distinctly superior in smoothness of flavor to that made by acid inversion as customarily practiced, and its manufacture may be feasible for supplying special commercial requirements.

The application of invertase inversion to the confectionery industry has already been described by one of the writers.[10] Invertase inversion in this industry has attained extended use in the United States, Canada, and Australia.

As a result of the investigations here outlined, invertase has been placed upon the market in commercial quantity in the United States by three manufacturers[11] and it is now available as a standardized preparation.

[8] Jackson and Gillis, *Science*, **53**, 265 (1921); Herzfeld and Möller, *Z. Ver. Rübenzuckerind.*, **32**, 693 (1895); Girol, *Bull. assoc. chim. sucr. dist.*, **25**, 120 (1907).

[9] *U. S. Dept. Agr., Crops and Markets*, December 29, 1923.

[10] Paine, THIS JOURNAL, **16**, 513 (1924); Paine and Hamilton, U. S. Patents 1,437,816 and 1,502,207 (December 5, 1922, and July 22, 1924).

[11] Wallerstein Laboratories, 171 Madison Ave., New York, N. Y.; Digestive Ferments Co., 920 Henry St., Detroit, Mich.; Industrial Research Laboratories, 220 W. Ontario St., Chicago, Ill.

Whole and Skimmed Milk Powders as Food[1]

Observations on a New Vitamin for Reproduction

By L. T. Anderegg and V. E. Nelson

Iowa State College, Ames, Iowa

Whole and skimmed milk powders have been tested by the biological method concerning their food value. It is definitely shown that whole milk powder properly supplemented with iron salts and carbohydrate or iron salts alone furnishes everything necessary for growth, reproduction, and rearing of young. The relative amounts of protein, fat, and salts have a decided influence upon the nutritive value of the ration. The amount of iron salts added to whole milk powder has a pronounced effect upon reproduction.

Skimmed milk powder has an entirely different food value than whole milk powder. On a ration of skimmed milk powder supplemented so as to conform in composition with a whole milk powder diet, which was very favorable for reproduction, the results were entirely different. The addition of either yeast or wheat embryo to a skimmed milk powder diet, on which there was no reproduction, changed it so that young were born and reared by the first generation; the second generation on these experiments grew normally but did not reproduce. Yeast and wheat embryo must therefore be furnishing the same supplementing substance.

AT PRESENT the factors that are essential, both qualitatively and quantitatively, for the optimum animal diet are very far from being known and understood, and this in spite of the tremendous amount of investigation in this field during the last decade and a half. Any information which tends to shed light on this problem is therefore of the utmost importance.

One food which it is reasonable to suppose should be a close approach to the ideal is milk. Professor Mathews[1,*] has phrased this thought very nicely in the following words:

> Milk is a food for the young and growing. It is a most interesting food, since it represents the answer Nature has given to the question as to the best food for developing mammals. After a very long period of experimentation in the monotremes, marsupials and lower placental mammals, the milk of the higher placentals was evolved. It is probable that there are good reasons for the presence in milk of most, if not all, of its constituents.

The importance of milk, and of the various food products derived from milk, in relation to human and animal dietary regimes is of such importance that further information concerning the nutritive values in this field of food products is highly desirable.

Although much information along this line can be obtained by chemical and physical studies of milk, it is the biological method which has been most fruitful of results. The rat, because of its small food consumption, omnivorous habit, comparatively short reproductive cycle and span of life, serves exceptionally well as a test animal. With these animals it is possible to obtain accurate data concerning any class of food product in a comparatively short time.

It is now well established that a diet which may be adequate for apparently normal growth to the adult stage may, nevertheless, be found lacking when the experiment is continued so as to include observations on reproduction and the rearing of young. Frequently the females fail to become pregnant or, becoming pregnant, the young may be few in number and may even be born dead though apparently normal in development. Again, if born alive, the young may succumb within a few days or perhaps at about weaning time. It appears that parturition, the first few days of life, and the weaning stage are critical periods in the life of the rat.

This paper will describe some investigations which have to do especially with the nutritive values of whole and skimmed milk powders. Owing to the amount of water present in liquid whole milk, or in liquid skimmed milk, it is questionable whether the animals consume a sufficient quantity to satisfy their energy requirements. Should the process employed in the desiccation of liquid milk unfavorably affect it, the milk powder might not appear so good, from a nutritive point of view, as the original liquid milk really is. On the other hand, any observations tending to emphasize the positive aspect of the food value of powdered milk would certainly be applicable to the original material. Concerning the method of making the milk powders employed in these investigations the manufacturers state:[2]

> Natural milk is first pasteurized by the holding process and partially concentrated by the vacuum process. Then it is sprayed under heavy pressure into a chamber through which a current of filtered warm air is passing. The milk is broken up into almost invisible spray and upon reaching the warm air loses its moisture by evaporation. The humid air passes out through a vent and the solids fall as a dry powder of less than 3 per cent moisture.

The important feature of this process is that the milk never reaches the boiling point and therefore does not carry the cooked flavor to the product—Klim; nor, even more important, does it lose one iota of its food value. Each milk particle, a perfect sphere as it enters the room, is reduced in size as its moisture is evaporated, until, still a sphere, it falls as a dry powder to the floor of the chamber. The maintenance of the spheroidal shape indicates uniform evaporation from the outside to the center.

After numerous analyses the following values have been selected to represent the per cents of protein, fat, and ash in the milk powders used in these experiments:

	Protein	Fat	Ash
Whole milk powder	26.4	27.5	6.0
Skimmed milk powder	37.0	1.3	8.0

In general, it may be stated that the expressed opinions of other investigators are to the effect that milk when tested by the biological method is found to be in some way inadequate. Thus, specifically, Mattill and Stone[3] carried out observations on the following diets:

Whole milk powder	Starch	Lard	Salts
50	38	10	2.0
60	28.4	10	1.6
70	18.8	10	1.2
80	9.2	10	0.8
100	Iron citrate, 0.2 per cent		

[1] Reported before the Iowa Academy of Science, May, 1924. Received January 13, 1925.

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

These investigators state that growth was at first better than normal on these diets, but after 75 days there was a retardation, and the slowing up of growth was more pronounced in the female than the male. Reproduction was unsuccessful, for of 30 females studied only 6 were reported as pregnant and young were seen in but two instances and were either dead when found or else perished shortly after birth. Furthermore, there appeared to be a total lack of the maternal instinct, as no nests were prepared by the females and their young were allowed to lie scattered about the cage.

Diet Necessary for Reproduction

Given an opportunity to make a selection from a variety of possible foods, an animal may select in a way which is favorable to its physical well-being. In order tentatively to test out the nutritive value of whole milk powder, a group of rats weighing from 50 to 80 grams each was placed in a cage where there was free access to water, purified butter fat, agar-agar, purified casein, salt mixture, and powdered whole milk, each in a separate container. At first butter fat and milk powder appeared to be chiefly consumed, but when the rats had reached an average weight of about 125 to 150 grams they turned from the butter fat to the casein. Several of the females gave birth to young and from two litters of 5 and 6 young, 3 and 5, respectively, were weaned. This observation suggests that the optimum diet of the young rat may be different from that of the adult, in that it may permit of the presence of a greater amount of fat, which may be a very significant point. Moreover, this at once suggested that the reproductive performance of rats on whole milk powder to which lard had been added might be enhanced by the removal of some of the fat. In addition, still another possibility suggested itself. Observations by Nelson, Heller, and Fulmer[4] indicated that the percentage of salt in the diet may have an important influence on reproduction. With a salt content approximating 5 per cent in the diets they employed, sterility was evident, whereas at a level of 3.7 per cent reproduction occurred. Assuming that whole milk powder will, as a rule, contain very nearly 6 per cent of ash, it is evident that the diets of Mattill and Stone[3] carried a salt content of about 5 per cent. In view of the observations in this laboratory, just mentioned, it is conceivable that the salt content of the milk powder diets might be the cause of the lack of reproduction.

Effect of Relative Amounts of Protein, Fat, and Salts

In order to test the effect of removing some of the fat, and also of the effect of the salt content, Diets 1 and 2 of Table I were devised. Sixty per cent of whole milk powder was selected as this contains 3.6 per cent of ash, an amount believed favorable for reproduction. As milk is notably deficient in iron, 0.2 per cent of iron citrate was added. In order to obviate the possibility of a deficiency in the protein moiety, 6 per cent of thoroughly water-washed casein was added. These substances, together with 4 per cent of agar-agar for roughage, and dextrin to 100, made up Diet 1. Diet 2 is similar to Diet 1 but has 2.4 per cent of dextrin replaced by an equal amount of McCollum's salt mixture 185.[5] The salt content of this diet is hence 6.2 per cent, or about that of whole milk powder itself.

Every female on both of these diets became pregnant, gave birth to young and nursed some of them in an apparently natural way. To great surprise the animals of Lot 53 on Diet 2 containing the larger amount of salt—namely, 6.2 per cent—had better records for reproduction and rearing of young than did those of Lot 52 on Diet 1 with less salt. However, those with less salt, though they reproduced later in life, and were neither so prolific nor so successful in the rearing of their young as those with more salt, were uniformly larger animals than those on the higher salt diet. Should this observation be confirmed, it indicates that a diet which is optimum as concerns growth may not be optimum when reproduction and rearing of young are the goal. The best single record was that of a female on Diet 2, who gave birth to four litters of 42 young and reared 39 of them. Fourth generation young were reared on this diet. In Table II setting forth the reproduction and growth records of the different lots, the data for the three females having the best records have been selected. Even so, it frequently happened that a female and her young were discarded before the young were weaned. Obviously, such selection will make the number of young born and reared somewhat higher than a general average; but by so doing it is believed that certain deaths due to accident, rather than the fault of the diet, are eliminated.

It should be stated that on a diet exactly duplicating one of those of Mattill and Stone—namely, Diet 3 in Table I—Lot 89 conformed exactly to the behavior described by them for their animals. There was never any evidence of an advanced pregnancy though the animals were carried on the diet for a period of 32 weeks. However, when the lard was omitted, as in Diet 4, the results were entirely different. Lot 90 presents a very acceptable record. Growth was about normal and, as shown in the table, 3 of the females gave birth to fourteen litters of 94 young of which number 74 were weaned. The second generation animals on the diet, Lot 121, grew at the normal rate, but reproduction was delayed until they had been on the diet for 20 weeks, while on the best of the diets used by the writers reproduction occurs about 7 weeks after the animals have been started. The small amount of protein, 13.2 per cent, is suspected as being responsible for the delay. Each female produced one litter. The three litters comprised 24 young and 22 of them were weaned, when the experiment was discontinued.

Table I—Composition of Diets
(Figures in per cent)

Diet	Whole milk powder	Skimmed milk powder	Casein	Salt mixture	Iron citrate	Agar-agar	Dextrin	Starch	Lard	Butter	Cod-liver oil	Wheat embryo	Yeast
1	60.0		6.0		0.2	4.0	29.8						
2	60.0		6.0	2.4	0.2	4.0	27.4						
3	50.0			2.0				38	10				
4	50.0			2.0		4.0	44						
5	50.0		20.0	2.0				18	10				
6	60.0		6.0	4.2	0.2	4.0	25.6						
7	99.8				0.2								
8	99.0				1.0								
9	85.0				0.5	4.0	10.5						
10	60.0				0.5			11.5	28				
11	30.0		20.0	3.7		4.0	42.3						
12	15.0		20.0	3.7		4.0	57.3						
13	5.0		20.0	3.7		4.0	62.3			5.0			
14		60			0.2	4.0	30.8			5.0			
15		60			0.2	4.0	30.8				5.0		
16		60			0.2		26.8			5.0		8.0	
17		60			0.2		29.8			5.0			5.0
18		65		1.0	0.2	4.0	13.8			16.0			

The significant difference between Diet 3, on which there was an entire lack of reproduction, and Diet 4, on which reproduction and rearing of young were both very satisfactory, lies solely in the substitution of carbohydrate for a portion of the fat. Diet 5 was devised in an attempt to overcome the deleterious effect of the fat in Diet 3. Starch, to the extent of 20 per cent, was replaced by an equal amount of water-washed casein. The growth of the animals of Lot 114 was markedly better than normal. Each female gave birth to and reared young. Of a total of 88 young, 50 were weaned.

Table II—Growth, Reproduction, and Rearing of Young on Powdered Milk Diets

Lot	Diet	Generation	Females	Weeks on diet	Litters	Total young seen	Young weaned	Young dead 48 hours after birth	Rate of growth[a]
52	1	1	3	29	11	57	45	12	$N+$
53	2	1	3	29	11	94	87	7	N
89	3	1	3	32	0				$N-$
90	4	1	3	32	14	94	74	20	N
121	4	2	3	24	3	24	22		N
114	5	1	3	24	9	65	50	2	$N++$
138	5	2	3	19	3	13	4	9	$N+$
122	6	1	3	22	8	64	58	6	$N+$
152	6	2	3	15	3	26	12	11	$N+$
78	7	1	3	20	3	15	4	11	N
161	7	1	3	23	0				N
154	8	1	3	26	4	31	13	18	$N+$
170	8	2	3	13	0				$N+$
172	9	1	3	13	3	30	28	2	$N+$
136	10	1	3	27	3	18	12		N
164	10	2	3	16	0				N
94	11	1	3	27	7	44	32	12	$N+$
116	11	2	3	20	2	13	11		$N+$
93	12	1	2	27	6	36	15		N
92	13	1	3	18	0				$N-$
159	14	1	3	21	0				N
160	15	1	3	21	0				N
140	16	1	3	27	7	49	46		$N+$
142	17	1	3	27	5	25	13	8	$N+$
103	18	1	3	28	6	32	7	25	N

[a] N designates normal growth, $N-$ below normal, $N+$ better than normal, and $N++$ very much better than normal growth.

As indicated, those 3 females which were most successful reared 50 of their 65 young. Though the second generation, Lot 138, made growth at better than the normal rate, their record for reproduction is not very satisfactory, as only 4 young were weaned. Numerous other observations in this laboratory confirm the belief that high concentrations of protein and fat have a tendency to ameliorate each other's harmful effects and the combination may permit of practically normal growth as concerns weight increase, but that it is not possible to balance these against each other in extreme concentrations so that there will be no interference with normal reproduction and rearing of young. Diet 3, on which there was no evidence of reproduction even in the first generation, could be so modified—first, by dropping out the added lard and substituting an equal weight of the carbohydrate dextrin, or, second, by retaining all the fat of the diet replacing a portion of the starch by an equal weight of washed casein—that experimental animals could be carried on it with successful weaning of some of the third generation. This illustrates the extreme importance of a proper quantitative balance between the well-known food constituents of the diet.

Since, from the record of Lot 53, added salt appeared to have a favorable effect on reproduction and the rearing of young, Diet 6, which contains 8 per cent of salt, was devised. Lot 122 was continued on this diet for 22 weeks. Growth was better than normal, the females reproduced repeatedly and reared their young. Three of the females gave birth to eight litters of 64 young and of these 58 were weaned, while the rest were found dead shortly after birth. The second generation animals, Lot 152, grew equally well and reproduction took place. They were remarkably thrifty in appearance, being unusually smooth and clean. Two of the litters of their young were weaned, when the experiment was discontinued. Clearly, the salt content was not the limiting factor in the work of the other investigators.

The calculated calorific value of Diet 6 is about 4.4 calories per gram, while that of Nelson, Heller, and Fulmer, previously mentioned and containing 5 per cent of salt and on which the animals were almost without exception sterile, is about 4 calories per gram. Since growth was good in both cases, it may be assumed that the food consumption, from the energy standpoint, was comparable in the two experiments. To secure 1000 calories would require the consumption of 227 grams of Diet 6, while 250 grams of the other diet under consideration would be required. This amount of the first diet contains about 18 grams of salt while the latter contains only about 12.5 grams of salt. Evidently, in consuming equivalent amounts of the two diets, from the energy content standpoint, the animals of Lot 122 consumed roughly 50 per cent more salt than did those on the diet on which reproduction was very unfavorable. There is apparently a very marked interrelationship of the various constituents of the diet.

Influence of Iron Salts

It was of interest to determine the behavior of animals on a diet consisting of whole milk powder supplemented by iron citrate alone. The beneficial action of iron added to the diet upon the reproduction of the pig has recently been pointed out by McGowan and Crichton.[6] Two different groups of rats have been carried on Diet 7, consisting of whole milk powder 99.8 and iron citrate 0.2 per cent. Growth is about normal. In Lot 78 several of the females reproduced, but only 4 young were weaned and they were decidedly inferior young. The animals of Lot 161, on the same diet, gave no evidence of reproduction though on the diet for 23 weeks. When, as in Diet 8, the content of iron was increased by adding 1.0 per cent of iron citrate, the results were notably better. Three females gave birth to young and, though only four litters were actually seen, it is certain that at least three more must have been born. Only young from the first litters were weaned. Lot 170, consisting of 2 males and 4 females, was continued on the diet as second generation for 13 weeks. Notwithstanding their good growth there was no evidence of reproduction. It was previously reported[7] that on a diet of whole milk powder 85, agar-agar 4, iron citrate 0.2, and dextrin 10.8 per cent, the young all perished within a very short time after birth. Later, on increasing the iron to 0.5 per cent, as was done in Diet 9, there was an improvement in the nutritive value of the diet. Each of 5 females gave birth to a litter of young and of the 45 born 43 were weaned. This experiment was discontinued at the end of 13 weeks. In view of the data presented, and of experiments now in progress but incomplete, it is believed that the influence of iron

in the diet upon reproduction may be very great, but it is a question whether it will be possible to supplement whole milk powder with iron alone in such a way as to cause the combination to induce normal reproduction and rearing of the young.

Having observed the effect of the added iron, the writers wished to repeat an early experiment of Osborne and Mendel[8] which has been widely cited in evidence of the adequacy of powdered whole milk as a food. Their diet consisted of whole milk powder 60, lard 28, and starch 12. The writers modified this, slightly changing the starch to 11.5 and adding 0.5 per cent of iron citrate. Lot 136 on this diet consisted of 3 males and 6 females. Growth was about normal and each female became pregnant, but apparently only once. Two of them died in parturition and autopsy revealed 5 and 12 apparently fully developed fetuses. One female gave birth to 4 young which were dead at birth and the remaining 3 gave birth to 18 young, of which 12 were weaned. The second generation, Lot 164, consisting of a male and 6 females, was continued on the diet for 16 weeks. There was no evidence of an advanced pregnancy, though growth seemed to be normal. Apparently, the added iron was beneficial but it did not completely overcome the handicap due to the high lard content of the diet.

Comparison of Whole and Skimmed Milk Powder

Osborne and Mendel[9] and McCollum and Davis[10] have reported on the vitamin content of milk powder. The former found about 24 per cent of whole milk powder necessary to give rise to vigorous growth when used as a source of vitamin B, while the latter found that the equal amount of skimmed milk powder gave very good growth when serving as the source of the same vitamin. The writers have made some trials with whole milk powder as a source of vitamin B and these incidentally bring out another interesting point in connection with reproduction. As indicated in the table, when 30 per cent of whole milk powder furnished all the vitamins in the diet it was possible to get the second generation animals to rear part of their young. Growth was uniformly better than normal. When 15 per cent of whole milk powder furnished all the vitamins there was repeated reproduction in the first generation. One of the females had to be killed on account of an abnormal tooth and this left only two females in the lot, as is indicated for Lot 93 in the table. The lot of second generation animals on this diet made sustained growth but at considerably below the normal and there was no reproduction among these animals. Lot 92, which derived its vitamins from 5 per cent of whole milk powder together with 5 per cent of butter fat, grew for only about 4 weeks. This group, Lot 92, received a total of about 7.2 per cent of butter fat in the diet, while Lot 93, getting all its vitamins from 15 per cent of whole milk powder, received only about 4.1 per cent of butter fat in the diet. Lot 94, getting its vitamins from 30 per cent of whole milk powder, had about 8.3 per cent of butter fat in the diet. Reproduction is possible, therefore, on diets containing small amounts of butter fat.

Having been successful in the employment of whole milk powder as a source of protein and vitamins in the diet for growth, reproduction, and rearing of young, it was natural to assume that skimmed milk powder so supplemented as to resemble whole milk powder in composition could be used equally well. However, this turned out to be not at all the case. Various diets have been devised, but as yet it has not been possible to get a diet containing skimmed milk powder which is anywhere near as satisfactory as some of the whole milk powder diets. Even though an attempt was made to imitate the composition of the best whole milk powder diet very closely, as concerns composition, by adding suitable amounts of butter fat, agar-agar, iron citrate, and dextrin, the results were totally different. Diet 18 compares closely in general composition with Diet 2. But the record for reproduction of Lot 103 on this diet is very unlike that of Lot 53. Of the comparatively few young born only a very few were weaned. Moreover, the first litters were not produced until the animals had been on the diet more than twice as long as was necessary in the case of Lot 53. An adequate explanation for this difference has not yet been given.

Thinking that there might be a difference in the method of manufacturing the two milk powders which could account for these findings, they were stated to the manufacturers, who replied that there was no difference in their method of powdering these two milk products, which would account for this difference in nutritive values.

Skimmed milk powder 60, iron citrate 0.2, agar-agar 4, butter fat 5 (cod-liver oil 5 per cent in one case), and dextrin to 100 was tried; and although there were 3 males and 5 females in each of these groups, Lots 159 and 160, not a single advanced pregnancy was ever noted. After being on the diet about 5 months the males averaged about 265 grams, the females about 195 grams.

Value of Wheat Embryo and Yeast

Two diets were devised to test the supplementing value of wheat embryo and of yeast. Lot 140, consisting of 2 males and 4 females, was fed a diet composed of skimmed milk powder 60, butter fat 5, iron citrate 0.2, wheat embryo (unextracted) 8, and dextrin to 100. Each female gave birth to a litter of young after having been on the diet about 7 weeks, the length of time usually required on the better whole milk powder diets, and furthermore, every one of the 32 young comprising these four litters was successfully weaned. Seven additional litters of young were apparently born, although only five litters consisting of 29 young were actually seen. Of the 61 young seen 56 were weaned. Of these young 2 males and 4 females were fed the same diet for a period of 5 months. They were fine appearing animals, but there never was any evidence of a pregnancy. In this case 8 per cent of wheat embryo supplemented a diet so that growth and reproduction were nearly or altogether normal during the first generation, although reproduction did not occur in the second generation. Without the wheat embryo even the first generation would have been sterile. Similarly, Lot 142 received skimmed milk powder 60, butter fat 5, iron citrate 0.2, air-dried yeast 5, and dextrin to 100. On this diet each of the 4 females produced a litter of young at the end of about 7 weeks after being started, and of the 22 young 19 were weaned. Two of the females produced an additional litter of 5 and of 6 young. Of these, 5 from the latter litter only were weaned. Here again 2 males and 4 females from these young were continued on the diet. Although they grew well and appeared entirely normal, there was no advanced pregnancy though they were observed until 5 months of age. Apparently, the 8 per cent of wheat embryo added was a little better in producing results than was the 5 per cent of added yeast. Clearly, wheat embryo and yeast supplement the skimmed milk powder, making it resemble somewhat nearer the whole milk powder as concerns its nutritive value for reproduction. The assumption of a vitamin having to do specifically with reproduction makes easy the explanation of the observations. If it is a vitamin that has to do specifically with reproduction, then it appears to be present in the air-dried yeast to an extent comparable to that present in wheat embryo.

Sure[11] has also studied the nutritive value of skimmed milk powder and has obtained some reproduction on skimmed

milk powders variously supplemented. In one diet there are included 35 per cent of skimmed milk powder and 61.9 per cent of rolled oats. In this laboratory very good reproduction was observed in the first generation on a diet in which 60 per cent of oat groats furnished all the protein and all the vitamins. Another diet employed by Sure contained 35 per cent of skimmed milk powder and 61.9 per cent of polished rice. From the chart it appears that the females weighed about 70 grams when started on this diet. The writers have had some success with reproduction on Diets 14 and 15, but in this case the rats were started at an initial weight of from 80 to 100 grams. Some young were weaned on Diet 14. No doubt this was possible only because of the comparatively advanced age of the experimental animals when placed on the diet. On a diet of polished rice 50, commercial casein 40, dextrin 10, and a liberal supply of whole milk, Sure secured four successful generations. The favorable effect of whole milk in the diet upon reproduction has been clearly pointed out by Palmer and Kennedy,[12] who say:

> Our results might also be interpreted to indicate a lack of something required for normal lactation, were it not for extensive unpublished data which we have showing that the addition of 10 cc. of whole milk (1.25 grams of milk solids) to the diet of rats which fail to grow normally, as well as reproduce, has resulted in the securing of normal rats in experiments which have, to date, reached the third generation.

Evans[13] has indicated that the oil of the wheat germ is a very potent source of a factor which favorably influences reproduction. There are in progress experiments designed to test the supplementary value of an ether extract of wheat germ, as well as a variety of other materials. Should these additions favorably affect reproduction on a ration well balanced with reference to salt, protein, the known vitamins, fat, and carbohydrate, it will be considered evidence in favor of a factor, probably a vitamin, having to do with reproduction.

In the meantime, the writers wish to accumulate further experimental data in an attempt to determine whether the assumption of an additional vitamin, or some other explanation, is the correct one.

Acknowledgment

The writers desire to thank the Merrell-Soule Company for the liberal supply of milk powders and the Fleischmann Company for the yeast.

Bibliography

1—Mathews, "Physiological Chemistry," 3rd. ed.
2—Merrell-Soule Co., "Klim," a pamphlet, **1921**.
3—Mattill and Stone, *J. Biol. Chem.*, **55**, 443 (1923).
4—Nelson, Heller, and Fulmer, *Ibid.*, **57**, 415 (1923).
5—McCollum and Davis, *Ibid.*, **19**, 245 (1914).
6—McGowan and Crichton, *Biochem. J.*, **18**, 265 (1924).
7—Anderegg, *J. Biol. Chem.*, **59**, 587 (1924).
8—Osborne and Mendel, *Ibid.*, **15**, 311 (1913).
9—Osborne and Mendel, *Ibid.*, **34**, 537 (1918).
10—McCollum and Davis, *Ibid.*, **20**, 415 (1915).
11—Sure, *Ibid.*, **58**, 681, 693 (1924).
12—Palmer and Kennedy, *Proc. Soc. Exptl. Biol. Med.*, **20**, 506 (1923).
13—Evans, *Science*, **60**, 20 (1924).

Water Solubility of Various Wood Tars[1]

By H. N. Calderwood, Jr.

FOREST PRODUCTS LABORATORY, MADISON, WIS.

IN THE course of an investigation of the suitability of various wood tars for treating fish-net twine, A. V. Ruiz, of Vera Cruz, Mexico, determined the solubility in water of the different tars used. The method used was one devised by the writer[2] for solubility studies of the dissolved tar from hard maple.

The tar and distilled water were mixed in definite proportions in a separatory funnel and stirred vigorously for an hour at room temperature with a motor-driven stirrer. The tar and water mixture was then allowed to stand overnight before separation. A portion of the water layer was then distilled for dissolved tar by the usual method.[3] The results of this work are shown in the accompanying table. All the hardwood tars had been prepared in the experimental retort in this laboratory, but the pine tar was a commercial sample. The ratios of water to tar are expressed in parts by weight. These ratios correspond to those existing between the tars and their respective pyroligneous acids.

Solubility of Various Wood Tars in Water

(Grams of tar per 100 ml. of water)

KIND OF TAR	RATIO		Solubility
	Water	Tar	
Hard maple:			
Raw settled	10	1	1.05
Boiled	10	1	0.60
Steamed	10	1	(*a*)
Dissolved	3.38	1	8.60
Pine tar, raw	5	1	0.225

(*a*) This tar was so viscous that good mixing with the water was impossible.

The raw settled hardwood tar was the material obtained by allowing the crude condensate from the retort to stand until it was no longer turbid. The boiled tar was obtained from the raw settled tar by heating in an oil bath held at 150° C. until no further distillate was secured. The steamed tar was obtained by subjecting a portion of the boiled tar to steam distillation until the oil condensate had a specific gravity greater than the water condensate. The preparation of the dissolved tar has been described elsewhere.[2]

Examination of the results shows that removal of the more volatile constituents decreases very markedly the water solubility of the hardwood settled tar. Probably the constituents whose removal caused the decreased solubility were those soluble in the aqueous portions of the distillates, although this point was not checked by returning the oil portions of the distillates to their respective tars and again determining the water solubility. This point would not be of commercial importance, because the wood distillation plants are able to dispose of the oil distillates very readily as "chemical oils," while the residual hardwood tars are very rarely disposed of other than as a source of fuel in the plant. A discussion of the solubility of the dissolved tar has been given elsewhere.[2] Other than to mention the low solubility of the pine tar no discussion can be given because its history is unknown.

The data are of value in all cases where any of these tars are used in mixture with water or in cases where after application they will be exposed to action of water.

[1] Received February 19, 1925.

[2] Dissertation, University of Wisconsin, 1923. Abstract in THIS JOURNAL, **17**, 149 (1925).

[3] *U. S. Dept. Agr., Bull.* **129**, p. 6.

Selenium Compounds as Spray Materials[1,2]

By F. Marion Lougee with B. S. Hopkins

UNIVERSITY OF ILLINOIS, URBANA, ILL.

THE object of the present investigation was to study the relative toxicities of selenium and selenium compounds in order to determine their suitability for use as insecticides, fungicides, herbicides, and the like. Inasmuch as selenium and sulfur are strikingly alike in their properties, except that compounds of selenium in general are more toxic than those of sulfur, it was believed possible that selenium may find successful application along these lines.

Sulfur is the basis of many of our more important sprays. Since selenium is more toxic than sulfur, it should be more efficient in destroying parasitic forms of life. Many solutions containing selenium in a variety of forms have been tried as spray materials against apple scab and bitter rot. Leaf injury is too great to permit the successful use of selenium for these purposes, but there is prospect of success in their use as dormant sprays against such pests as pear blight and oyster-shell scale. The most promising use of these selenium solutions is for the eradication of broad-leaved plants such as dandelions and plantain from fields and lawns.

The physiological effects of selenium and its compounds have been the subject of rather extensive investigations. In the living organism selenates are reduced to selenites and the latter to metallic selenium, which is subsequently transformed, according to Maassen,[3] into selenium ethyl, $Se(C_2H_5)_2$, in the case of animals, or into selenium methyl, $Se(CH_3)_2$, in the case of microbes.

Chabrié and Lapicque,[4] Czapek and Weil,[5] Jones,[6] Woodruff and Gies,[7] and Lehman,[8] who have made careful studies of the effect of selenium and its compounds on the animal organism, were unable to demonstrate any direct toxic action on the cells. They conclude that selenium compounds act poisonously on the animal body as a whole and that selenites are more poisonous than selenates, whereas elementary selenium is nonpoisonous.

Some attempts have been made to find applications of selenium compounds in medicine, especially as remedies for cancer, but the utility of selenium for this purpose is extremely doubtful and Keysser[9] maintains that selenium compounds are not true curative agents for cancer.

Numerous investigators have studied the effects of selenium compounds on widely divergent types of bacteria. Because of their ease of reduction, selenites are coming into rather extensive use for the detection of bacterial life. The particular effects vary with the bacterial species.

A few studies have also been made of the effects of selenium compounds on fungi. In 1902, Maassen and Rosenheim[10] called attention to the fact that analogous organic compounds of arsenic, selenium, and tellurium are formed by the action of fungi and bacteria, and that it is therefore necessary, in applying the biological test for arsenic, to take into consideration the possible presence of selenium and tellurium. Nemec and Kas[11] have made a study of the influence of selenium on the metabolism of certain molds.

The effect of selenium on plants has recently become a subject of considerable interest. Turina[12] examined the action of selenites and selenates as well as other salts, on the germination of barley, mustard, and Lepidium plants, and on the mature plants. He concluded that these salts entered the plant system by way of the root-cap. Stoklasa[13] undertook to determine the influence of selenium on vegetable growth in the presence and in the absence of radioactivity. He found that selenites were invariably more toxic than selenates and that the toxicity of selenium compounds was inhibited by radium emanations.

Such in brief is the history of selenium from the biological standpoint. Although the toxicity of selenium and its compounds has been studied in considerable detail, no attempts have apparently been made to apply either selenium or its compounds along horticultural lines as spray materials. Such attempts were made in the present investigation.

Preliminary Experiments of 1920–21

Assuming that the principal chemical reaction involved in the manufacture of lime-sulfur is represented by the equation

$$3Ca(OH)_2 + 12S \rightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$$

selenium[14] analogs were prepared, using the proportions called for by the following equations:

$$3CaO + 12Se \rightarrow 2CaSe_5 + CaSe_2O_3$$
$$6NaOH + 12Se \rightarrow 2Na_2Se_5 + Na_2Se_2O_3 + 3H_2O$$

Since the lime and selenium did not unite readily when cooked up according to the ordinary rules for lime-sulfur, the lime-selenium was prepared by fusing the materials together in a covered crucible. The resulting product, on treatment with boiling water, dissolved to a wine-red solution, leaving considerable residue.

The soda-selenium was easily obtained by evaporating down on a steam bath aqueous sodium hydroxide and selenium in the proper proportions. The product was, when freshly prepared, completely soluble in water to a mahogany-red solution, but the solubility decreased on standing, owing to the separation of elementary selenium.

These materials were subjected to a series of laboratory

[1] Received September 27, 1924.

[2] Submitted by Miss Lougee to the faculty of the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of doctor of philosophy.

[3] *Arb. kais. Gesundh.*, **18A**, 475 (1902).

[4] *Compt. rend.*, **110**, 152 (1890).

[5] *Arch. exp. Path. Pharmakol.*, **32**, 438 (1893).

[6] *Biochem. J.*, **4**, 405 (1909).

[7] *Am. J. Physiol.*, **6**, 29 (1902).

[8] *Biochem. Z.*, **134**, 390 (1922).

[9] *Z. Chemotherap. 11 Orig.*, 188 (1914).

[10] *Proc. Chem. Soc. (London)*, **18**, 138 (1902).

[11] *Compt. rend.*, **171**, 746 (1920).

[12] *Biochem. Z.*, **129**, 507 (1922).

[13] *Compt. rend.*, **174**, 1075 (1922); **174**, 1256 (1922); *Biochem. Z.*, **130**, 604 (1922).

[14] The selenium used in all experiments, unless otherwise specified, was the gray, metallic selenium supplied by the Baltimore Copper Smelting and Refining Company. Selenious acid from the same source was also used in the later experiments.

and field tests in the horticulture department of the university. The laboratory tests with lime-selenium showed that this material was toxic, but field tests failed to confirm the favorable results, because great difficulty was experienced in getting the lime-selenium into solution and the toxic powers of the spray did not measure up to expectations. The soda-selenium could not be criticized on grounds of insolubility, but any possible advantages were counterbalanced by its extremely caustic properties which defoliated the trees and caused the fruits to drop.

Field tests were also made with atomic selenium—finely powdered, gray, metallic selenium—but the indications were that this material was altogether too coarse to be of any value as an insecticide or fungicide.

Colloidal red selenium was used in the next field tests. This was prepared by boiling selenium with aqueous sodium sulfite solution, diluting and acidifying with a few drops of dilute sulfuric acid according to the method of Julius Meyer[15] who represents the chemical reactions as follows:

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3$$
$$Na_2SeSO_3 + H_2SO_4 \rightarrow Se + SO_2 + H_2O + Na_2SO_4$$

This material was tried out on a single tree against *Venturiapomi*, the fungus causing apple scab, and the first series of applications apparently gave as good results as those obtained with lime-sulfur and lead arsenate, the standard spray, as there was a heavy infection of scab on the fruit of the trees used as checks. Unfortunately, however, serious injury to the trees later developed.

Experiments of 1921–22

Since the results of the earlier experiments were by no means conclusive and the necessity of testing the sprays under a variety of conditions was recognized, it was deemed advisable to coöperate with the department of horticulture in carrying out a series of laboratory and field tests to establish more definitely the possibilities of selenium sprays.

During the fall and winter of 1921-22, Emil Guba, research assistant for W. A. Ruth, assistant professor of pomological pathology, carried out a series of laboratory tests against *Phyllosticta solitaria*, E & E, the fungus causing apple blotch, using solutions of 200-mesh lime-selenium, freshly prepared soda-selenium, potassium polyselenide, and sodium selenite, with the corresponding sulfur compounds to serve as checks.

The potassium polyselenide was designated in the earlier experiments as "potassium selenosulfocarbonate," because it was made by passing hydrogen selenide in excess into the calculated amounts of strong potash solution and carbon disulfide in the expectation of obtaining a solution of K_2CSeS_2, analogous to potassium sulfocarbonate, K_2CS_3, which is used to destroy the phylloxera of grapevines. That such a compound was not formed, however, and that the dark wine-red liquid obtained was a solution of potassium polyselenide became apparent later when it was found that the volume of carbon disulfide remained unchanged after the hydrogen selenide was passed into it. The true chemical reactions, therefore, may be represented as follows:

$$H_2Se + 2KOH \rightarrow K_2Se + 2H_2O$$
$$2H_2Se + O_2 \rightarrow 2Se + 2H_2O$$
$$K_2Se + (X - 1)\,Se \rightarrow K_2Se_x$$

The sodium selenite was made by neutralizing commercial selenious acid with caustic soda in accordance with the equation

$$H_2SeO_3 + 2NaOH \rightarrow Na_2SeO_3 + 2H_2O$$

The laboratory tests with the lime-selenium and soda-selenium indicated that the toxicity of these compounds was comparatively low, but the potassium polyselenide and sodium selenite were sufficiently promising to warrant further tests in the field. Accordingly, trees infected with the fungus causing apple blotch were sprayed with these solutions at the rate of 7.6 liters (2 gallons) per tree. Each solution was made up in such a way that the concentration of selenium was 6304 parts per million, since this corresponded to the concentrations used in the laboratory experiments. These sprays gave good control of the apple blotch fungus but the foliage of the trees was severely injured.

Experiments of 1922–23

In view of the foregoing results it was thought best to conduct a series of laboratory and field experiments to determine the upper and lower limits of the toxicity of selenium compounds. This work was done with the assistance of H. W. Anderson, assistant professor of pomological pathology. The considerations governing the choice of spray materials for the laboratory tests were ease of preparation and stability of compounds; hence the decision to use selenious acid and sodium selenite. Owing to the few difficulties offered in the way of propagating and maintaining a satisfactory supply of spores, the fungus chosen was the organism causing bitter rot, *Glomerella cingulata* (Stoneman) Spaulding and Von Schrenk.

Laboratory Work—Six slides were sprayed by means of an atomizer with a standard solution of selenious acid, and six other slides with sodium selenite. After the spray had dried, five drops of water in which spores were held in suspension were placed on each slide, which was then put in a Petri dish along with a check in the form of an unsprayed slide also bearing five drops of water holding suspended spores. The Petri dishes were kept in a 20° C. incubator and counts of the germinated spores made at regular intervals. In the standard solutions of selenious acid and sodium selenite the concentration of selenium was 6304 parts per million. These solutions were used at different dilutions ranging from 6304 to 63.04 parts per million.

Repeated experiments showed that the minimum strength of selenious acid that permitted no germination of spores was one-third that of the standard solution, while none of the concentrations of sodium selenite used gave complete inhibition.

The next step was to test the sprays under field conditions in order to determine whether or not the strength that prevented germination of spores in the laboratory would show equal efficiency in the orchard without any accompanying injury to the trees.

Field Work—Before application of the sprays on the large scale, preliminary tests were made by spraying separate branches with the solutions, using an atomizer. In this way it was found that the concentration that prevented germination of spores in the laboratory experiments injured the oliage of the trees in every case. Hence the sprays were further diluted for application on the large scale. The concentration of selenium in the selenious acid used was 350 parts per million; in the sodium selenite, 500 parts per million; and in the potassium polyselenide, which was also used in the field tests, 2100 parts per million. A power spray rig was used for the application of the materials and two Ben Davis trees were sprayed with each solution, allowing 56.7 liters (15 gallons) per tree. A seventh unsprayed tree served as a check.

The first spray applied was the calyx spray, May 14, 1923. A heavy rainstorm followed about an hour after application so that it was impossible to determine the effects of the solutions. The next spray was put on a little over a week later, on May 25. The trees were subsequently kept under observation and it was soon evident that considerable in-

[15] *Z. Elektrochem.*, **25**, 80 (1919).

jury was developing. As approximately half of the leaf surface turned brown, it was considered wise not to apply the full number of sprays, as it seemed highly probable that concentrations weak enough to insure against injury to the foliage would not be strong enough to prevent the growth of the undesirable fungi.

Experiments of 1923–24

In spite of these rather discouraging results, it was still believed possible that the toxicity of selenium might find some useful applications. Inasmuch as selenium compounds had shown themselves injurious to the foliage of trees as well as to fungi, it seemed likely that these compounds might prove effective as dormant sprays, or as sprays to be applied to the trunks or branches of trees, which are comparatively resistant. Furthermore, consideration of the fact that the intensity of injury from the selenium compounds corresponded roughly to the amount of leaf surface presented, suggested the possibility of using these compounds for the eradication of weeds.

In order to test the correctness of this theory, rather extensive experiments were carried out in the summer and fall, using selenium compounds as sprays against various obnoxious weeds. Selenious acid and sodium selenite in varying volumes at concentrations of selenium ranging from 791 to 19,180 parts per million in the case of the selenious acid and 791 to 18,978 parts per million in the case of the sodium selenite, were applied to plots of known area on which dandelions, plantain, burdock, grass, and clover were growing and observations were made at regular intervals. The stronger solutions attacked and injured all the vegetation, but with selenious acid at a concentration of 791 parts of selenium per million applied at the rate of 1.2 liters per square meter (1 liter per square yard), the dandelions, plantain, and burdock were completely shriveled, while the grass and clover suffered very little injury.

A second series of experiments made in early spring, using a concentration of selenious acid equivalent to 614 parts of selenium per million applied at the rate of 1350 cc. per square meter (125 cc. per square foot), resulted in severe injury to the grass and clover as well as to the dandelions, plantain, and burdock. These results, which failed to harmonize with the results of the earlier experiments, might possibly be explained on the basis of the relatively greater susceptibility to injury shown by all young vegetation. An application of 100 cc. of selenious acid containing 6140 parts of selenium per million to individual dandelions destroyed these without any attendant injury to the surrounding vegetation.

In pursuance of the idea that selenium compounds might prove effective as dormant sprays, or as sprays that would not of necessity involve application to the leafy parts of the trees, it was thought possible that pear blight might be combated successfully by means of selenium preparations. Hence a pure culture of *Bacillus amylovorus* (Burr) Trev. was secured and a series of laboratory tests made in order to determine which compounds would be effective.

A loopful of a beef broth culture of the organism causing pear blight was transferred to 5 cc. of each of the various solutions, and after the bacteria had been exposed to the action of the chemicals for a definite number of minutes, a loopful was removed from each test tube, introduced into sterile beef broth, and left for incubation at room temperature or in the 30° C. incubator. Growth of bacteria was indicated by turbidity of the medium.

The solutions used were sodium selenite, selenious acid, alcoholic selenious acid, furfural and selenious acid, furfural alone, and ammoniacal zinc selenite made by dissolving precipitated zinc selenite in concentrated ammonium hydroxide. The inclusion of the last-named compound in the test materials was prompted by recollection of the experiments of Hayward Reed, of Sacramento, Calif., who attained some degree of success in his experiments with zinc chloride against the pear-blight bacillus.[16]

The most promising of all the materials tested was selenious acid. This acid at a selenium concentration of 6140 parts per million caused the death of the organisms in the case of cultures 1, 2, and 3 months old, whereas 24-hour cultures were killed by a concentration of 682 parts of selenium per million, as shown by the following table:

Effect of Selenious Acid on 24-Hour Cultures

Concn. of selenium P. p. m.	Time of Exposure: 20 Minutes 1	2	3	4	25 Minutes 1	2	3	4
6140	−	−	−	−	−	−	−	−
3070	−	−	−	−	−	−	−	−
2146	−	−	−	−	−	−	−	−
1535	−	−	−	−	−	−	−	−
1228	−	−	−	−	−	−	−	−
1023	−	−	−	−	−	−	−	−
877	−	−	−	−	+	−	−	−
767	−	−	−	−	−	−	−	−
682	−	−	−	−	−	−	−	−
614	−	−	−	+	−	−	−	+
558	+	−	−	−	−	−	−	−
512		−	−	−		−	−	−
472		−	−	−		−	−	−
438		−	−	+		−	−	+
409		−	−	+		−	−	−
384		−	−	−		−	−	−
361		+	−	+		−	−	+
341		−	−	−		−	−	−
323		+	−	−		−	−	−
317		+	+	+		−	−	+

Inasmuch as bacteria of various ages would be encountered under field conditions, it was deemed advisable to adopt selenious acid containing 6140 parts of selenium per million as the standard solution for subsequent field work on pear blight. Accordingly, in preparation for the field tests, an attempt was made April 16, 1924, to inoculate twigs of pear trees in one of the university orchards by means of the laboratory cultures. The field tests were never carried out, however, owing to the failure of the attempted inoculation, which might have been due to a lack of virulence on the part of the cultures, or to very unfavorable weather conditions. A few minor experiments were carried out against oyster-shell scale, *Lepidosaphes ulmi*, with the idea that the same concentration of selenious acid that had proved effective under laboratory conditions against the organism causing pear blight might also be effective in this case. Two small willow trees about 1 and 1.7 meters (3 and 5 feet) high, respectively, were sprayed March 27, 1924, with the standard selenious acid at the rate of 1.9 liters (0.5 gallon) per tree, 3.78 liters (1 gallon) of the spray were also applied April 5, 1924, to a white lilac bush about 2 meters (7 feet) high, which was badly infested with the scale. A week later the scale was dry, showing a tendency to slough off, and observations made on the lilac bush at various times during the spring indicated that it was in a healthy condition. More extensive experiments with the selenious acid against pear blight and oyster-shell scale could not be undertaken at the time, but it is hoped that the investigation can be continued at a later date.

Conclusions

1—The selenium sprays so far tested are unsatisfactory for application to the leafy parts of trees, because the concentrations that prevent germination of fungal spores of such diseases as apple blotch and bitter rot are injurious to the foliage of trees.

2—The caustic properties of selenium compounds which make them undesirable for spraying trees in leaf may not prevent their possible usefulness as dormant sprays or sprays to be applied to the more resistant parts of trees or other

[16] *Am. Fruit Growers' Mag.*, June, 1923.

plants. Among the diseases or insect pests which might be combated successfully by means of such sprays are pear blight, oyster-shell scale, blister canker, crown-gall, and the like.

3—Selenium compounds are deleterious to certain plants such as dandelions, plantain, burdock, etc., while the injury to grass and clover is less severe; hence these chemicals may prove useful as weed eradicators.

The Determination of Cyanamide[1]

By L. A. Pinck

Fixed Nitrogen Research Laboratory, Washington, D. C.

In the course of an investigation at this laboratory on cyanamide and some of its derivatives, unsatisfactory results were obtained in the quantitative determination of cyanamide, particularly in the presence of relatively large amounts of derivatives, such as dicyanodiamide, urea, guanylurea, and guanidine. A study was therefore made of the effect of various concentrations of these compounds on the determination of cyanamide in the two most promising analytical methods. The results of this study are briefly presented together with a description of an analytical procedure for cyanamide which was developed and has been found to be very satisfactory in the work at this laboratory.

SEVERAL methods and many modifications have been proposed for the quantitative determination of cyanamide. Nearly all of them are based on the precipitation of cyanamide as a silver salt, and the determination of the cyanamide on the basis of nitrogen or silver.

Previous Methods

Perotti[2] first developed a titration method consisting in the addition of an ammoniacal extract of calcium cyanamide to a definite quantity of silver nitrate solution, the filtration of the silver cyanamide precipitate, and the titration of the excess silver nitrate with standard thiocyanate solution. Kappen[3] modified this method by acidifying the cyanamide solution to convert the calcium into a neutral salt and then adding a slight excess of ammonia. He also stipulated the use of dilute solutions. Grube and Krüger[4] modified the Kappen method by adding the silver nitrate to an acid solution and then making it ammoniacal. In the Caro method[5] the precipitation was made with an ammoniacal silver acetate solution and the cyanamide was determined by kjeldahling the silver cyanamide precipitate. Brioux[6] modified the Caro method by using silver nitrate instead of the acetate and titrating silver in the silver cyanamide. Another method, consisting in the hydrolysis of cyanamide to urea and the determination of the latter, had been proposed by a number of investigators,[7] but the writer did not find that method quantitative. Marquerol and co-workers[8] made a comparative study of most of the methods and found them all to be inaccurate; however, the Caro method gave the best results.

The method employed in the early work of this laboratory was a combination of the Caro and Brioux methods (hereafter referred to as the Caro-Brioux method), consisting of the addition of silver nitrate solution to an ammoniacal solution of cyanamide and the determination of the nitrogen in the silver cyanamide by the Kjeldahl-Gunning method. The results were unsatisfactory, being high in some cases and low in others. That the solubility of the silver cyanamide, either in the solution from which it was precipitated or in distilled water, was not in part responsible for the unsatisfactory results was soon demonstrated, and hence attention was directed to the effect of the presence of various quantities of cyanamide derivatives.

Experimental

A series of cyanamide determinations was therefore made on crude calcium cyanamide extracts to which varying amounts of urea, guanylurea sulfate, guanidine nitrate, and dicyanodiamide were added. To each 50-cc. aliquot of crude calcium cyanamide extract, containing approximately 50 mg. of cyanamide nitrogen, 5, 25, 50, and 100 mg. of the above substances were added. The results are given in Table I. Since the first set of results on the extracts containing dicyanodiamide was divergent, that set was repeated.

Table I—Effect of Various Cyanamide Derivatives on Determination of Cyanamide by the Caro-Brioux Method

Material added to 0.25 gram crude $CaCN_2$	Per cent Cyanamide N as Determined in Presence of				
		Guanylurea	Guanidine	Dicyanodiamide	
Gram	Urea	sulfate	nitrate	1st set	2nd set
None	19.12	18.97	18.87	18.95	18.87
0.005	19.09	18.97	18.92	19.76	19.58
0.025	19.13	19.15	19.07	20.86	21.59
				20.38	21.66
				20.65	21.66
0.050	19.20	19.24	19.29	21.70	21.48
				21.66	21.19
				21.55	21.64
0.100	19.24	19.29	19.44	20.20	22.90
				22.55	22.08
				22.54	22.37

These results show that the method is not reliable for samples containing large amounts of cyanamide derivatives, dicyanodiamide interfering most.

The development of a volumetric method in which cyanamide derivatives would not interfere was then undertaken. To a 50-cc. aliquot of crude calcium cyanamide extract there were added 1 cc. of concentrated ammonium hydroxide and varying amounts of ammoniacal silver nitrate solution. The silver cyanamide precipitate was filtered off at the end of 2 hours. The silver was determined either in the filtrate or in the precipitate by means of potassium thiocyanate in acid solution. The Caro-Brioux method was used as a check. Table II shows the results obtained with different samples of calcium cyanamide (or mixtures containing cyanamide) and with varying amounts of silver nitrate.

[1] Received March 7, 1925.

[2] *Gaz. chim. ital.*, **35**, II, 230 (1905).

[3] *Landw.Vers.-Sta.*, **70**, 455 (1909).

[4] *Z. angew. Chem.*, **27**, I, 326 (1914).

[5] *Ibid.*, **23**, 2405 (1910).

[6] *Ann. sci. agron.*, April, 1910.

[7] Monnier, *Chem. Ztg.*, **35**, 601 (1911); Fosse, et al., *Compt. rend.*, **179**, 408 (1924).

[8] *Ann. chim. anal.*, [2] **2**, 164 (1920).

Table II—Comparison of Caro-Brioux and Volumetric Methods Using Varying Amounts of $AgNO_3$

Sample	Caro-Brioux Method Per cent cyanamide N	Volumetric Method Excess 0.25 *N* $AgNO_3$ Cc.	Per cent cyanamide N		Remarks
1 Crude	18.09	1	18.03	18.03	
$CaCN_2$	18.12	2	18.07	...	
2 Crude	19.32	2	19.32	19.28	
$CaCN_2$	19.32	6	19.30	19.30	
3 H_2CN_2	65.03	6	65.02	65.21	
4 Crude $CaCN_2$	3.73	1	3.65	3.67	
$+K_2SO_4$	3.75	5	3.75	3.74	
5 Crude $CaCN_2$ $+KCl$	2.36	..	1.71	1.71	4.91% dicyanodiamide N 1.82% urea *N*
6 Crude	7.34	3	6.46	6.44	4.92% dicyanodiamide N 2.24% urea *N*
$CaCN_2$	7.45	6	6.44	6.43	

This table shows that the results of the two methods are in very close agreement for samples of cyanamide which do not contain any dicyanodiamide or urea, but that they differ in the presence of these compounds. Moreover, the results are constant with varying amounts of ammoniacal silver nitrate.

A comparison of the two methods was then made on a cyanamide extract and on the same extract to which dicyanodiamide and urea had been added. The composition of the latter solution was approximated as follows: cyanamide nitrogen, 15 per cent; dicyanodiamide nitrogen, 75 per cent; and urea nitrogen, 10 per cent. The results are shown in Table III.

Table III—Determination of Cyanamide in Solutions Having a High Concentration of Cyanamide Derivatives

(Figures in per cent)

Cyanamide Solution Alone		Cyanamide Solution Containing Dicyanodiamide and Urea		
Caro-Brioux method	Volumetric method	Caro-Brioux Method Ag titration	Caro-Brioux Method Kjeldahl N	Volumetric method
19.25	19.22	22.98	22.43	19.68
19.17	19.15	23.82	21.87	19.64
19.22	19.22	22.36	23.25	19.64

These results again indicated that by the Caro-Brioux method of precipitation of silver cyanamide in the presence of dicyanodiamide some silver dicyanodiamide was also precipitated. Kappen[3] found that his method was quantitative for pure cyanamide or calcium cyanamide not containing any other nitrogenous compounds and that dicyanodiamide interfered most. The volumetric method also gave results somewhat too high (0.4 per cent), and it was therefore concluded that reprecipitation was necessary. This was effected by dissolving the filtered and washed precipitate with dilute nitric acid and reprecipitating by the addition of ammonium hydroxide. Low results were occasionally obtained, however, owing to the combined solvent action of the ammonium nitrate in the presence of excess ammonia, previously pointed out by Grube and Krüger,[4] and as shown by the following experiment:

Cyanamide determinations were made by the volumetric method on 50-cc. aliquots of a crude calcium cyanamide extract to which 2 grams of ammonium nitrate were added. To one sample the usual excess of ammonia was added while in another the cyanamide was precipitated without the addition of ammonia. The results are given in Table IV.

Table IV

Sample Containing	Per cent cyanamide N
No NH_4NO_3	20.95
	20.92
2 grams NH_4NO_3 + 1 cc. NH_4OH	20.52
2 grams NH_4NO_3	20.70

That the solvent action of ammonium nitrate could be reduced by proper dilution was shown by an experiment in which 2 grams of ammonium nitrate were added to 25-cc. aliquots of cyanamide solution. One solution was diluted with 100 cc. of water, another with 200 cc., and then 40 cc. of 0.1 *N* ammoniacal silver nitrate were slowly added to each. The precipitate was filtered, dissolved, and titrated in the usual manner. The results are shown in Table V.

Table V

Sample Containing	Mg. cyanamide N
No NH_4NO_3	58.5
	58.5
2 grams NH_4NO_3 and diluted with 100 cc. H_2O	58.6
	58.5
2 grams NH_4NO_3 and diluted with 200 cc. H_2O	58.6
	58.7

Reprecipitation with the proper dilution was tried on the solution previously mentioned, containing 15 per cent of the nitrogen in the form of cyanamide, 10 per cent as urea, and 75 per cent as dicyanodiamide. The cyanamide determination checked very closely with the amount of cyanamide put in the solution, the potassium thiocyanate titration for cyanamide alone being 8.83 cc. and that for the solution containing dicyanodiamide and urea, 8.85 cc.

Method

A 2-gram sample of crude calcium cyanamide is extracted for 2 hours with 400 cc. of water in a shaking machine. After filtering, 50-cc. aliquots are pipetted into 250-cc. beakers, 1 cc. concentrated ammonia is added, and ammoniacal silver nitrate run in with constant stirring from a buret at such a rate that the drops can be counted very readily. If the sample is in solution, an aliquot equivalent to about 50 mg. nitrogen is taken for analysis. After standing for 15 minutes the precipitate is filtered off through a Gooch crucible containing an asbestos mat. The silver cyanamide precipitate is washed eight to ten times with distilled water, then dissolved with dilute nitric acid (approximately 1 *N*) and titrated with standard thiocyanate solution in the presence of ferric alum indicator.

In the presence of a very large amount of dicyanodiamide it is necessary to redissolve the silver cyanamide precipitate in dilute nitric acid. This can easily be accomplished by running dilute nitric acid (not over 25 cc. normal acid) through the Gooch containing the silver cyanamide with the use of suction. The Gooch is well washed with distilled water. Reprecipitation is made by first diluting the solution to 150–200 cc. and then adding a few cubic centimeters of ammoniacal silver nitrate and as much ammonia as is necessary to make the solution barely alkaline. The solution is well stirred, and after standing for at least 2 hours it is filtered, the precipitate washed, dissolved, and titrated with standard potassium thiocyanate as described above.

If carbide is present in the sample it is necessary to kjeldahl the silver cyanamide precipitate instead of titrating it.

Japanese Dyestuff Subsidy Continued—According to a cable received from Acting Commercial Attache Rhea, Tokyo, the Japanese Diet, before its adjournment on March 31, passed an act encouraging the Japanese dyestuffs industry. The act carries a subsidy not to exceed 1,000,000 yen per year, for six years (1 yen = $0.416, at the exchange prevailing April 2), which is about one-half the former figure.

The government has been guaranteeing an 8 per cent dividend on the stock of the Nippon Senryo Sciso Kaisha (Japan Dye Manufacturing Company), which has been subsidized to the extent of approximately 2,000,000 yen yer year.

It is said that as many as sixty varieties of coloring materials have been manufactured, of which only about thirty-five have proved successful. There has been a tendency to import the more expensive and complicated dyes, and to manufacture the cheaper and less difficult.

Imports of dyes into Japan have been very heavy during the past year, and it has been impossible for domestic dyes to compete in the market on either a color or a price basis.

Test for Comparing Detergent Efficiencies of Soaps[1]

By Robert M. Chapin

Biochemic Division, Bureau of Animal Industry, Washington, D. C.

A test for the relative deflocculating or detergent efficiencies of soaps is based upon the observation that when dilute soap solutions are shaken with powdered flake graphite in presence of air the appearance of a white band at the lower boundary of the froth indicates the presence of an excess of soap. The graphite is standardized against an ammonium palmitate solution containing sufficient excess of ammonia to insure maximum detergent power. A table shows the analyses, the detergent coefficients, and the costs per unit of detergency, of eleven unidentified samples of commercial cake soaps.

FOR the valuation of a complex and variable material intended for a single specific application a properly designed test for *performance* often affords data of greater practical usefulness than the results of a chemical analysis. Still more often the one very advantageously supplements the other. Soaps, as a class, constitute a material of notoriously complex and variable composition, which is used primarily for the single purpose of cleansing. Notwithstanding long recognition of the obvious need, no test for cleansing efficiency yet proposed has received general acceptance, and chemists still depend almost entirely upon data of composition for determining the relative merits of competitive samples.

Heermann[2] has recently described an elaborate test which is essentially a miniature washing experiment on a standard fabric previously impregnated with a standard soiling material. There can be no objection to a test which so closely parallels service conditions provided only that it is not impractically cumbersome and that it actually proves capable of distinguishing between various samples with sufficient precision.

Tests based on the determination of surface tension or interfacial tension appear not entirely satisfactory. They are really only tests of wetting power[3] and are therefore too inclusive, for many substances greatly promote wetting power without notably increasing detergency. It is not enough for a detergent solution merely to wet the dirt, it must emulsify or deflocculate it; that is, the mutual attraction between the particles of dirt must be overcome so that each particle floats free in the medium and therefore may, under the influence of sufficient agitation, wander out from amid the fibers of the goods into the bulk of the washing solution. A comparison between the emulsifying powers of various soap solutions upon a standard oil might thus constitute a useful index of their relative detergent efficiencies were it not that there seems no way to standardize the size of the globules so that equal volumes of oil shall correspond to equal interfacial areas. The same objection, to neglect others, applies with equal force to "suds tests" in which emulsions of air are compared with one another. It therefore becomes necessary to employ a test substance of preformed and fixed surface area, such as a finely divided uniform powder which is insoluble in and chemically inert toward the medium. McBain[4] and his co-workers have adopted a certain brand of carbon black and estimate the deflocculating power of a soap solution by determining how much of the test substance is carried through the pores of a standard filter paper on simple filtration, expressing the result as the "carbon number" of that solution. This test ought to be of some value in the study of soap solutions, but the data presented were too scanty to enable a definite estimate of its capabilities. If it is to be utilized as a test for comparing the potential detergent efficiencies of different soaps, it seems that a definite carbon number will have to be adopted as standard and then the minimum concentration of each soap necessary to reach that carbon number determined.

Rationale of Proposed Test

The proposed test, like that of McBain, Harborne, and King, utilizes a finely divided inert powder as the standard dirt, but powdered flake graphite is chosen for the purpose. Its advantage over any form of charcoal lies in its freedom from porosity so that equilibrium in adsorption is reached in a far briefer time. The use of anything in the way of standard fabric is eliminated on the assumption that a determination of the efficiency of a soap solution in separating dirt from dirt will be practically as useful an index to its cleansing power as its ability to separate dirt from fabric.

After pure flake graphite has been shaken with pure water in presence of air it quickly subsides, leaving a slight film upon the surface but no froth. When a minimal proportion of soap is also present a scanty but persistent stiff black froth is produced. Under a magnifying glass the individual bubbles appear completely armored with a coherent coating of graphite flakes. In such concentrations the soap apparently is not acting as a detergent and, in fact, very likely renders the "dirt" more "sticky" than it would be in pure water. But when sufficient soap is present the aspect of the froth greatly changes. It is much more voluminous and much paler, and inspection with a magnifying glass shows the few particles of graphite entangled in it to have lost all mutual attraction and to be individually sliding down within the films under the pull of gravity. Certainly the soap, thus forming a typical "suds," is now fully functioning as a detergent. Somewhere between the extremes must lie a critical concentration at which the soap is no longer completely exhausted by the graphite but is just beginning to impart an excess of deflocculating or detergent power to the liquid. Fortunately, there exists a phenomenon which seems to indicate this critical concentration with fair precision. So long as graphite is in excess the froth appears uniformly gray from top to bottom. As soon as a slight excess of soap is present the bottom of the quiescent froth becomes notably paler than the overlying portion owing to the slow rise of many minute persistent bubbles, unplated by graphite, from the main bulk of the solution after the major part of the froth has risen into place. The first appearance of a white band in distinct contrast to the overlying darker froth after the well-shaken mixture has stood at rest for a few minutes thus constitutes an "end point" whereby an unknown soap solu-

[1] Received February 27, 1925.

[2] *Z. deut. Öl-Fett-Ind.*, **44**, 361, 378, 391 (1924); through *C. A.*, **18**, 3485 (1924).

[3] Compare work by Harkins and Feldman, *J. Am. Chem. Soc.*, **44**, 2665 (1922).

[4] McBain, Harborne, and King, *J. Soc. Chem. Ind.*, **42**, 373T (1923).

tion may be titrated against standardized graphite and its detergent efficiency estimated in a manner that appears both theoretically sound and practically feasible.

Experimental

The first steps in working out details of the test involved a determination as to whether it would reveal the effect of the addition of alkali and alkaline salts to a given soap solution.

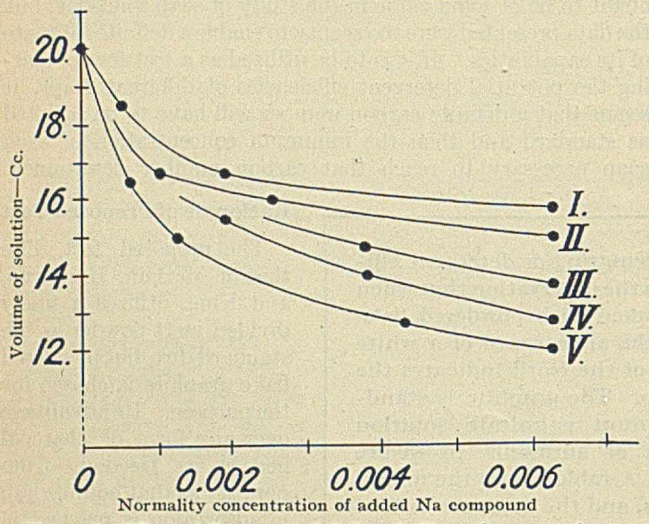


Figure 1—Effect of Presence of Other Sodium Compounds upon Deflocculating Efficiency of 0.0025 *N* Sodium Oleate at 30° C. in Experiment 1

I—Chloride
II—Borate
III—Silicate
IV—Carbonate
V—Hydroxide

EXPERIMENT 1—A specimen of "Oleic acid, U. S. P.," apparently of good quality and showing by acidimetric titration a mean molecular weight of 285, was made into an aqueous stock solution with the calculated quantity of sodium hydroxide, and the neutrality of the resulting soap was proved by phenolphthalein in an alcoholic dilution. Into each of a series of similar test tubes, holding nearly 50 cc., was weighed 1 gram of purified graphite No. 635. After addition of the desired quantity of the solution under test and closing with a clean rubber stopper, each tube was tilted back and forth a sufficient length of time to insure equilibrium, vigorously shaken, twirled vertically between the palms of the hands for a few seconds, and then left vertically at rest for the froth to rise. The end point was taken as half way between the volume of solution at which no white band was apparent and that at which it was clearly present even after a repeated twirling. The temperature throughout was that of the room, not far from 30° C. The solutions were all 0.0025 *N* in soap content and the concentrations of the other sodium compounds present were also reckoned on the basis of normality of sodium content. The water used for all solutions had been freed from carbon dioxide by reboiling after distillation. The results are plotted in Figure 1.

The addition of the common ion, sodium, inhibited the hydrolysis of sodium oleate and so increased its apparent detergent efficiency. The effect was much more pronounced when hydroxyl ions were simultaneously introduced. It will be noted that the curves of the various sodium compounds fall into the order they would be expected to take on the basis of the relative concentrations of hydroxyl ions in their solutions.

It next seemed desirable to ascertain how the test would work with soaps prepared from various pure fatty acids, with a view to determining their relative efficiencies. From Experiment 1 it is evident that the full capacity of a fatty acid to act as a detergent is developed only in the presence of considerable excess alkali. But with the fixed alkalies a point is too soon reached at which the soap becomes "salted out" and naturally becomes difficult to manage. Ammonia was therefore selected as the most appropriate alkali, and it was first necessary to determine how high a concentration is needed to develop a constant detergent capacity in case of a given fatty acid.

EXPERIMENT 2—After several preliminary experiments, four test tubes were prepared, each containing 3.2 grams purified graphite No. 632–2, and 0.0075 gram palmitic acid in a volume of 20 cc. total liquid, but varying in ammonia content through the series 3, 4, 6, and 8 cc. of concentrated ammonia water assaying 26 per cent NH_3. The stoppered tubes were tilted in a water bath till equilibrium was reached, then removed, shaken briskly for 5 seconds, and at once replaced in the bath at an angle of about 20 degrees from the vertical. In this position the minute bubbles at the end point accumulate in a crescentic or lenticular mass more sharply distinguishable than the complete ring formed in a vertical position. The proportion of graphite had been so chosen as to afford but an incipient end point, thus making perceptible even small differences between the tubes. All the tubes were found so similar as to be indistinguishable at 25°, 30°, and 35° C. The end points appeared slightly more pronounced at 30° C. than at either of the other temperatures.

It appears, then, that the maximum detergent capacity of an ammonium soap will be assured when the solution is prepared with one-fifth of its volume of full-strength concentrated ammonia water.

EXPERIMENT 3—The oleic acid was the specimen already described. The lauric acid was claimed to melt at 37° to 38° C., the myristic acid at 52° to 53° C., the palmitic acid at 61.5° to 62° C., and the stearic acid at 67° C. All tests carried 1 gram of purified graphite No. 635 in a final volume of 20 cc. of a 1:4 dilution of concentrated ammonia water. The end point was taken at the first clearly defined appearance of a white crescent in the inclined tube as in Experiment 2. Thus the only variables were the temperature and the weight of ammonium soap. The latter was calculated from the weight of fatty acid known to be present, through its theoretical molecular weight. The results are plotted in Figure 2.

EXPERIMENT 4—To gain some idea of the effect of dilution, a solution of ammonium myristate was tested at 25° C. in a final volume of 20 cc. and a final concentration of 20 per cent ammonia water against varying weights of graphite No. 635. The results were as follows:

Graphite Gram	Ammonium myristate Mg.
1	10
0.5	6.5
0.25	4.5

Discussion

It will first be in order to observe what the test reveals regarding the principles that govern the detergent action of soaps, and then to determine how it should be executed in practice in accord with these principles so as to afford a true comparison between the potential detergent values of commercial soaps.

From Figure 2 it is apparent that a given soap may be most efficient at a certain temperature and that the optimal temperatures for various samples may differ considerably. Therefore, if one desires to determine the comparative value of different samples for a specific washing operation, he must execute the test at the temperature at which that washing operation is to be actually performed. If this temperature

is greatly above room temperature, it will obviously be necessary to provide an oven within which the tubes can be placed in a rack and mechanically shaken at constant temperature and within which they can be observed through a window. It is probable that the majority of washing operations are carried on at a temperature only a little above blood heat; therefore, it is suggested that the standard temperature for general testing shall be 45° C., in which case an open water bath will serve.

Experiment 4 indicates that the apparent detergent power of a given weight of soap falls off with increasing dilution. That fact does not constitute an objection to the test, for a similar falling off must occur in actual washing operations. But it does necessitate that soaps should be tested at approximately the concentration at which they would naturally be used in practice. For general testing it is suggested that a 0.04 per cent solution of ammonium palmitate, made in a 1:4 dilution of concentrated ammonia water, be the standard. As will later be shown, this strength corresponds to a 0.2 to 0.4 per cent solution of the ordinary cake soaps. Ammonium myristate would be more convenient on account of its greater solubility, but it affords a distinctly vaguer end point. At a given temperature, the lower the molecular weight of the fatty acid the easier its soap solution foams to form a fine-grained suds. With increasing temperature the higher fatty acids acquire an increasing resemblance to the lower acids in this respect. But the end point is sharper in the coarser grained suds and therefore palmitate is superior to myristate for the critical operation of standardizing the graphite. From Experiment 2 and Figure 2 it is evident that the most desirable temperature for this standardization will be 30° C. Of course, standardization by ammonium palmitate is entirely unnecessary for merely arriving at the relative values of samples to be compared directly with one another, but in all work of more than temporary importance it is exceedingly desirable to express results in terms of a definite standard, reproducible at any other time and place by any other analyst. The standardization of a given lot of graphite has to be performed but once, after which it may be used for any other soap at any temperature desired.

It is very important to prepare the test solution of any commercial soap with the water actually to be used in the washing operation for which the soap is desired, or at least in a water fairly representative of the waters likely to be used. Many soaps are purposely compounded for use with hard waters, and if the water actually to be used in washing is hard it would be manifestly unfair to such soaps to use distilled water in the test. On the other hand, it would be equally unfair to soaps intended for use with soft water to test them in water harder than that to be used in practice. The choice of the water to be used in the test therefore seems unavoidably the responsibility of the individual analyst.

Directions Recommended for a Standard Test

PREPARATION OF THE GRAPHITE—The graphite must be originally free from oil. (An oiled sample presents a dull appearance in contrast to the glistening luster of the "dry" material. Satisfactory extraction of the oil appears impracticable.) For this reason the variety provisionally recommended is "Flake Graphite Package 632, No. 2," although it is undesirably coarse. One pound of the graphite in a 1500-cc. stout beaker is digested in a mixture of 100 cc. concentrated hydrochloric acid with 700 to 900 cc. water on the steam bath for several hours, with frequent stirring. After partial cooling and settling, remaining froth is skimmed off with a small watch glass; then the graphite is filtered with suction on a hardened paper in a Büchner funnel and washed with 1 liter of distilled water. The cake is loosened by a spatula run around its edge, dropped into an evaporating dish, and transferred to the original beaker in which it is digested on the steam bath for one-half hour in a mixture of 50 cc. concentrated ammonia water and 700 to 900 cc. water, with frequent stirring. It is then again filtered, washed with distilled water till freed from chloride, and thoroughly dried at above 100° C. The portion passing a 60-mesh sieve is bottled for use after thorough mixing.

STANDARDIZATION OF GRAPHITE—A weight of 0.1875 gram of palmitic acid melting not below 61.5° C. is washed by a jet of cold water into a 500-cc. Pyrex volumetric flask to which are also added 100 cc. of full strength C. P. concentrated ammonia water and sufficient distilled water to fill the flask about three-fourths. The flask is heated at 50° C. with frequent gentle agitation until solution is complete, then slowly filled to the mark with distilled water at 50° C. It must be kept tightly stoppered throughout except for brief openings to relieve pressure at the beginning.

To a 175 × 20 mm. Pyrex test tube is transferred a weighed quantity of the purified graphite, 20 cc. of the ammonium palmitate solution at 50° C. and uniformly mixed are pipetted in, and the tube is at once tightly closed with a clean rubber stopper and tilted or shaken until the graphite has become thoroughly distributed, then placed horizontally in a water bath at 30° C. After it has had time to reach standard temperature the tube is gently tilted for at least 2 minutes while immersed in the bath, removed, quickly wiped off with a dry towel, briskly shaken for 5 seconds, and then at once replaced in the bath in a rack adjusted to hold it at an angle of about 20 degrees from the vertical. In exactly 2 minutes the tube is inspected for the presence of a distinct white crescent or lens of minute bubbles in the lower part of the froth. If none is apparent the test must be repeated with a smaller weight of graphite in another tube. If the end point is unquestionably passed, the test must be repeated with a larger weight of graphite. By sufficient repetitions thus is finally obtained the greatest weight of graphite with which 20 cc. of standard ammonium palmi-

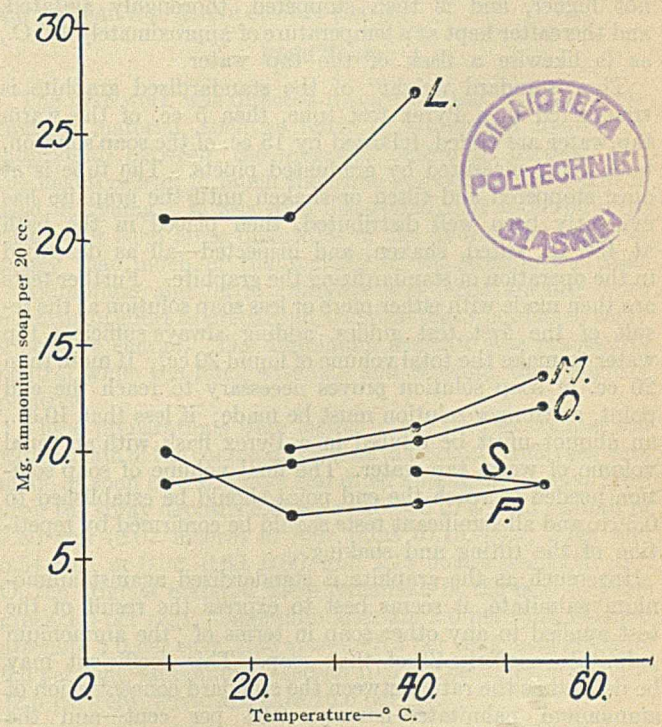


Figure 2—Deflocculating Efficiencies of Various Ammonium Soaps in Experiment 3

L = Laurate
M = Myristate
O = Oleate
S = Stearate
P = Palmitate

tate solution will afford a distinct end point. This weight of graphite is the "standard weight" of that particular graphite for all subsequent work.

Because of the ready escape of ammonia from the ammonium palmitate solution the latter must be kept tightly stoppered except while the pipet is being filled. The pipet should be provided with a bulb or similar means for applying suction other than the unprotected mouth.

The above prescribed minimum time for tilting the tubes in the water bath—namely, 2 minutes—may not always be quite sufficient to insure equilibrium close to the end point; consequently no result may be regarded as final until confirmed by a repetition of the tilting and shaking.

As with most indicators employed to determine the end point of a titration, there is a certain indeterminate zone over which the result is dubious. The end point is not reached unless a rather sharply defined crescentic or lenticular area that is nearly white is conspicuously present. Pale streaks or spots of no definite shape must be ignored. Of course, any particular tube may be subjected to as many repeated shakings and inspections as one desires to assure himself of its exact status with respect to the end point.

EXECUTION OF THE TEST—About 2 grams of the sample to be tested are weighed by difference into a 500-cc. Pyrex volumetric flask; 50 cc. of "tap water"—meaning thereby the water selected for use in the test—are added, and the flask is left upon the steam bath with frequent agitation until the soap is as completely dissolved as possible. The flask is allowed to cool somewhat and then is slowly filled to the mark with tap water freshly heated to 45° C., but not higher, and is then stoppered, thoroughly agitated, and thereafter kept at a temperature of approximately 45° C., as is likewise a flask of the tap water.

The "standard weight" of the standardized graphite is transferred to a Pyrex test tube, then 5 cc. of the warm tap water are added, followed by 15 cc. of the soap solution, both being measured by graduated pipets. The tube is at once stoppered and tilted or shaken until the graphite has evidently been well distributed, then placed in the bath at 45° C., tilted, shaken, and inspected—all as described in the operation of standardizing the graphite. Further tests are then made with either more or less soap solution as the result of the first test guides, adding always sufficient tap water to make the total volume of liquid 20 cc. If more than 20 cc. of soap solution proves necessary to reach the end point, a stronger solution must be made; if less than 10 cc., an aliquot must be diluted in a Pyrex flask with an equal volume of warm tap water. The final volume of soap solution needed to reach the end point should be established to 0.5 cc. and all significant tests should be confirmed by repetition of the tilting and shaking.

Inasmuch as the graphite is standardized against ammonium palmitate, it seems best to express the result of the test applied to any other soap in terms of "the ammonium palmitate coefficient" of that soap. This coefficient may be defined as the ratio between the standard concentration of ammonium palmitate—namely, 0.04 per cent—and the concentration of the soap under test which is found equivalent thereto under the conditions of the test. It is most simply calculated from the formula $4/(W \times V)$, in which W represents the weight in grams of soap per 500 cc. of the soap solution prepared for the test, and V represents the minimum volume in cubic centimeters of that soap solution necessary, when made up to 20 cc., to produce a definite end point.

In reporting an ammonium palmitate coefficient it will obviously always be necessary to append a description of the water used. If the test is made at any temperature other than 45° C., or against any multiple or fraction of the standard weight of graphite, it will also be necessary to add such details. Whatever modifications may be made in testing the soap solution, none should be made in the method of standardizing the graphite, which should be invariably at 30° C. against a 0.04 per cent solution of ammonium palmitate in ammoniacal distilled water; otherwise confusion will certainly arise. It is suggested that the report should be made in the general form

$$\text{Ammonium palmitate coef. at } T° = G/S \times C$$

in which T is the temperature at which the test is made, G the weight of graphite used, S the standard weight of that graphite, and C the apparent coefficient calculated directly from the formula $4/(W \times V)$. Thus, if one should find an apparent coefficient of 0.14 at 80° C., using 3 grams of a graphite of which the standard weight against 0.04 per cent ammonium palmitate is 1.5 grams, the result would be reported as

$$\text{Ammonium palmitate coef. (80° C.)} = 2 \times 0.14$$

Equipment for the test need be but simple. The water bath here used was a galvanized iron foot bath placed over a 3-heat electric hot plate. For tilting the tubes in the bath an ordinary square (15 × 15 cm.) of nichrome gauze was provided with two rows of four loops each, one row of wire, the other of small and thin rubber tubing. Through the center of the gauze, secured with nuts and washers, was the threaded end of a brass shaft, at the other end of which was mounted a pulley and bearing. The shaft was inclined from the vertical as much as possible without raising the ends of the tubes above the water level during rotation, which was at the rate of about 40 r. p. m. More simply, the gauze may be merely crimped over two brass wires laid along opposite edges and the wires brought up and twisted together to form a handle by which the apparatus may be manually tilted. Ordinary soft-glass flasks and test tubes should not be used, for they are often susceptible to rapid attack by soap solutions.

Results of Examination of Some Commercial Soaps

The most tempting field in which first to apply a test for cleansing efficiency is afforded by the common cake soaps sold in such enormous quantities for general cleaning and household laundering. The samples comprised single cakes of eleven brands purchased from local chain groceries. The methods of analysis used probably need but brief discussion. The "excess alkali" was calculated from the difference between the titrations for total alkali and total fatty acid. The "actual soap" was obtained from the dried residue from the latter titration and so was the "apparent molecular weight" of the fatty acids. Since unsaponified matter was not separated from the fatty acids, both these values are likely to be somewhat high. Inasmuch as the moisture content of a cake of soap taken from the shelf in a grocery is somewhat fortuitous it has seemed best to calculate all results presented in the table to the dry basis, and to omit the percentage of moisture actually found. The cake is the unit and it makes no real difference how much water it may have lost during storage after it was manufactured. The samples are arranged in the table in the descending order of their contents in "actual soap" on the dry basis. Thus they naturally fall into three groups: first a white soap which frankly sells at a higher price than the rest; second, Samples B to H, inclusive, which are all yellow soaps; and the last three, which are white soaps, evidently silicated.

The figures in the last column, headed "Cost per detergent unit," are obtained by dividing the cost per dry kilogram by the detergent coefficient, and therefore represent the cost of that dry weight of each soap which would be equivalent in detergent power, under the conditions of the test, to 1 kg. of ammonium palmitate. It must be noted that the water used in determining the detergent coefficients was the

city supply drawn from the tap in the laboratory after running freely for several minutes.

Examination of Commercial Cake Soaps
(Results on dry basis)

Brand	Actual soap Per cent	Excess alkali as Na_2O Per cent	Undetermined Per cent	Apparent mol. wt. fatty acids	Cost per dry kilo	Ammonium palmitate coefficient (dry)[a]	Cost per detergent unit
A	99.0	0.1	0.9	257	$0.589	0.205	$2.87
B	95.6	1.9	2.5	290	0.289	0.209	1.38
C	95.3	1.9	2.8	294	0.284	0.205	1.38
D	91.8	3.4	4.8	297	0.246	0.216	1.14
E	90.4	3.5	6.1	290	0.251	0.193	1.30
F	90.0	3.1	6.9	289	0.326	0.212	1.56
G	83.1	2.9	14.0	299	0.303	0.163	1.86
H	75.7	9.3	15.0	292	0.286	0.194	1.48
I	71.7	7.4	20.9	239	0.320	0.198	1.62
J	70.7	6.6	22.7	252	0.277	0.198	1.40
K	66.6	7.4	26.0	252	0.308	0.194	1.59

[a] Washington city tap water, at 45° C.

The writer desires to draw no general conclusions respecting the relative merits of different types or brands of soaps from the limited number of results presented in the table. The whole subject of the detergent action of soaps is too complex, too closely bound to other considerations, such as action upon the goods, and too economically important to warrant any generalizations unsupported by a very comprehensive and painstaking investigation of all the factors. It is not likely that the writer, in his present position, will be able to follow out this line of investigation; consequently the data are presented merely to illustrate how the test may help to solve some of the problems which bother alike manufacturers and consumers of a most important commodity. One such is the utility of sodium silicate. From the data conveyed in Figure 1, which cover merely distilled water up to a temperature of 60° C., it must not be inferred that sodium silicate always functions solely by virtue of its concentration in sodium ions and hydroxyl ions. The possibility still remains that it may possess notably specific water-softening and soap-saving powers when used with certain hard waters at certain temperatures.

The writer has in progress a study of the fundamental principles of detergency as revealed by the described test.

Adherent Arsenical Preparations[1]

By William Moore

American Cyanamid Co., New York, N. Y.

WHILE a member of the Department of Entomology of the University of Minnesota, the writer became interested in the possibility of applying some of the principles of colloid chemistry to the use of insecticides. After listening to a lecture on the precipitation of oppositely charged colloids, the question arose as to whether this electric phenomenon might not be applied to the use of insecticides. Could the poor adherence of arsenical particle to the leaf surface when exposed to the washing effect of rains and dews be caused by the absence of an electric charge or to the presence of like charges? If such were the case, the adherence should be increased by the presence of opposite electric charges.

It is well known that glass has a negative electric charge when wet. Preliminary tests with glass slides and a suspension of lead arsenate indicated that the adherence could be greatly increased by the addition of positively charged aluminium hydroxide. Seeding citrus trees in the greenhouse were sprayed with a suspension of lead arsenate and with a suspension of lead arsenate to which aluminium hydroxide had been added. After the sprays had dried the plants were sprinkled with water for 5 hours. When the plants had dried it was quite apparent that the lead arsenate–aluminium hydroxide spray had many times the adherence of the lead arsenate alone.

Charges on Arsenical Particles and on Leaf Surface

The common arsenates and arsenites found on the market were ground as fine as possible in an agate mortar, suspended in water, and their reactions in the electric field observed. Whenever the particles migrated at all, the migration was toward the positive electrode, indicating that those exhibiting an electric charge were negative.

The surface of leaves react with dyes as though they were electrically negative. Cellulose is electrically negative when wet. A study of the movement of water through a leaf or over its surface when placed in an electric field indicated that the water migrated toward the negative electrode and that the leaf had a negative electric charge.[2]

Field Tests

The first work was directed toward the use of a positively charged material, such as ferric or aluminium hydroxide, interposed between the negative arsenical particle and the negative leaf, in much the same manner as a mordant is used in dyeing. It was soon discovered that to accomplish this result such large quantities of the hydroxide were necessary that much of the toxicity of the arsenic was lost.

Aluminium and ferric arsenates and ferric arsenite were made in an effort to prepare an arsenical that would itself carry a positive charge. The aluminium arsenate was practically neutral while the ferric arsenate and arsenite were slightly positive.

These preparations were tested in the field in comparison with certain of the common arsenical materials. Analyses were made as soon as the sprays had dried and again 17 days later after the spray deposits had been exposed to a total rainfall of 7.80 cm. (3.07 inches) in four rains (0.15, 0.07, 2.03, and 5.54 cm., or 0.06, 0.03, 0.80, and 2.18 inches, respectively). Of the original material there remained, in the case of Paris green 1.5 per cent, magnesium arsenate 2.0 per cent, calcium arsenate 5.0 per cent, zinc arsenite 5.3 per cent, lead arsenate 6.6 per cent, aluminium arsenate 10.0 per cent, ferric arsenite 12.5 per cent, ferric arsenate 16.6 per cent.

Preparation of Positively Charged Arsenicals

Ferric Arsenate—A study of ferric arsenate showed that, when freshly prepared, the entire precipitate may be peptized with ferric chloride. Much depends upon the concentration of the solutions. Mixing equal parts of molar or half molar solutions of disodium arsenate and ferric chloride gave no precipitate. Fifth molar solutions produced an opaque colloidal solution, whereas with twentieth molar solutions a precipitate formed at once and settled out com-

[1] Received December 17, 1924.

[2] University of Minnesota, Agr. Expt. Sta., *Tech. Bull.* 2 (June, 1921).

pletely. With fortieth molar solutions there was again a tendency to stay in suspension and no precipitate formed when hundredth molar solutions were used.

The precipitate obtained from the twentieth molar solutions after filtering and washing was found to be electrically neutral. The addition of a small amount of ferric chloride tended to peptize the precipitate. The particles were reduced in size and stayed well in suspension. The precipitate was difficult to filter, but after being filtered and washed, it was found to be electrically positive.

LEAD ARSENATE—It was impossible to prepare a good positively charged lead arsenate from lead arsenate precipitated from lead nitrate with disodium arsenate, but it was very easy to make it from lead arsenate precipitated from lead acetate. It is known that an acid lead arsenate is made if lead nitrate is used but that a basic lead arsenate is formed from the acetate. Analyses showed that it was the basic arsenate which so readily took on a positive electric charge. When the acid lead arsenate made from lead nitrate was treated with sodium hydroxide or lead acetate, it was converted to the basic arsenate and then readily took on a positive charge if treated with a slight excess of lead acetate.

COPPER ARSENATE—A study of the copper compounds of arsenic indicated that a positively charged copper arsenite may be made from copper chloride or sulfate, but a copper arsenate was made difficult to prepare from these salts. The desired copper arsenate was readily formed from a copper salt of a weak acid such as the acetate.

OTHER ARSENATES—Studies of various arsenates and arsenites of zinc, chromium, cerium, magnesium, and calcium confirmed the foregoing observations.

The results of these experiments indicated that a positively charged arsenical was one, the particles of which contained an adsorbed metallic ion, such as iron, aluminium, zinc, lead, copper, magnesium, or calcium.[3] The conditions favoring the adsorption of the ion were found to be the formation of a basic arsenic compound in the presence of a slight excess of a soluble metallic salt, preferably in some cases the salt of a weak acid. The combination may be roughly represented as follows:

$$(FeAsO_4)_x\ Fe^{+++} + 3Cl^- + H_2O$$
$$(Cu_3\ (AsO_4)_2)_x\ Cu^{++} + 2(CH_3CO_2)^- + H_2O$$

Some hydroxides or oxides of the metal may be, and no doubt usually are, present.

Working on this basis it was found possible to go a step further and impart the desired electric charge to a manufactured arsenical by treating it with the proper metallic salt. The arsenate may be made by any method desired and the positive electric charge imparted to it as the last step in its manufacture.

Calcium Arsenate That Adheres

Calcium arsenate has become the standard boll weevil poison, and such large amounts have been used that at times there has been a shortage of arsenic. The use of a positively charged calcium arsenate would resist the washing effect of rains and dews, reduce the number of dustings necessary for the control of the weevil, and serve to relieve the shortage of arsenic. Such a calcium arsenate has been made, during the past season, under commercial manufacturing conditions and has been tested in the field.

In the tests standard calcium arsenate manufactured under the same conditions as the positive calcium was used for comparison. The plants were dusted when dry and exposed to the ordinary weather conditions. Analyses showed that at the end of 5 days, during which there were two rains (0.30 and 0.51 cm., or 0.11 and 0.20 inch, respectively) and a dew every night, the adherence of the positive calcium arsenate was 259 per cent better than the standard material. A second test was run for 9 days, during which there were two rains (0.46 and 1.02 cm. or 0.18 and 0.40 inch, respectively) and a dew each night. The adherence of the special material was 245 per cent greater than the standard calcium arsenate. In a third test the plants, after being exposed to the weather for 7 days during which time there were two rains thoroughly sprinkled to equal the washing effect of a very heavy rain. Analyses indicated that in this test the adherence of the positive calcium arsenate exceeded the standard by 196 per cent.

[3] U. S. Patent 1,376,153 (April 26, 1921).

Summary

The common arsenical spraying and dusting materials as now manufactured either have no electric charge or a negative charge when wet, and are therefore easily washed off the plants by the action of rain or dew.

The common basic arsenical materials may be so manufactured or treated that they will have an adsorbed positive ion which will give the arsenical particle a positive electric charge when wet.

Such positively charged arsenical particles are attracted and held to the negatively charged leaf surface, resisting the washing effect of rains and dews.

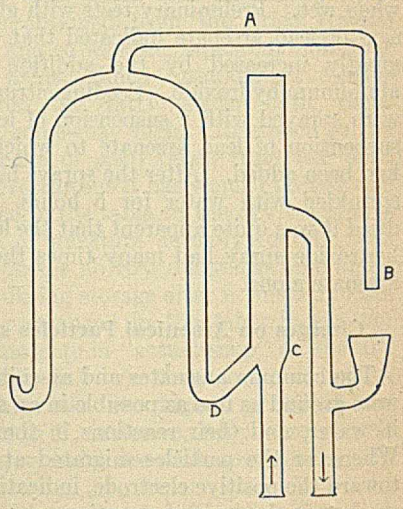
A positive calcium arsenate has been made under commercial manufacturing conditions and tested in the field, where the adherence was found to be from 196 to 259 per cent greater than the standard calcium arsenate.

A Constant-Level Regulating Device[1]

By R. L. Stehle

MCGILL UNIVERSITY, MONTREAL, CANADA

SEVERAL constant-level regulating devices have been described recently in THIS JOURNAL,[2] but none of them is wholly satisfactory. Air is continually being liberated from the incoming cold water during its passage through the hot inlet tube and eventually the siphon breaks. In the device figured this has been obviated by the addition of a second siphon, *A*, which constantly removes the air liberated; thus the apparatus will function indefinitely. The rate at which siphoning occurs may be readily adjusted by lengthening or shortening the tube *B* by means of a short piece of small-bore rubber tubing or by constricting the end of *B*. Since large bubbles of air sometimes accompany the tap water, the free escape of these is insured by the enlargement of the inlet tube at *C* and the downward bend in the main siphon at *D*.



[1] Received March 23, 1925.

[2] Wilde, THIS JOURNAL, **16**, 904 (1924); Jefferson, *Ibid.*, **16**, 1230 (1924).

Disintegration of Portland Cement in Sulfate Waters[1,2]

By Thorbergur Thorvaldson, Rae H. Harris,[3] and David Wolochow[3]

UNIVERSITY OF SASKATCHEWAN, SASKATOON, SASK.

A study of the development of alkalinity in solutions of sodium sulfate shaken with set Portland cement showed that the alkalinity, as measured by titration, was caustic, increased with the concentration of sodium sulfate in the solution, and was, below a certain limit of alkalinity (probably a pH of approximately 12), almost proportional to the amount of cement present. The pH of the various sulfate solutions after coming to equilibrium with the cement was, however, nearly constant.

Extraction of set cement by consecutive portions of 1.64 per cent solution of sodium sulfate (the alkalinity never rising to the limit mentioned above) indicates that the rate of extraction of lime decreases progressively to an almost constant value. The extract contains mainly lime, although, especially during the later extractions, the other constituents such as alumina and silica are also removed. Eighty-four per cent of the lime present was removed in this way and the limit of extraction had not been reached. No essential difference was observed between extraction with the solution of sodium sulfate under these conditions and with distilled water, except that the first was more rapid.

The presence of calcium chloride in solution inhibits slightly the liberation of free lime from Portland cement, whereas the presence of sodium chloride has a slight accelerating effect.

The effect of 0.5 *M* sodium sulfate solution on the liberation of lime from the cement is not increased by the presence of 0.5 *M* sodium chloride.

Solutions of sodium sulfate, magnesium sulfate, and mixtures of these were shaken with set Portland cement and then analyzed. An explanation of the action of solutions of sodium and magnesium sulfate on set Portland cement is proposed on the basis of these analytical data and the other experiments described.

THERE are on record some striking examples of failures of concrete structures exposed to sea water,[4] and while the consensus of opinion among engineers seems to be that well-made concrete will resist the chemical action of sea water indefinitely, there is little doubt that many of these failures are due to the action of the magnesium salts and sulfates in sea water on the Portland cement in these structures.

Some time ago engineers observed very serious failures of concrete structures exposed to ground water in many parts of the Western States and the Prairie Provinces of Canada.[5] Although there was disagreement at first as to the cause, it is now acknowledged that the trouble lies with the sulfates so abundant in the soil of these localities. It has now been shown that, whereas structures of inferior cement and workmanship disintegrate very rapidly in low concentrations of sulfates, even the most carefully made concrete prepared from Portland cement of the highest quality will disintegrate in time under the influence of high concentrations.[6]

The study of disintegration of Portland cement concrete through the action of sulfates has been in progress in this laboratory for several years. The main plan followed has been the preparation in the pure state of the various constituents of Portland cement and the study of the action of sulfate solutions on these. The results of this work will soon be published.

A preliminary study of the action of water and sulfate solutions, with and without the presence of other salts, on Portland cement was first undertaken. Although many such studies have been made before,[5,7] it was considered worth while to carry out experiments to obtain further quantitative data on the subject.

General Experimental Procedure and Materials

Briquets of neat cement were prepared according to the usual engineering practice but using distilled water and in every way avoiding contamination. These were stored in a damp closet or in distilled water for at least 28 days, then dried, ground finely, and a weighed quantity was treated with the various solutions in stoppered glass flasks. Thorough mixing was assured by shaking the flasks in a rotary shaker. From time to time the flasks were allowed to stand and the clear supernatant liquid was removed for analysis.

The Portland cement used in the experiments (Cement A) was one that has been used to make cement blocks for an extensive field investigation in western Canada on the action of ground waters on concrete. The results of physical tests (supplied by the Department of Civil Engineering of the University of Saskatchewan) were as follows:

Normal consistency	23 per cent
Passing No. 200 sieve	84.2 per cent
Soundness in steam	O. K.
Time of setting (Gillmore):	
Initial	5 hours 15 minutes
Final	7 hours 15 minutes
Tensile strength, 1 to 3 briquets standard sand mortar:	
7-day, 247 pounds per square inch	
28-day, 350 pounds per square inch	

Chemical analysis of the cement and of the ground briquets (the latter lost 7.5 per cent on drying to constant weight at 105° C. in a current of carbon dioxide–free air and a further 10.4 per cent on ignition) gave the following results:

	Cement A Per cent	Briquets Per cent
Loss on ignition	3.45	17.90
Silica (SiO_2)	21.19	18.01
Iron oxide (Fe_2O_3)	2.72	2.26
Alumina (Al_2O_3)	6.71	5.93
Lime (CaO)	60.47	51.39
Magnesia (MgO)	3.19	2.79
Sulfuric anhydride (SO_3)	1.66	1.47
	99.39	99.75
Manganese	Trace	Trace
Insoluble (standard cement analysis)	0.29	0.24

[1] Received December 8, 1924.

[2] This work was done under the auspices of a research committee of the Engineering Institute of Canada with the financial support of the Research Council of Canada, the Canada Cement Co., the Canadian Pacific Railway, and the three Prairie Provinces of Canada.

[3] Bursarists, Research Council of Canada.

[4] *Proc. Inst. Civil Eng.*, **107**, 73, 370 (1891). First report, Committee of the Institute of Civil Engineers on Deterioration of Structures Exposed to Sea Water, **1920**, p. 26. Marine Structures, Report of Committee on Marine Piling Investigation, National Research Council, **1924**, p. 152.

[5] Burke and Pinckney, Montana Agr. Coll. Expt. Sta., *Bull.* **81** (1910). Series of papers read at the Second General Professional Meeting of the Engineering Institute of Canada at Saskatoon, **1918**. *J. Eng. Inst. Canada*, **1**, 150, 200 (1918).

[6] Williams, *J. Eng. Inst. Canada*, **4**, 446 (1921); *U. S. Bur. Standards, Tech. Paper* **214**, also unpublished reports of the Committee of the Engineering Institute of Canada on the Deterioration of Concrete in Alkali Soils.

[7] Bates, Phillips, and Wig, *U. S. Bur. Standards, Tech. Paper* **12**; Steik, University of Wyoming, Agr. Expt. Sta., *Bull.* **113** and **122**.

The various salts used in the experimental work were purified by recrystallization until they contained only very slight traces of impurities.

Action of Sodium Sulfate

It is well known that when Portland cement clinker is treated with water, alkalinity is developed due to the setting free of calcium hydroxide from the calcium silicates during hydration. Some of this alkalinity is also due to the reaction of water with the tricalcium aluminate in the cement. Thus by following the development of alkalinity in a liquid shaken with finely ground cement, one might expect to be able to determine the effect of the presence of various substances on the decomposition of the calcium silicates. Tables I, II, and III record the results of such experiments. It should be remembered that the neat cement used had been "cured" for at least 28 days and that it was therefore partly hydrated when the shaking experiments were begun.

Hydrated Portland Cement in Water and in Sodium Sulfate

Table I

Weight of hydrated cement: 10 grams
Volume of liquid (initial): 1000 cc.
Temperature: Same for all samples, averaging 20° C., but varied at times as much as 5° C. from this mean
Titer: In terms of cc. 0.1 *N* acid per 20 cc. of liquid—(1) phenolphthalein as indicator, (2) methyl orange as indicator

	Distilled water		0.05 *M* Na_2SO_4 (0.7%)		0.5 *M* Na_2SO_4 (7%)	
Time Shaken	(1)	(2)	(1)	(2)	(1)	(2)
2 hours	4.02	4.69	5.70	5.83	7.20	7.48
5 hours	5.33	5.39	6.30	6.42	7.60	7.94
10 hours	5.80	5.90	6.83	6.95	8.23	8.45
20 hours	5.80	5.90	7.05	7.14	8.55	8.81
30 hours	6.39	6.43	7.17	7.26	8.80	9.14
54 hours	6.67	6.72	7.31	7.40	9.15	9.41
5 days	6.78	6.82	8.03	8.12	10.00	10.23
12 days	7.42	7.46	8.25	8.35	10.82	11.08
1 month	8.20	8.26	9.48	9.58	12.30	12.45
2.5 months	8.50	8.54	9.86	9.99	12.70	12.87
7 months	7.54	7.65	9.04	9.25	11.86	12.15
7.5 months	7.40	7.49	9.07	9.23	11.56	11.89

Effect of Ratio of Cement to Liquid on Alkalinity

Table II

Volume of liquid: 1000 cc.
Temperature: Same for all the samples averaging 20° C., with a variation of 5° C. from this mean
Titer: In terms of cc. 0.1 *N* acid per 25 cc. of liquid, methyl orange as indicator

	Distilled Water		8.22% Na_2SO_4	
Hydrated cement, weight	10 grams	20 grams	10 grams	20 grams
Time Shaken				
22 hours	7.47	10.24	10.10	17.69
75 hours	8.25	11.31	11.24	19.06
5 days	8.64	11.80	11.75	19.80
8 days	8.96	12.18	12.18	20.60
11 days	9.19	12.45	12.56	21.30
16 days	9.61	11.86	13.49	22.78
1.5 months	9.89	12.39	13.93	24.16
3 months	9.98	11.90	13.87	24.49
7 months	9.43	11.02	13.38	24.44
7.5 months	9.30	10.93	13.20	24.19
Mean value of alkalinity with phenolphthalein as indicator	0.09 less	0.10 less	0.22 less	0.27 less

Effect of Concentration of Sodium Sulfate on Alkalinity

Two cements were used for this experiment, Portland cement A and a natural cement for which resistance to sulfate water was claimed, known as "Cement B." Seven grams of the cement were shaken with 500 cc. of the solution for about 680 hours. The alkalinity is expressed in cubic centimeters of 0.1 *N* acid per 25 cc. of liquid.

Table III

	(1)	(2)	(3)	(4)	(5)	(6)
Concn. of Na_2SO_4, per cent	0.165	0.41	0.82	1.65	4.11	8.22
Titer Cement A	13.7	13.5	13.6	14.8	16.3	18.0
Titer Cement B	3.1	7.0	8.2	9.1	9.6	11.1
pH Cement A	12.67	12.68	12.64	12.66	12.65	12.63
pH Cement B	12.09	12.42	12.46	12.47	12.42	12.46

Thus the alkalinity developed during the treatment of hydrated Portland cement with water and with solutions of sodium sulfate is entirely hydroxide alkalinity. The amount increases with the concentration of sodium sulfate. The alkalinity in a solution of sodium sulfate is almost proportional to the weight of cement. It should be borne in mind that when a large quantity of cement is shaken with water the liquid soon becomes saturated with calcium hydroxide and further decomposition of the calcium silicates results in the formation of crystals of hydrated lime in the solid phase while the liquid phase remains unaltered. The 20-gram sample (Table II) has practically reached the state of saturation in 22 hours, while the 10-gram sample has not reached that point in 7.5 months. When a sulfate such as sodium sulfate is present in the liquid phase, the calcium hydroxide reacts with it forming the slightly soluble calcium sulfate which on reaching saturation separates out as crystals of gypsum leaving a corresponding amount of sodium hydroxide in solution. Thus the alkalinity developed may be far above that of a saturated solution of hydrated lime and would be expected to give a measure of the free lime liberated by the cement.

In each case there is a characteristic increase in the alkalinity to a maximum followed by a distinct decrease. The maximum in the case of 20 grams cement in water (Table II) is greater than the solubility of hydrated lime under the conditions of the experiment and can therefore not be due to calcium hydroxide alone, while the final value is practically equivalent to this. In work in this laboratory with tricalcium aluminate this characteristic drop in alkalinity has been obtained and has been shown to be due to the separation of less soluble hydrated aluminates. We may therefore conclude that the peak value for the alkalinity in Tables I and II is due to both calcium hydroxide (or sodium hydroxide) and hydrated tricalcium aluminate in solution and that the decrease in alkalinity is due to the separation of less soluble aluminates.

Extraction of Lime from Portland Cement by Solutions of Sodium Sulfate

Two experiments were carried out to determine quantitatively the extraction of lime from the cement: (1) by allowing the cement to come once to an equilibrium with concentrated solutions of sodium sulfate, and (2) by successive extraction of the cement with a sulfate solution and with water.

(1) Twenty-gram portions of the hydrated cement were shaken with 1 liter of sulfate solution for 10 months and the total alkalinity was determined.

	(*a*)	(*b*)
Concn. of Na_2SO_4, per cent	4.63	9.26
pH of liquid (final)	12.5	12.5
Total alkalinity, cc. normal acid	85.1	89.6
CaO equivalent of alkalinity, grams	2.38	2.51
CaO in original cement, grams	10.3	10.3
CaO extracted, per cent	23.1	24.4

(2) Twenty-gram portions of the hydrated cement were extracted successively (*a*) with liter portions of water, and (*b*) with liter portions of 1.64 per cent solution of sodium sulfate. The extraction of lime was followed by titration of each portion of liquid.

Extraction number	Time of extraction	Total titer cc. normal acid (*a*)	(*b*)
1	2 days	45	56
2	3 days	34	36.6
5	3 days	11.8	15.1
10	1 week	6.4	8.0
20	3 weeks	4.0	5.0
25	2 weeks	3.2	3.8
30	1 week	2.4	3.4
31	1 week	2.4	3.8
32	1 week	2.4	3.8

Thus, after extraction with thirty-two 1-liter portions during the course of a whole year, the alkalinity developed during a week's shaking had reached almost a constant value. The experiment was discontinued and analysis of the residual solid showed that 72 per cent of the lime had been extracted by the water and 84 per cent by the sulfate solution. During the treatment a much smaller proportion of the alumina and silica was removed. These experiments indicate

that, although the main action is the extraction of lime from the cement, yet during the later stages both silica and alumina are removed, owing possibly to the slight solubility of the hydrated aluminates and silicates in the liquids and to the formation of stable colloidal suspensions. The extraction is speeded up in the presence of sodium sulfate and the effect increases with the concentration, but there is no evidence of a difference in the nature of the reactions involved with water and with solutions of sodium sulfate. Under the conditions of the experiment it seems likely that in either case all the calcium can be extracted by continued treatment. This indicates the importance of making impermeable concrete even when in contact with only fresh water.

Effect of Chlorides

It seems to be generally considered that the presence of chlorides is a contributing factor in the distintegration of cement by sulfates. Experiments on mortar bars in this laboratory have not confirmed this. A series of experiments was therefore carried out to determine the effect of chlorides on the development of alkalinity in Portland cement–water and Portland cement–sulfate mixtures.

Table IV

Weight of neat cement, 10 grams
Volume of liquid, 1000 cc.
Temperature, mean 20° C., var. 5° C.
Concentration of salts in terms of molar solution
Titer: Cc. 0.1 *N* acid per 20 cc. of liquid, indicator methyl orange

		$CaCl_2$		NaCl		Na_2SO_4	
Time	H_2O	0.05 *M*	0.5 *M*	0.05 *M*	0.5 *M*	0.5 *M*	0.5 *M* + 0.5 *M* NaCl
2 hours	4.69	4.76	4.30	5.47	6.26	7.48	7.35
5 hours	5.39	5.09	4.41	5.87	7.01	7.94	7.58
10 hours	5.90	5.37	4.80	6.23	7.00	8.45	8.34
20 hours	5.89	5.37	4.99	6.74	7.23	8.81	8.37
30 hours	6.43	5.80	5.23	7.01	7.36	9.14	9.07
54 hours	6.72	5.74	5.23	7.00	7.39	9.41	9.50
5 days	6.82	6.33	5.64	7.59	8.07	10.23	10.09
12 days	7.46	6.42	5.68	7.89	8.33	11.05	10.90
1 month	8.26	7.22	6.21	8.78	9.25	12.45	12.27
2.5 months	8.54	7.23	5.92	9.07	9.61	12.87	12.89
Mean value of alkalinity with phenolphthalein as indicator:		0.07 less	0.08 less	0.15 less	0.07 less	0.10 less	0.25 less	0.20 less

Thus calcium chloride has an inhibiting action, as is to be expected on account of the presence of the calcium ion in solution. Although the solutions of sodium chloride alone give a marked increase in alkalinity over that produced in distilled water, yet a solution that is 0.5 molar with respect to both sodium sulfate and sodium chloride does not give an increase in alkalinity over 0.5 molar solution of sodium sulfate. As far as disintegration of cement in sulfate solutions is shown by the increased liberation of free calcium hydroxide from the cement, it appears that presence of sodium chloride in 0.5 molar solution of sodium sulfate has no effect.

Action of Magnesium Sulfate

Although the extent to which the silicates of calcium in a cement are decomposed in solution of sodium sulfate is apparently indicated by the development of alkalinity in the solution, this cannot be so when magnesium sulfate or other soluble magnesium salts are present. Here the liberated calcium hydroxide reacts with the magnesium sulfate forming the insoluble magnesium hydroxide and the slightly soluble calcium sulfate and the liquid remains nearly neutral as long as magnesium salts remain in the solution. Information as to the progress of the liberation of lime from the cement, however, may be obtained by following the rate loss of magnesium by the liquid. A complete analysis of the liquid will also indicate the extent of the formation of calcium sulfate as well as any further reaction of the sulfate with the cement. As is to be expected, when magnesium sulfate is present in experiments such as the above, the extraction of lime from the cement is accelerated. This does not necessarily mean that the destruction of a block of concrete is more rapid when it is immersed in a solution of magnesium sulfate than in sodium sulfate of corresponding concentration, as the deposition of the products of the reaction in the pores of the block will affect the diffusion of the solution through the concrete. Field and laboratory tests indicate that the deterioration of concrete in solutions of magnesium sulfate is only slightly, if any, more rapid than in sodium sulfate.

A series of experiments was made in which 15-gram portions of set Cement A were shaken with 1-liter portions of sulfate solutions of various concentrations (sodium and magnesium). After 6 weeks samples of the clear liquid were removed and the alkalinity, content of calcium, loss of sulfate, and loss of magnesium were determined. By making certain assumptions one can calculate from these data, in two different ways, the amount of lime removed from the cement. On the assumption that the sulfate is removed from the solution only as calcium sulfate (or as calcium sulfoaluminate), the amount of lime removed from the cement is equivalent to the sulfate removed plus the calcium in solution. In the second place, provided the sodium and magnesium sulfates react only with the free lime liberated by the cement, the sum of the lime equivalents of the magnesium precipitated and the alkalinity developed should be equal to the amount of lime removed. Table V gives the data of these experiments and the calculations based on the foregoing assumptions.

Notes:

(1) The liquid of Expt. 2 contained 0.378 gram of alumina (Al_2O_3) in solution. This is equivalent to 42 per cent of the total alumina in the cement. Expt. 3 contained 0.02 gram or a little over 2 per cent of the total alumina. In Expt. 1 it was absent and in Expts. 4, 5, and 6 traces of alumina were present.

(2) Expt. 2 contained 0.143 gram of silica in solution or 5.3 per cent of the total silica in the cement. In Expts. 1, 3, 4, 5, and 6 there was no silica in the liquid.

Examination of the results in Table V, which are representative of a large number of similar experiments conducted in this laboratory, suggests an explanation of the action of sulfate solutions on hydrated cement. The action of magnesium sulfate as shown in Expt. 4 represents the simplest case. Here the magnesium precipitated is equivalent to the calcium sulfate formed—i. e., the two methods used to calculate the calcium extracted from the cement give agreeing results. We may consider that the magnesium sulfate reacts with the lime liberated through the natural hydration of the cement, and the products are removed on account of their slight solubility. The liberation of free lime is consequently speeded up and continues until all the available lime has been removed and has reacted with the magnesium sulfate. The high percentage of lime removed (94 per cent) indicates that if ultimate products of hydrolysis containing lime are formed, then the calcium in these is at least partly replaced directly by magnesium. The same applies to Expt. 5, except that here all the magnesium sulfate in solution is removed before the cement is completely decomposed, and alkalinity then develops owing to liberation of free lime as in the normal case with water.

With sodium sulfate (Expts. 2 and 3) calculation of the lime removed from the cement by the two methods used in Table V gives widely different results. The formation and precipitation of calcium sulfate during the initial stage speeds up the liberation of lime from the cement with the development of abnormally high caustic alkalinity and the presence of caustic soda in the solution. When the alkalinity has thus risen to a fairly high figure (the data indicate a rapid reaction at pH = 12.7), a second reaction begins to take

Table V

Experiment number	(1)	(2)	(3)	(4)	(5)	(6)
Grams of salt in 1000 cc. solution	Distilled water	17.68 Na_2SO_4	1.768 Na_2SO_4	17.82 $MgSO_4$	1.782 $MgSO_4$	4.45 $MgSO_4$ 4.42 Na_2SO_4
Caustic alkalinity, cc. normal in 1000 cc.	48.0	60.6	52.3	0	37.5	29.8
CaO equivalent of alkalinity, grams (I).	1.344	1.70	1.46	0	1.05	0.83
CaO by analysis, grams in liquid (II)	1.355	0.74	1.12	0.71	1.19	0.84
Original SO_3, grams	Nil	9.96	0.996	11.85	1.185	5.45
Final SO_3, grams	Nil	3.41	0.004	2.53	0.132	2.31
SO_3 lost by liquid, grams	Nil	6.55	0.992	9.32	1.053	3.14
CaO equiv. of SO_3 lost by liquid, grams (III)	Nil	4.58	0.69	6.52	0.737	2.20
Original MgO, grams	Nil	Nil	Nil	5.97	0.597	1.49
Final MgO, grams	Trace	Trace	Trace	0.81	Trace	Trace
MgO lost, grams	Nil	Nil	Nil	5.16	0.597	1.49
CaO equivalent of MgO, lost by liquid, grams (IV)	Nil	Nil	Nil	7.16	0.829	2.07
CaO lost by cement, grams:						
Calcd. from (I) and (IV)	1.344	1.70	1.46	7.16	1.88	2.90
Calcd. from (II) and (III)	1.355	5.32	1.81	7.23	1.93	3.04
Per cent CaO removed, (II) and (III)	17	69	23	94	25	39
Final pH of liquid	12.60	12.72	12.67	9.46	12.53	12.39

place, involving the formation of calcium sulfate without a corresponding increase in the alkalinity. This probably represents the direct displacement of the calcium in the aluminates and silicates by sodium. The fact that nearly one-half of the alumina present in the cement and a considerable amount of silica are found in the solution in Expt. 2, which contains an excess of sodium sulfate, supports this view. Thus the first reaction due to the presence of sodium sulfate—i. e., the speeding up of the natural process of hydration of the cement—might be expected to have a beneficial result on the strength developed, whereas the actual disintegration takes place through the second reaction. This is found to be in accordance with the abnormal behavior of briquets of cement mortar mixed with sulfate waters or cured in a solution of sodium sulfate.[8]

In mixtures of sodium and magnesium sulfate the magnesium sulfate disintegration controls as long as there is any of that salt present. Only after this is removed and the alkalinity rises can the sodium sulfate disintegration play its part. This is evident from the comparatively slight discrepancy between the lime removed in Expt. 6 (Table V) as calculated by the two methods. In an experiment, not recorded above, where the liquid contained 22 grams of sodium sulfate and 4.455 grams of magnesium sulfate per liter, the lime removed as calculated from alkalinity and the magnesium precipitated gave a result 16 per cent lower than when calculated from the calcium in solution and the sulfate removed.

The difference in appearance of cement mortars and concretes when disintegrated by various sulfate solutions is of interest. When sodium sulfate is the disintegrating agent the product when wet is soft and almost like putty, whereas when magnesium sulfate is used the product is granular and harder. When mixtures of sodium and magnesium sulfates are used the appearance of the product is characteristic of the magnesium sulfate disintegration.

It will be noted that the foregoing explanation does not take into account the much talked of physical effect of the crystallization of substances during sulfate disintegration with an increase in volume and consequent disruption of the concrete. The results of the foregoing experiments indicate that complete disintegration of Portland cement may take place in sulfate solutions without such crystallization playing any part. On the other hand, under certain conditions, especially when a structure is exposed to alternate drying and wetting, such crystal formation and frost action represent the final cause of the disruption of material already weakened through chemical disintegration.

[8] C. J. Mackenzie in 1920 obtained results which showed that standard sand briquets thus made or stored gained greater strength than when good water was used. Continued storing in solutions of sodium sulfate showed loss in strength and ultimately disintegration.

Detection of Traces of Iodides[1,2]

By Frank B. Wade

Shortridge High School, Indianapolis, Ind.

THIS simple and effective method is published in the belief that it may be of service to others in keeping check on the uniformity of distribution of iodides in iodized salt or as a means of detecting traces of iodides as impurities in other substances.

Mix 1 gram of starch with 5 cc. of water and add the mixture to 45 cc. of boiling water in an Erlenmeyer flask over a burner. Boil to clear the starch. Cool and pour over a filter paper in a shallow dish. When the paper is wet *pour off all surplus* starch solution. Prepare a small chlorine generator. (A test tube containing 1 gram of potassium permanganate and provided with a one-hole rubber stopper and a right-angle delivery tube is handy. When ready for use add 1 or 2 cc. of concentrated hydrochloric acid.) Sprinkle the salt to be tested *sparingly* over the wet filter paper in order to get a uniform layer of salt as nearly as possible one crystal thick. This will dampen the salt with the starch solution, but there should not be enough water present to dissolve the salt perceptibly. Now "gas" the surface of the salt with a little chlorine from the generator (at a hood or at a window with a strong outward draft). The starch solution will at once turn blue wherever there was any iodide and the distribution of the latter can at once be noted by the "pattern" that appears in blue. Avoid excess of chlorine.

The merit of the method apparently is that it gives a high concentration of the iodide and a relatively low concentration of the accompanying chloride at each of the tiny centers where the iodide lies. Thus there is no adverse mass action effect to drive back the iodide into an associated condition. The iodide, being present in minute quantities, is practically all dissolved and dissociated and ready to react with the chlorine to release free iodine, which colors the starch blue. The chloride is in the main undissolved and undissociated, and does not interfere with the delicacy of the reaction.

[1] Received March 2, 1925.

[2] This method was based upon a suggestion from A. D. Thorburn, of Indianapolis, and worked up under the writer's direction by two of his pupils, Barbara Blatt and Hilda Renchen.

Pyrrole from New Sources—Some Uses[1]

By Joseph Michelman

20 Seaver St., Roxbury, Mass.

Extension of the results obtained from the destructive distillation of leather scrap and of gelatin has suggested glue stock as another source for the industrial preparation of the pyrroles and pyrocoll. From a chemical standpoint, prepared glue stock is satisfactory. However, an abundance of cheap raw materials in an excellent condition characterizes leather scrap and makes it preëminently suitable for this purpose.

A few uses for the pyrroles are suggested. The reduction into pyrrolidine derivatives, which might be used as substitutes for nicotine as an agricultural poison, is pointed out. Readily accessible pyrrole offers opportunities for the synthesis of some of the alkaloids of the pyrrolidine series and of compounds of pronounced physiological activity.

AN INVESTIGATION of the decomposition products from leather scrap[2] led to the conclusion that leather and gelatin decompose upon destructive distillation into substances common to both. The products obtained by Weidel and Ciamician[3] upon destructively distilling gelatin were in accord with those obtained by the writer upon subjecting leather scrap to the same treatment, excluding, obviously, those substances arising from the tanning matter. The most characteristic of these decomposition products are pyrocoll and the pyrroles; the absence of pyridine bases and fatty acid nitriles is equally noteworthy. It is now possible to make a further generalization that pyrrole and pyrrole derivatives, especially pyrocoll, are the characteristic distillation products arising from animal matter composed of internal and external gelatinous and membranous substances and connective tissue, a necessary criterion for such animal matter being that it should be capable of passing into a gelatinous or glutinous condition upon boiling with water.

The foregoing generalization may have some biochemical significance, but only its industrial applications will be considered at this time. In this connection, it suggests another source, in addition to scrap leather, for obtaining pyrocoll and the pyrroles on an industrial scale.

Raw Materials

As is well known, animal offal of various descriptions has been subjected to destructive distillation, frequently for the recovery of ammonia and animal charcoal, and sometimes merely for its disposal. This practice of using raw materials from the varied and indiscriminate sources results in a mixture of distillation products of such complexity that isolation and purification of its constituents become impractical. Even bones, which can supposedly be selected with more care than the average animal offal, give a distillate, "bone oil," containing, among many other substances, pyridine bases, fatty acid nitriles, and the pyrroles. Some of these are not sufficiently valuable, and others complicate the extraction and recovery of the more valuable constituents. The presence of these associated impurities can be avoided by selecting raw materials closely related to gelatin, which has been shown by Weidel and Ciamician[4] to yield principally the pyrroles and pyrocoll uncontaminated by pyridine bases or fatty acid nitriles. The chemical distinction between gelatin and glue is merely one of purity, and they would yield the same distillation products, but both are too costly for this purpose. However, "glue stock," which constantly accumulates in considerable quantities in abattoirs and tanneries and from which glue is manufactured, is more suitable industrially and economically.

The composition of the glue stock for this process is confined to hides, hide trimmings, fleshings, skivings, shavings, etc., and to similar matter, including scrap leather, that has been "detanned"—that is, from which the tanning substances have been removed. As has been shown, it is desirable to have these raw materials in a state of purity approximating gelatin or glue, and if they are not already in this condition, they may be subjected to a liming process as is ordinarily used in dehairing and defleshing hides. By the action of the lime solution the epidermal layers are loosened and the fatty matter is saponified. The substances that would give rise to the formation of pyridine bases and fatty acid nitriles are thereby to a large extent removed. (Weidel and Ciamician[4] postulated that the presence of the pyridine bases in bone oil was due to the condensation of the acrolein from the fats with ammonia and aliphatic amines.) The alkali need not be removed from the stock, which is dried and destructively distilled similarly to scrap leather. Since glue stock and leather scrap yield in the main the same distillation products, excluding those substances arising from the added tanning matter, the methods of recovery of the products from glue stock are the same as those outlined for leather scrap.

Costs

The condition, the cheapness, and the present plentiful supply of leather scrap give it outstanding advantages over glue stock as an industrial source for the pyrroles. Leather scrap is $5 to $10 a ton at the present time, has a moisture content of only 6 to 15 per cent, and requires little if any preparatory treatment, as has been shown in the preceding paper.[2] Glue stock is variously quoted—for instance, hide trimmings are about $20 a ton—but as such materials have an exceedingly variable content of glue-yielding substance and a large amount of moisture, and may require preparatory treatment, the cost per ton mounts considerably higher.

Yields

The yield of the pyrroles and pyrocoll varies with the amount of animal matter present in the raw materials, and is larger from chrome-tanned than from vegetable-tanned leathers. The hide substance contents of these leathers are 50 to 75 per cent and 35 to 50 per cent, respectively. Thus, glue stock for this process is to be evaluated upon its content of gelatinous matter, which is generally lower than that in leather. The pyrocoll, which is readily separated from the

[1] Received November 25, 1924.

[2] This Journal, **17**, 247 (1925).

[3] *Monatsh.*, **1**, 279 (1880).

[4] *Ber.*, **13**, 55 (1880).

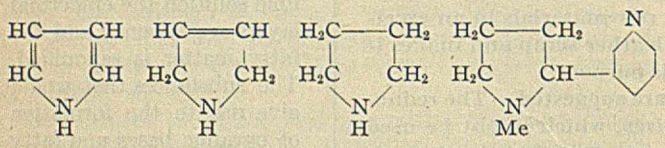
other distillation products and purified, can be used with reasonable accuracy as indicative of the yields of the pyrroles as well. It was thus observed that the yield of pyrocoll decreases with more compact baling of the scrap—that is, with an increase in the all-over density of the raw materials in the bales or billets. On the other hand, more compact baling results in a char of greater density, which is very desirable. The industrial value of the products will determine the method of operation, which is controllable over a wide range.

The utilization of other waste products composed of leather, such as discarded footwear, leather board, old belting, etc., is also possible but not economically feasible at present.

Pyrrole in Synthetic Chemistry

Scrap leather and glue stock are thus fruitful sources of pyrrole and its derivatives, which offer numerous possibilities for synthesis. A few of these applications will be discussed very briefly.

HYDROGENATION—The hydrogenation of pyrrole and its homologs yields exceedingly interesting products possessing pronounced alkaloidal character. The relationship of pyrrole through pyrrolidine to nicotine is apparent from their formulas:



Pyrrole Pyrroline Pyrrolidine Nicotine

This relationship of chemical constitution is also manifest in their similarity of pharmacological behavior. Tunnicliffe and Rosenheim[5] have investigated the physiological action of the reduced pyrroles and noted the close relationship in this respect between pyrrolidine and nicotine. This suggests a very important use for the reduced pyrroles as an agricultural poison as a substitute for nicotine sulfate. For this purpose the reduced homologs of pyrrole should be very efficacious, because, as Tunnicliffe and Rosenheim have pointed out, the pharmacological effects of the pyrrolidine ring are greatly intensified by the introduction of a side group—for instance, the inactive pyridine ring. The hydrogenation of the pyrroles may proceed in two stages:

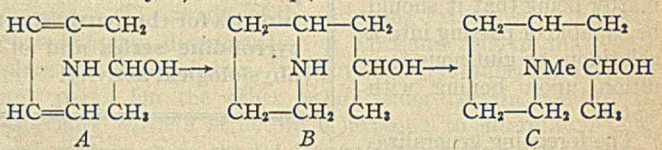
Reduction to Pyrroline—The electrolytic reduction of the pyrroles to the corresponding pyrrolines as proposed by Dennstedt[6] gives yields claimed to be almost quantitative. Knorr and Rabe,[7] using metals and mineral acids, obtained pyrrolines and some members of the pyrrolidine series, however, with yields less than one-half.

Reduction to Pyrrolidine—Padoa[8] obtained pyrrolidine by passing pyrrole vapor and hydrogen through a tube containing reduced nickel, with a yield of 25 per cent. Putochin[9] recently repeated this work and analyzed the by-products of the reaction. Willstätter[10] attempted to hydrogenate pyrrole derivatives in ether solution with platinum black and hydrogen, but without success; pyrroline derivatives could be reduced, however. Pure pyrrole in acetic acid can be reduced to pyrrolidine by this method with a yield of about 80 per cent. Kurt Hess[11] has accomplished the quantitative reduction of pyrrole to pyrrolidine by catalytic hydrogenation with platinum black out of contact with the air.

HALOGENATION—Ciamician and Silber[12] prepared tetraiodopyrrole, or iodol, by the action of iodine on pyrrole in the presence of alkali. There are several other methods.[13] Iodol is said to possess the same physiological properties as iodoform, but it differs from the latter in being odorless and nonpoisonous. The action of sulfuryl chloride on pyrrole yields a series of progressively chlorinated products.

POLYMERIZATION—The polymeric change of the pyrroles into the corresponding indoles was discussed in the preceding paper.[2] To this may be added that Plancher and Ciusa[14] effected the conversion by using zinc acetate and acetic acid. The use of indole as a perfume base in synthetic civet, jasmine, and neroli oils is well known.[15] The indoles have been proposed frequently as various dye intermediates, but little if any development has occurred in this direction, probably because of their prohibitive cost, which is $6 per ounce for indole at present.[16]

SYNTHESIS OF ALKALOIDS—The presence of a pyrrolidine group in the alkaloids, cocaine, atropine, tropine, tropacocaine, homatropine, etc., is well recognized. The preparation of pyrroles substituted by derivatives of propane presents the possibility of synthesizing some of the alkaloids of the pyrrolidine group, which is reflected in Kurt Hess'[17] synthesis of the alkaloid hygrine and in a series of patents of Bayer & Company. Compound *A*[18] may be prepared from pyrrole and α-propylene oxide through the Grignard reagent. The compound *A* is readily reduced with good yields to the compound *B*.[19] After the imide hydrogen atom of *B* is replaced by a methyl group through the action of formaldehyde, the compound *C* results.[20]



A *B* *C*

The similarity of the structure of compound *C* to that of tropine is noteworthy. Compounds of the type *A*, *B*, and *C* are intended as "intermediates in the preparation of pharmaceutical products."

Note—Since this paper was written, the writer has received a private communication stating that the synthesis of tropine from pyrrole has actually been carried out. Accordingly, the syntheses of tropacocaine, and possibly homatropine, are in sight.

A voluminous literature has accumulated upon the chemistry of pyrrole and its derivatives, which has been well summarized by Ciamician,[21] J. Schmidt,[22] and Meyer-Jacobson.[23]

[5] *Zentr. Physiol.*, **16**, 93 (1902); *Chem. Zentr.*, **73** (II), 390 (1902).
[6] German Patent 127,086 (1902); *Chem. Zentr.*, **73** (I), 338 (1902).
[7] *Ibid.*, **72** (I), 71 (1901).
[8] *Gazz. chim. ital.*, **36** (II), 317 (1906).
[9] *Ber.*, **55**, 2742 (1922).
[10] *Ibid.*, **45**, 1477 (1912); *Ann.*, **385**, 207 (1911).
[11] *Ber.*, **46**, 3120, 4104 (1913).
[12] *Ber.*, **18**, 1766 (1885).
[13] German Patents 35,130 and 38,423 (1886).
[14] *Atti accad. Lincei*, **15**, 447 (1906).
[15] German Patent 139,822 (1903).
[16] *Drug. Chem. Markets*, October 15, 1924.
[17] *Ber.*, **46**, 3113, 4104 (1913).
[18] *Chem. Zentr.*, **85** (II), 1136 (1914).
[19] *Ibid.*, **86** (I), 583, 926 (1915).
[20] *Ibid.*, **86** (II), 1033 (1915); **88** (II), 146 (1917).
[21] *Ber.*, **37**, 4200 (1904).
[22] "Die Chemie des Pyrroles," Stuttgart, **1904**.
[23] "Organische Chemie," Vol. II, **1920**, p. 146.

Du Pont Organizes Viscoloid Company—Plans have been completed for the formation of the du Pont Viscoloid Company to manufacture and deal in pyroxylin plastic articles. The company will take over the business heretofore conducted by the Viscoloid Company, Inc., with plant at Leominster, Mass., and the pyralin business formerly conducted by the du Pont Company with plants at Arlington, N. J., Poughkeepsie, N. Y., and Norwich, Conn. The main office will be in New York. B. F. Davis, general manager of the du Pont company's pyralin department, will be president of the new organization.

Cracking of Low-Temperature Coal Tar and Conversion Products[1]

By Jacque C. Morrell and Gustav Egloff

UNIVERSAL OIL PRODUCTS CO., CHICAGO, ILL.

THE production of a smokeless fuel, together with the economic consideration of decreasing the price differential between bituminous and anthracite coal, has stimulated research and investigations into the possibilities of low-temperature carbonization. Such processes are operated at a temperature of from 500° to 600° C., compared with 1000° to 1300° C., for high-temperature carbonization. In general, low-temperature carbonization includes all those processes where the temperatures are maintained low enough to avoid substantial decomposition of the primary liquid products.

One of the major sources of gasoline for automotive use in the future will be the cracking of tars derived from low-temperature carbonization of coal. The annual production of bituminous coal in the United States is approximately 600 million tons. This quantity of coal low-temperature treated would yield about 360 million barrels of tar, which when subjected to heat and pressure distillation would produce over 100 million barrels of motor fuel, or approximately 50 per cent of the motor fuel produced in the United States.

The ultimate yield of motor fuel from the cracking of low-temperature tars would be 30 per cent as a minimum, and the motor fuel produced would be composed substantially of aromatic and unsaturated hydrocarbons—a superior type of motor fuel.

In carrying out the processes of low-temperature carbonization various types of equipment have been utilized, including horizontal and vertical retorts of varying form, with and without moving elements for keeping the charge in motion. The mechanical difficulties encountered are many and, as with the heat treatment of large masses of carbonaceous matter in general for large-scale production, many improvements have yet to be made. The chief problem here, as with all coking operations, is the great difficulty of subjecting a mass of such material to uniform temperature conditions owing to the low heat conductivity of these carbonaceous materials. As an example of such difficulty the data given by Parr[2] show that during a 35-hour coking period the center of the mass did not reach the stage of decomposition, given as 250° C. (482° F.), until after 20 hours. Thus it is seen that each successive layer of coal is being subjected to different temperature conditions. The ideal, then, is to find some mechanical means by which each particle of coal is subjected to the same temperature conditions. Another difficulty is the expansion of the coal mass on heating, the maximum expansion being around 550° C.

Aside from mechanical difficulties, it is believed that the chief determining factor in the economic future of low-temperature carbonization will be the utilization of the tars produced during the process. It is with this phase of the subject that the writers are at present interested. The annual production of bituminous coal in the United States is about 600 million tons, with new fields being continuously chartered. No doubt the production of bituminous coal would increase greatly were the demand increased—i. e., if wider uses could be found for same. However, on the assumption of the above production, and taking as an average yield approximately 0.6 barrel per ton of coal (American practice), about 360 million barrels of low-temperature tar would be produced if all the coal were so utilized. Assuming an average ultimate yield of motor fuel of 30 per cent by cracking this tar, which the writers believe can be obtained, a total of more than 100 million barrels of motor fuel could be produced from this source alone. This would represent about 50 per cent of the present motor fuel production in this country. Of course, it is realized that all bituminous coal produced will not be subjected to low-temperature carbonization, but the foregoing figures are cited as a possibility.

Concerning this problem in Great Britain, Tupholme[3] says: "It has therefore to be recognized that the most promising internal supply of both motor spirit and fuel oil lies in the direction of the low-temperature distillation of coal."

As stated previously, the production of low-temperature tar differs from that of general practice by a marked reduction in the temperature. The temperature range of 1000° to 1300° C. for ordinary carbonization is reduced practically one-half for low-temperature carbonization. The optimum temperature will vary with types of coal and other factors, and may in some cases exceed 700° C. The volume of gas produced in low-temperature carbonization is much less than that produced in high-temperature carbonization, but the amount of tar is greatly increased. It is generally accepted that a high-temperature tar represents a secondary product from the heat treatment during the formation of low-temperature tar.

The extensive work on low-temperature carbonization by Curtis and co-workers[4] is illustrated with regard to products and yields by the data in Table I.

Table I—General Results of Low-Temperature Carbonization with Miscellaneous Coals

Source	H_2O in coal Per cent	Ash in coal Per cent	B. t. u. in coal Per lb.	B. t. u. in carbocoal Per lb.	Yields per Ton of Dry Coal: Carbocoal Lb.	Dry tar Gal.	Light oil Gal.	$(NH_4)_2SO_4$ Lb.	Gas Cu. ft.	B. t. u. of gas Cu. ft.	Sp. gr. of tar Cu. ft.
Wilder, Va.	2.2	8.2	14,225	12,458	1543	29.1	2.2	19	7644	640	1.07
Upshur Co., W. Va.[a]	1.3	7.7	14,110	12,950	1346	32.55	1.09	18	7555	581	1.08
Lundale, W. Va.	1.2	5.3	14,481	13,419	1404	34.73	1.83	21	9070	573	1.07
Rock Springs, Wyo.	10.4	3.2	13,117	13,364	1125	31.04	1.84	34	9345	487	1.06
Bush, Ill.	5.4	16.6	12,329	12,096	1373	24.54	1.64	19	7871	541	1.12
Neff, Ohio	2.9	11.0	12,906	11,195	1285	37.12	2.79	21	6835	608	1.10

[a] Briquet mix: 80 per cent semi-Carbocoal, 10 per cent coke-oven pitch, 10 per cent bituminous coal.

[1] Presented before the Division of Petroleum Chemistry at the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924.

[2] *Gas. Age-Record*, **50**, 531 (1922).

[3] *Chem. Met. Eng.*, **30**, 1019 (1924).

[4] Curtis and Geldard, *Ibid.*, **28**, 61 (1923).

In Table II Tupholme[5] gives a comparison of low- and high-temperature carbonization.

Table II—Yield from 1 Ton of Average Coal (25 to 30 per cent Volatile Matter)

	Low-Temperature, Coalite Process	High-Temperature Gas Works	Carbonization Coke Ovens
Temp. of carbonization	520° C. (1000° F.)	965° C. (1800° F.)	965° C. (1800° F.)
Gas	6000 to 6500 cu. ft. rich gas 700 to 750 B. t. u. per cu. ft.	12,000 cu. ft. medium quality (Town's) gas, 550 B. t. u. per cu. ft.	11,500 cu. ft. poor quality coke-oven gas 450 B. t. u. per cu. ft.
Liquid	20 gal. Coalite oil	10 gal. coal tar	8 gal. coal tar
Ammonium sulfate	15 lbs.	25 lbs.	28 lbs.
Residue in retort	14 cwt. smokeless fuel	13.5 cwt. soft coke	14–14.5 cwt. hard coke

The chief differences in composition of the two types of tar as noted by various workers are a decrease in the amount of tar acids and a change in the nature of the bases as the temperature of carbonization is increased. Other differences with regard to the percentage of unsaturated hydrocarbons, aromatic hydrocarbons, naphthenes, and paraffin hydrocarbons have been noted. Naphthalene and anthracene are absent in the low-temperature tar, whereas the high-temperature tars contain considerable quantities of these substances.

Analyses and Cracking of Charging Oils

In the present work three different low-temperature carbonization products were cracked. These included a dry tar, a neutral oil, and straight distillate. The results obtained from the cracking of these low-temperature tars are very encouraging from the viewpoint of motor fuel production. Further, it is known that the yields of motor fuel obtained from low-temperature coal tar or distillates shown herein can be increased.

Table III—Analysis of Charging Stock

	Dry Tar		Neutral Oil		Straight Distillate	
Coke, per cent[a]	11.3		1.5[b]		Trace	
Distillation[c]	° C. (° F.)	Sp. gr.	° C. (° F.)	Sp. gr.	° C. (° F.)	Sp. gr.
Initial point	196 (385)	...	193 (380)	...	185 (365)	...
10%	246	0.935	235	0.898	224	0.925
20%	267	0.954	249	0.914	246	0.951
30%	290	0.968	261	0.924	249	0.959
40%	307	0.985	273	0.933	274	0.966
50%	343	0.995	281	0.946	290	0.971
60%	356	1.003	293	0.908	304	0.978
70%	368	1.009	307	0.957	321	0.988
80%	393	1.055	321	0.962	341	0.992
90%	...	...	338	0.971	370	1.006
Maximum	393 (740)	...	338 (640)	...	370 (698)	...
Water, per cent	0.3		...		...	
Per cent at 210° C.	2.3		0.6		2.4	
Per cent at 300° C.	36.7		56.5		56.7	
Gravity of distillate	0.957		0.931		0.962	
Gravity of residue	...		0.995		0.902	
Per cent residue	...		10.0		10.0	
Flash point, 107.2° C. (225° F.) Cleveland						
Fire point, 126.7° C. (260° F.) Open Cup						
Gravity, ° A. P. I.	1.0		17.7		12.8	
Gravity, specific	1.074		0.948		0.981	
Viscosity at 77° F.(25° C.), seconds	206 Saybolt Furol		...		...	

[a] By weight on 100-cc. Engler distillation.
[b] Liquid residue.
[c] 800-cc. charge (1000-cc. Engler flask).

Table IV—Results from Cracking Low-Temperature Coal Tar

	Sp. gr.	Bé. gr.	Cc.	Per cent of tar
Charge	1.074	1.0	8000	
Cracked distillate	0.8927	27.0	3200	40.0
Water			144	1.8
Residuum			None	
Carbon, 9.4 lbs. (4263.8 grams.)[a]				
Noncondensable gas, 24.59 cu. ft. (696.6 liters)				
Carbon, gas and loss				58.2
Pressure, 100 lbs.: maximum temp., 452° C. (845° F.)				
Motor fuel (navy end point), sp. gr., 0.8299 (Bé. gr. 39.0)				18.1
Initial boiling point, 49° C. (120° F.)				
End point, 224° C. (435° F.)				
Cracked distillate bottoms, sp. gr. 0.9478 (Bé. gr. 17.8)				21.3
Loss				0.6

[a] Approximately 50 per cent coke by weight.

[5] *Chem. Met. Eng.*, **29**, 233 (1923).

Table V—Results from Cracking Neutral Oil from Low-Temperature Coal Tar

	Sp. gr.	Bé. gr.	Cc.	Per cent of neutral oil
Charge	0.9484	17.7	8000	
Cracked distillate	0.8514	34.7	4000	50.0
Water			360	4.5
Residuum	1.036	5.1	3747	46.8
Carbon, 0.20 lb. (90.72 grams)				
Noncondensable gas, 9.88 cu. ft. (279.7 liters) (Gain)				1.3
Pressure, 175 lbs.: maximum temp., 427° C. (800° F.)				
Motor fuel (navy end point), sp. gr. 0.8090 (Bé. gr. 43.4)				31.9
Initial boiling point, 49° C. (120° F.)				
End point, 226° C. (439° F.)				
Cracked distillate bottoms, sp. gr. 0.9421 (Bé. gr. 18.7)				16.9
Loss				1.2

The results in Tables IV and V were obtained by subjecting the tar and distillates to heat and pressure distillation.

Study of Mechanism of the Reaction

The tar acids were determined by absorption with a dilute (10 per cent) solution of sodium hydroxide. Bases were removed by a 20 per cent solution of sulfuric acid. For purpose of the present work, hydrocarbons absorbed by 1.84 specific gravity sulfuric acid are referred to as unsaturated hydrocarbons. Those absorbed by fuming sulfuric acid, after the above treatment, are considered as aromatic hydrocarbons. Naphthenes and paraffin hydrocarbons were determined by difference.

This method of analysis is not free from objections, but the convenience of application for the present purpose more than offsets such objections. All present methods of separating hydrocarbon groups are open to some objections, however. Some of the errors involved are due to the following:

(*a*) Higher homologs of olefins are nonreactive with cold concentrated sulfuric acid. (*b*) The lower members of the naphthene series are attacked by concentrated sulfuric acid. (*c*) The lower members of the paraffin series are dissolved in fuming sulfuric acid, especially with more than 10 per cent sulfur trioxide. Further, it is recognized that aromatic hydrocarbons with unsaturated side chains may be dissolved in 1.84 specific gravity sulfuric acid. These generalizations are the result of many workers' reports in the literature.

Table VI—Analysis of Neutral Oil Distillate from Low-Temperature Coal Tar and Cracked Products from Neutral Oil and Tar

	Neutral oil Per cent	Combined cracked distillate and residuum from neutral oil Per cent	—Cracked Distillate— From neutral oil Per cent	From tar[a] Per cent
Tar acids	2.70	4.00	4.80	29.5
Bases	4.50	5.00	4.75	2.75
Unsaturated hydrocarbons	60.60	54.00	38.40	31.25
Aromatic hydrocarbons	9.40	12.75	19.40	25.75
Naphthenes and paraffin hydrocarbons	22.80	24.25	32.65	0.75

[a] Owing to the difficulty of obtaining marked separation of the heavy original tar from the reagents used no analysis was made of same.

These data indicate a decrease in unsaturated compounds on cracking, while the aromatic hydrocarbons show a small increase. The lower boiling components in the cracked distillate show a marked re-arrangement and distribution of aromatic hydrocarbons and saturated hydrocarbons.

Table VII—Analysis of 12.8 Bé. Gr. Straight Distillate from Low-Temperature Coal Tar and Cracked Distillate from Same[a]

	Straight distillate Per cent	Combined distillate and residuum from straight distillate Per cent	Cracked distillate from straight distillate Per cent
Tar acids	26.50	24.30	21.25
Bases	3.25	3.50	4.25
Unsaturated hydrocarbons	44.25	42.50	27.00
Aromatic hydrocarbons	9.50	10.25	20.25
Naphthenes and paraffin hydrocarbons	16.50	19.45	27.25

[a] Thirty per cent of cracked distillate was removed at 175 pounds pressure in this experiment. This distillate contained 17.7 per cent of motor fuel, based on the original charging stock, Bé. 42.6, initial boiling point 115° F., end point 435° F.

The analysis of straight distillate from low-temperature coal tar and cracked distillate from same, shown in Table VII, bears out the above finding with respect to the changes that the hydrocarbons undergo, although to a much less degree owing to a lesser degree of cracking.

The effect of tar acids present on utility of the motor fuel will be left for future consideration. Under any circumstances they may be removed for other uses if necessary.

Morgan and Soule[6] showed the presence of secondary and tertiary nitrogen bases in low-temperature coal tars. No primary amines were found by them. In the cracking of these low-temperature coal tars or distillates therefrom, the same type of bases are present as in the original charging stock—namely, secondary and tertiary. The presence of these bases was determined by the difference in solubility of the benzene sulfonyl chloride derivative. The dilute acid solution of bases is treated with potassium hydroxide and benzene sulfonyl chloride, heating to destroy excess of the latter. The secondary and tertiary amines are extracted with ether, which in turn is treated with hydrochloric acid to remove the tertiary amines. The secondary amines may be recovered by evaporation of the ether extract, the tertiary by neutralization of the hydrochloric acid solution, and the primary, where present, by neutralization of the original alkaline solution. No primary amines were found either before or after cracking.

The tar acids in the cracked product seemed to be principally cresols, judging from their boiling point range. No naphthalene was present either in the original low-temperature coal tar product or in the cracked product obtained therefrom. A cut was made between 190° and 245° C., which on cooling down below −29° C. separated out no solid. The boiling point of naphthalene is 218° C.

Only a mere trace, if any, of anthracene was present in the original tar or other original low-temperature carbonization product. The cracked products from these low-temperature carbonization materials, however, show considerable anthracene, especially in the residual oil from the cracking still. The anthracene cut was made between 343° and 371° C. (anthracene boiling point 360° C.). The crude anthracene cut was chilled, filtered, and recrystallized with absolute alcohol. The melting point of the recovered anthracene was from 205° to 207° C. (actual 213° C.). On oxidation to anthraquinone with chromic acid and partial reduction and formation of the disodium derivative of anthranol with zinc dust and sodium hydroxide solution, the characteristic blood-red color of the anthranol in alkaline solution was observed. The latter is converted by atmospheric oxidation into anthraquinone.

The formation of anthracene is especially remarkable as the maximum temperature was only 452° C., while anthracene has been looked upon as a high-temperature product. It is believed that the time factor is an important one in the formation of anthracene, even at low temperatures. However, until experiment shows otherwise, the writers believe that pressure distillation of itself may influence the reaction.

Analysis, within the limits of the method used, of the hydrocarbons present before and after cracking indicate, as previously stated, a decrease in the unsaturated hydrocarbons and increase in the aromatic, naphthene, and paraffin hydrocarbons. The distribution of the various hydrocarbons in the cracked distillate is particularly noteworthy, as here we have present hydrocarbons formed during the reaction. Here also there is a tendency toward a decrease in the unsaturated hydrocarbons and an increase in the aromatic, naphthene, and paraffin hydrocarbons. The percentage of motor fuel in the cracked distillates may be calculated from the summaries.

[6] *Chem. Met. Eng.*, **20**, 977 (1919).

The formation of aromatic hydrocarbons from olefin and paraffin hydrocarbons has been shown in the literature.[7] Soule and Morgan[8] favor the theory of dehydrogenation and dealkylation of unsaturated hydrocarbons, as well as the possibility of hydrogenation and dealkylation of phenols in the formation of aromatic hydrocarbons with increase in temperature. The conversion in the cracking process does not in the present case involve an increase in temperature, but only the added factors of increase in time and distillation under pressure.

Jones[9] looks upon phenols as primary products of coal distillation, regarding the phenols present in high-temperature tar as being formed from those in low-temperature tar. At higher temperatures, around 750° C., Fischer and Schrader[10] have shown that cresols are reduced to benzene and homologs when heated in the presence of hydrogen.

Jones and Wheeler,[9] Parr and Olin[11] Pictet Kaiser, and Labouchere,[12] have all investigated the presence of nitrogen bases in low-temperature coal tar. Morgan and Soule[13] show the presence of secondary and tertiary bases and the absence of primary bases. As stated above, like findings have been made in the present work both in the original materials and cracked products derived therefrom.

Coke Formation

It is to be recalled that the primary object of low-temperature carbonization is the production of a smokeless fuel. The question of coke formation in the cracking process is therefore an important one. In the cracking of the original tar about 50 per cent of coke was formed. Analysis of the coke showed the following: per cent ash 1.53; per cent sulfur 0.74; calorific value 15,500 B. t. u. per pound. The volatile matter in the coke is regulated by the cracking operation, and can be varied from about 5 per cent upward. The sulfur content, of course, depends upon the original sulfur content of the coal from which the tar is derived.

Contrasted with the production of motor fuel from oil shales, it is pointed out that, whereas the residue—namely, the coke—from the heat treatment of coal is the primary product, the residue from the heat treatment of oil shales represents a by-product of relatively low value. This comparison in the economies of the two processes is worth bearing in mind in the general development of motor fuel substitutes for gasoline.

Refining Process

In refining the crude distillates to produce marketable motor fuel, the tar acids must first be removed. The refining process is then similar to those described by the writers[14] in various articles, using such simple reagents as sulfuric acid, caustic soda, litharge, and under certain conditions some adsorbent, and, of course, water. It may be advisable from an economic viewpoint to remove the tar acids before cracking, as this would increase the yield of motor fuel from the cracking process per se.

Finally, all the processes from the cracking of these low-temperature coal tars to the production of finished motor fuel may be carried out in refineries without change of equipment, a fact which should make this new source of motor fuel of particular interest to the oil refiner.

[7] Rittman, *U. S. Bur. Mines., Bull.* **114**; Egloff and Twomey, *Met. Chem. Eng.*, **14**, 247 (1916); Jones, *J. Soc. Chem. Ind.*, **36**, 3 (1917).

[8] *Chem. Met. Eng.*, **26**, 1025 (1922).

[9] See also Jones and Wheeler, *J. Chem. Soc.*, **105**, 40 (1914).

[10] *Brennstoff.-Chem.*, **1**, 4, 22 (1920); **2**, 37 (1921).

[11] University of Illinois Expt. Sta., *Bull.* **60** and **79**.

[12] *Compt. rend.*, **165**, 113, 358 (1917).

[13] *Chem. Met. Eng.*, **26**, 977 (1922).

[14] *The Refiner*, **1923**.

Better Crank-Case Draining Service[1]

By C. M. Larson[2]

SINCLAIR REFINING CO., NEW YORK, N. Y.

This paper outlines the actual facts of dilution of crank-case oil without attempting to delve too deeply into the causes for crank-case dilution or remedial measures to correct dilution.

Data were gathered from dynamometer laboratory test work of scientific accuracy and also from actual road performance of automobiles. Curves are developed to display the relationship of dilution effect on engine performance. Other curves show the effect of different end point fuels, summer and winter weather changes, varying grades or viscosities of motor oils, and piston clearances, on the rate at which the percentage of dilution increases in the crank case of an automobile engine.

Two simple devices are described by the use of which the motorist can determine when his oil has become unfit for further use and may be considered dangerous. These devices constitute a pocket laboratory, and make it possible for the motorist to determine the proper times for changing crank-case oil based on the condition of the oil, and not on arbitrary or average mileage.

THE motorist of today has heard that his car needs draining. Some dealers tell him his engine should be drained every 700 miles, whereas his instruction booklet says another figure. On the other hand, the oil company's service station attendant, who tells the motorist that the crank case should be drained after every 400 miles run in winter and after 800 miles in summer weather, is frowned upon as trying to sell oil, not service. It is quite true that with the data on hand no figures of actual miles run as a guide to draining a certain make of car are reliable, and constitute only a rule-of-thumb method which may be harmful to the motor in some cases and wasteful of oil in others.

The effect of dilution on frictional horsepower (that derived from dynamometer calculations) is shown by Figure 1—a slight decrease in frictional horsepower at no load as the oil is diluted. Yet on the other hand, from the maximum brake horsepower curve it is readily seen that there is a decided power loss with increased dilution unless the initial oil is entirely too viscous. If there were no ill effect due to dilution, lubrication engineers would have an easy time getting various grades of motor oils placed on the approved list by motor manufacturers, for it stands to reason that a well-refined motor oil with ample body and medium high flash and fire would be better than a contaminated one having a viscosity slightly heavier than floor oil and with a flash as low as kerosene.

Inasmuch as the piston seal has a direct bearing on how the diluent reaches the crank case, naturally the viscosity, which is the characteristic classifying the grade of motor oil, materially affects the percentage of diluent that leaks into the crank case of an automotive engine. As shown in Figure 2,[3] a light motor oil will have to be drained at more frequent intervals than either the medium or the heavy grade, as the percentage of dilution is much greater per 100 miles. It is true that it is possible to get too heavy an oil so that for the first few miles excessive dilution will occur, as the oil cannot reach the walls of the cylinder to form a seal between the piston and cylinder walls until it is diluted to the proper viscosity. It follows that the motor that has been worn will have greater piston clearances, and therefore the effectiveness of piston seal will be more difficult to attain. This is clearly demonstrated in Figure 3.

Lately we have heard a great deal about *A*, *B*, *C*, and *D* grades of gasoline, and have been told that crank-case dilution

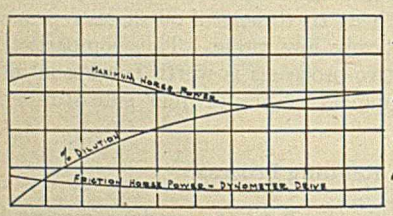


Figure 1—Effect of Dilution on Frictional Horsepower

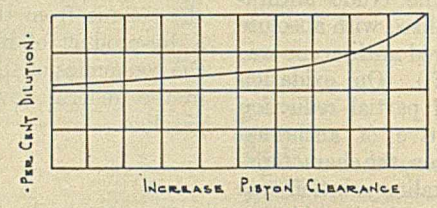


Figure 3—Data Taken from Dynamometer Runs on Oakland Motor, Using Five Increments of Undersize Pistons, Thus Duplicating the Stages of Wear Occurring throughout the Life of an Automotive Engine

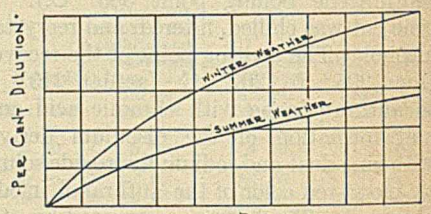


Figure 5—Composite Curves Plotted from Data Compiled from Runs Made by Sixteen Cars of Various Makes

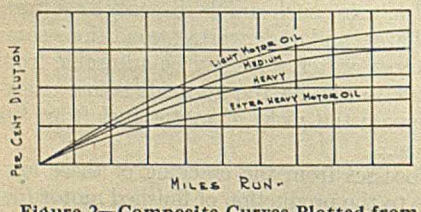


Figure 2—Composite Curves Plotted from Results of Dynamometer Test on Nine Grades of Motor Oil, Ranging from 185 to 1800 Seconds Saybolt at 100° F., and Road Test Made with Five Standard Makes of Cars, Using the Light, Medium, Heavy, and Extra Heavy Motor Oils of a Well-Known Brand

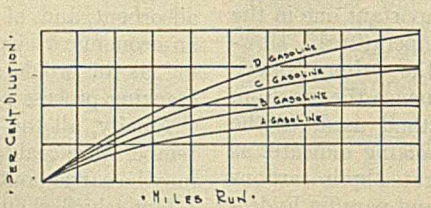


Figure 4—Composite Curves Compiled from Data Obtained from Sixteen Cars, Each Making Separate Runs on *A*, *B*, *C*, and *D* Gasoline

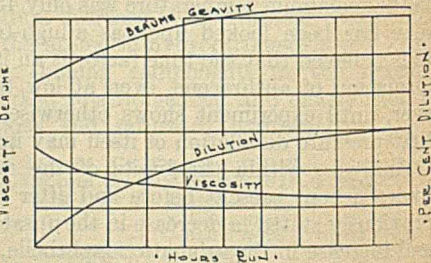


Figure 6—Composite Curves from Data Pertaining to Nine Different Grades of Oils, Varying in Viscosities and Base of Crude

[1] Presented under the title "Crank-Case Dilution" before the Division of Petroleum Chemistry at the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924.

[2] Supervising engineer.

[3] *J. Soc. Automotive Eng.*, **14**, 152 (1924), Tables 2 to 6.

increases progressively with decreasing volatility and the rate of increase is more marked for the heavier fuel. This increase in dilution with increased end points of the fuel is shown in Figure 4.

Through the tests run on the *A*, *B*, *C*, and *D* fuels it was also developed that during winter operations a more decided increase in percentage of dilution was noted than in summer. The curve for winter weather in Figure 5 shows a pronounced contamination of the crank-case oil due to dilution. Tests have also revealed that one or two applications of the choker in starting during cold weather will cause more dilution than several hundred miles of running.

Figure 7—Dilut-o-meter

Realizing that a more comprehensive service should be offered the motor public through the oil service stations, research work was started to make the "crank-case service" a practical, scientific one. As the foregoing charts show that the dilution of the crank-case oil for a certain make of car is dependent upon the viscosity of the new motor oil, the piston clearance, end point of fuel, and running temperature of the motor, as well as other factors not shown graphically, it was necessary to look elsewhere than to actual miles run. From Figure 6 it is readily seen that as the crank-case oil is diluted the Baumé gravity changes with the viscosity of the oil.

After repeated checking of used samples and then charting the data of gravity change with per cent dilution, an instrument called a "Dilut-o-meter" (Figure 7) was developed. This is simply a hydrometer, and like all such instruments depends for its readings on the density or specific gravity of the liquid being tested. In this case, however, the scale does not read in terms of Baumé gravity or specific gravity, but in terms which indicate the condition of the oil—whether good, fair, poor, or dangerous—obviating the necessity for interpretation of results and thus making it better adapted for general use.

The principle according to which the instrument operates is that as an oil is diluted by fuel it becomes lighter in gravity. At the same time there is a wide variation in the density or specific gravity of lubricating oils when new, some oils when new being as light as others after they are diluted beyond the point of satisfactory lubrication. This variation is taken care of by putting the indicating scale, not directly on the stem of the instrument, but on the sliding sleeve which may be moved up or down. The instrument may be set by putting it in the new oil and moving the scale to the zero point, or it may be set from tables furnished by the makers showing the proper scale settings for the well-known oils.

Since lubrication satisfaction depends on the viscosity or body of the oil and this body is decreased by dilution as shown in Figure 6, it was also possible to develop a pocket viscometer, or Visgage (Figure 8), for crank-case draining determinations.

The principle of the Visgage is that the travel of spheres through two oils is dependent upon their relative viscosities. Therefore, if we have two parallel inclined tubes of the same size containing the same oil at the same temperature, too small spheres will reach the bottom of the incline at the same moment. However, if one oil is twice as viscous as the other, the sphere in the heavier oil will be only half the way down the incline when the sphere in the lighter oil has reached the bottom. Thus, if the viscosity of the oil in one tube is known, it is possible to evolve a scale mathematically by which the viscosity of the unknown oil can be read directly. Inasmuch as the temperature of the oil in both tubes would be the same at the time of test, no temperature correction would be required.

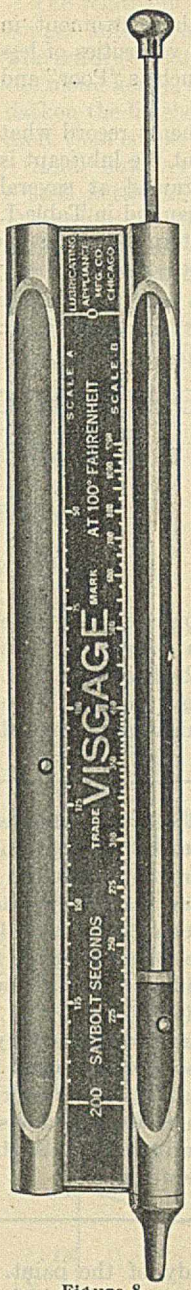


Figure 8

The accuracy of this instrument has been shown to run higher than 95 to 98 per cent in Saybolt seconds after the operator has become a little experienced, and at all times the error is negligible for practical work. It is so constructed that to make a test it is only necessary to insert the nozzle in the used oil and fill like a syringe. The determination is made and the viscosity at 100° F. read directly on the scale. To eject and clean the instrument it is only necessary to return the plunger handle to its original position. The entire operation does not require 30 seconds for a medium oil. Stop watch, thermometer, cleaning apparatus, conversion tables, and so forth, are eliminated and the difficult laboratory test of viscosity is reduced to a simple manipulation.

In order to simplify the scale for the motorist and at the same time give him a means whereby he can follow the manufacturer's recommendation, a scale as shown in Figure 9 was devised. By using the S. A. E. Handbook, Vol. I, D–151, crank-case lubricating viscosity oils specifications for Light (020 and 20), Medium (03 and 30), Heavy (50), etc., the zones were laid out to replace the

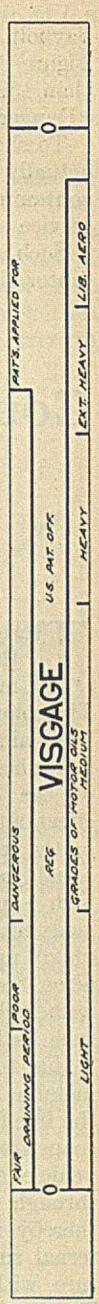


Figure 9

Table I

	Car Make	Mileage	Grade when New	—Condition of Oil Drained— Dilut-o-meter	Visgage Seconds
1	Buick	1000	Medium	Dangerous	90
2	Cadillac	600	Heavy	Very dangerous	Too black
3	Cadillac	700	Extra heavy	Dangerous	75
4	Cadillac	800	Extra heavy	Poor	85
5	Chevrolet	650	Medium	Top dangerous	45
6	Chevrolet	300	Medium	Top dangerous	45
7	Chevrolet	500	Medium	Dangerous	70
8	Chevrolet	639	Medium	Way over top	35
9	Chevrolet	1000	Medium	Dangerous	65
10	Chevrolet	500	Medium	Dangerous	60
11	Ford	600	Medium	Dangerous	70
12	Ford	500	Medium	Poor	135
13	Ford	350	Medium	Poor	125
14	Ford	600	Medium	Fair	145
15	Ford	270	Heavy	Poor, plus	105
16	Ford	600	Medium	Poor	125
17	Ford	1000	Medium	Between good and fair	205
18	Ford	800	Medium	Top dangerous	50
19	Studebaker	500	Medium	Very poor	75
20	Studebaker	500	Heavy	Very dangerous	50
21	Studebaker	500	Medium	Very dangerous (35%)	45

Saybolt viscosity readings supplied with the instrument in Figure 8. On the top side of the scale the viscosities of less than 180 seconds were graduated in zones such as "Poor" and "Dangerous."

To show more clearly how these instruments record what actually is taking place and to what extent the lubricant is contaminated, the tabulation of cars drained at several service stations during the same day is recorded in Table I.

Such devices allow the motorist to determine when his motor oil is getting badly contaminated and so light in body that it is not giving the proper piston seal. They also tell him that his fuel mixture is incorrect, that he is using choker too freely, or that the grade of fuel he is using accentuates dilution. The factors entering into this dilution problem are so numerous that the present stated period of draining the crank case does not remedy the situation. In draining the oil at predetermined periods, it is discovered either that the oil is past the point of suitability or that it still contains sufficient body to lubricate properly, and therefore should not be thrown away.

Comparison of Monel and Copper Kettles in Boiling Linseed Oil[1]

By C. Fichandler

Republic Varnish Co., Newark, N. J.

THIS investigation was undertaken in order to determine the effect of the material of which a varnish kettle is made on the properties of a kettle-bodied linseed oil. The color of the finished product is of primary importance to the paint man since the whiteness of a high-grade enamel is a function of the paleness of the bodied oil. The effect of the kettle reactions on the acidity of the oil is of equal importance. Too high a percentage of free acids in an oil will cause it to "body up" or even "liver," when brought into contact with highly basic pigments such as lead or zinc. This is due to the formation of metallic salts or soaps[2] of the free fatty acids. These soaps are insoluble in the oil vehicle and are dispersed through it as a colloid, thereby increasing the internal surface of the mixture, with a resultant increase in the body of the paint. Thus, oils of high acidity tend to produce enamels which become thick and pasty, with a loss of the desired brushing and flowing qualities.

Linseed oil "heat-bodied" in a monel metal kettle is found to be paler in color and to have a lower acid value than that cooked in a copper kettle. This is due to the fact that copper is not so resistant to attack by the free acids of the linseed oil as is monel metal. The soluble copper soaps formed cause a darkening of the oil and also tend to increase the rate of formation of free acids.

This was determined by bodying batches of linseed oil in monel and copper kettles under identical heat conditions. Samples were withdrawn from both at definite intervals, and viscosity, acid number, iodine number, and color were thus determined at each stage of the operation.

In view of these facts it is indeed surprising that very little systematic study has been conducted on the relation of the varnish kettle to the production of a pale, low-acid bodied oil. Although the varnish-maker has found that kettles of copper produce a paler oil than those of steel, there are practically no data on the subject in the literature.

However, a very interesting piece of work was carried on by Harrison[3] in an attempt to determine the effect of aluminium, copper, and iron kettles on the color of bodied linseed oil. He obtained three set-pots of about a half gallon capacity and bodied quart batches of oil at 610° F. in each set-pot. He then compared the color of the finished oils by simple ocular comparison and by means of a Lovibond tintometer, recording the relative darkness of his oils in terms of the number of units of yellow developed. After several determinations, he proved conclusively that the aluminium pot developed the palest oil, several shades lighter than that cooked in the copper pot, while the iron pot developed by far the darkest oil.

This investigation was criticized by Harrison's colleagues, however, on the ground that laboratory results frequently prove at variance with results on a commercial scale, and that he had neglected to correlate his color changes with any of the chemical reactions of the oil. It was in an effort to meet this criticism that the present work was undertaken. It was carried on under typical factory conditions so that data of value to the practical varnish man might be obtained.

Operation

A monel metal set-kettle of about 500 gallon capacity was compared with an ordinary 150-gallon copper varnish kettle.

(It was impossible to compare kettles of the same size as at the time of the experiment the plant was equipped with only the large type of monel kettle.) A batch of 300 gallons of oil was cooked in the former while the latter held 75 gallons. The size of the batches was so selected that the ratio of the mass of the oil to the area of the surface exposed to the air was approximately the same. Thus the factors that might operate in darkening the oils through oxidation were made identical in both kettles.

Heat was applied to both kettles at the same time and temperatures were observed every half hour. By regulating the kerosene burner that was heating the copper kettle, and by removing the kettle from the fire when necessary, it was possible practically to duplicate the temperature-time curve of the larger set kettle. In this way both masses of oil were cooked under the same conditions; thus any variation in the characteristics of the finished oil could then be ascribed to the composition of the kettles, rather than to viscosity differences caused by variations in heat treatment.

In 4 hours the oils reached the temperature range at which polymerizaton takes place (570° to 600° F.), and samples of each oil were withdrawn. Thereafter samples were taken every hour for 5 hours.

[1] Received November 7, 1924.

[2] Pickard, *Am. Paint J.*, April 10, 1922.

[3] Harrison, *Proc. Paint Varnish Soc.*, 1920.

The kettle reactions of the oils were next ascertained by examination of the samples that had been withdrawn at different stages of the polymerization. The color, viscosity, acid number, and iodine number of each sample were determined. The viscosity was determined by mixing 60 grams of oil with 30 grams of redistilled spirits of turpentine and noting the time necessary for 90 cc. of this mixture to run through a viscometer of the flow type at 70° F. The color was observed by placing the oils in small tubes of the same bore and examining them by transmitted light.

The acid number was determined by refluxing 2 to 4 grams of oil in 50 cc. of a neutral benzol-alcohol mixture for a half hour and then titrating against a decinormal solution of sodium hydroxide. The iodine number was determined by the Hanus method, keeping 50 to 60 per cent of Hanus solution in excess in each absorption.

The oil used was an alkali-refined oil and gave the following analysis:

Specific gravity	0.933
Iodine number (Hanus)	180.2
Acid number	0.92
Viscosity	10 seconds

Data

	Temperature ° F.		Viscosity Seconds		Iodine Number		Acid Number Mg.	
Time	Monel	Copper	Monel	Copper	Monel	Copper	Monel	Copper
6.45	Start	Start	10	10	180.2	180.2	0.92	0.92
7.15	170	220						
7.45	235	285						
8.15	300	300						
8.45	390	398						
9.15	455	450						
9.45	525	525						
10.15	572	580	11	11	165.6	166.5	1.71	1.69
10.45	570	575						
11.15	585	587	14	15	154.0	153.2	3.58	3.7
11.45	589	588						
12.15	588	588	19	20	144.0	144.2	5.5	6.35
12.45	587	587						
1.15	575	577	29	30	137.0	137.5	7.75	9.35
1.45	585	580						
2.15	576	570	46	48	134.5	134.0	9.2	11.1
2.45	580	575						
3.15	580	575	64	66	134.1	134.0	10.6	13.05
3.45	530	515	73	74			11.3	14.5

At every stage of the operation the oils withdrawn from the copper kettle were noticeably darker than the corresponding samples from the monel batch.

Discussion of Data

The viscosity curves (Figure 1) show that the control of the heat conditions of the two batches was successful. The viscosity of both oils was practically the same at every stage of the operation, indicating that polymerization took place at the same rate in both kettles. Hence, any variations in the other chemical properties of the oils cannot be laid to any variations in the heat treatment of the two batches, but are due solely to the reactions of the kettle surfaces with the oils.

The iodine number curves (Figure 2) show that the rate of polymerization and oxidation of the unsaturated glycerides was unaffected by the composition of the kettle. Nevertheless, the results were of interest as a check on the control of the operation. The iodine number of an oil varies inversely with the viscosity or degree of polymerization. Hence, the close agreement of the results at practically every stage of the operation furnishes additional evidence that heat conditions in both kettles were identical. Of purely theoretical interest is the rate of change of the iodine number. In reaching 580° F. it dropped 14 points, falling off only 9 points in the next hour, and dropping still less in the ensuing time. This would indicate that the polymerization of the more highly unsaturated linolenin with three double bonds, and linolin with two, begins quite early in the heating process and proceeds rapidly till most of their linkages have been closed. From then on, polymerization of the less unsaturated olein is much less rapid.

The relatively darker color of the samples taken from the copper kettle has been interpreted in two conflicting ways. The natural assumption is that the free acids in the oil attack the metal kettle, forming soluble metallic soaps which tend to darken the finished oils. Thus, iron soaps would discolor oil more than copper and copper more than aluminium.

Reid,[3] however, claims that in examination of oil boiled in a steel kettle he was able to find scarcely a trace of iron. Discarding the solubility theory, he asserts that the catalytic action of the metal in contact with the oil in the presence of air causes considerable oxidation followed by appreciable darkening of the oil. He explains the fact that some kettles yield darker oils than others by the relative catalytic strength of iron, copper, and aluminium in that order.

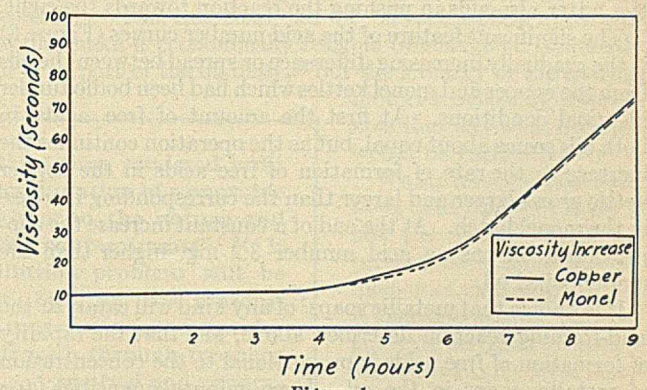


Figure 1

Nevertheless, the weight of evidence seems to point to the solubility explanation mentioned previously. Gardner[4] has recently conducted some valuable experiments on the availability of various metals and alloys for use in constructing varnish kettles. On immersing strips of metal of approximately 4.5 square inches surface area in high-acid linseed oil at 500° F. for 2 hours, he found that the resistance of monel metal to the fatty acids of linseed oil was considerably greater than that of copper. On reweighing a strip of monel metal originally weighing 21 grams, he found that its loss in weight was 0.0003 gram, whereas a strip of copper weighing 19 grams lost 0.0006 gram, exactly twice as much under identical conditions.

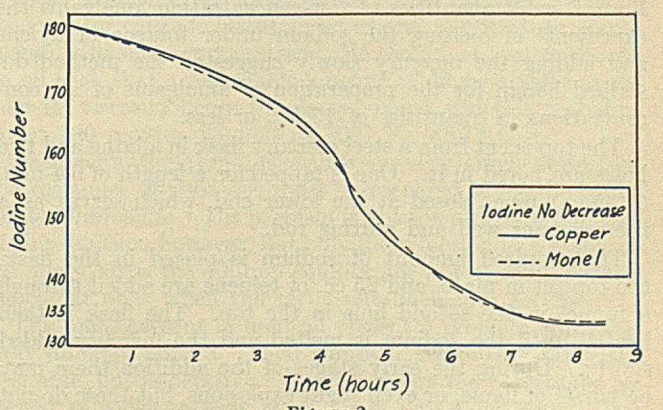


Figure 2

This bears out the theory that the relative darkening of the copper-boiled oil can be ascribed directly to the presence of dissolved copper in the form of soluble soaps, whereas a very much smaller amount of metal went into solution from the monel kettle. Still further evidence in favor of this explanation will be found on considering the curves on acid numbers.

Linseed oil is composed of glycerides of linolenic and linolic acids, with smaller amounts of oleic and stearic acids. Prac-

[4] Gardner, *Paint Mfrs. Assoc., Circ.* **125** (May, 1921).

tically all treatments, such as aging, oxidation, and polymerization, bring about a splitting of these fatty acids from the glycerol. Thus it is seen that the acid numbers of both oils increase as the polymerization advances. This is explained by Coffey[5] as due to the hydrolysis of the glycerides by water, traces of which are to be found in raw linseed oil.

$$C_3H_5\begin{matrix}\diagup\ OLn\\ —\ OL\\ \diagdown\ OSt\end{matrix} + 3H_2O \rightarrow \underset{\text{Glycerol}}{C_3H_5(OH)_3} + \underset{\text{Linolenic acid}}{HLn} + \underset{\text{Linolic acid}}{HL} + \underset{\text{Stearic acid}}{HSt}$$

At the high heats reached the glycerol is rapidly volatilized, so that, following the mass law, the reaction goes on towards completion. Moreover, the glycerol is continually being broken up into acrolein and water; the constant formation of the latter also aids in pushing the reaction towards the right.

The significant feature of the acid number curves (Figure 3) is the gradually increasing difference or spread between the oils from the copper and monel kettles which had been bodied under identical conditions. At first the amount of free acids in both oils seems about equal, but as the operation continues the increase in the rate of formation of free acids in the copper kettle grows larger and larger than the corresponding increase in the monel batch. At the end of a constant increase the copper-boiled oil has an acid number 3.2 mg. higher than the monel-boiled oil.

It is known that metallic soaps[2] of any kind will catalyze the acid-forming reaction described above, and that the rapidity of formation of free acids is proportional to the concentration of metallic soaps in the oil. Even minute quantities, too small to be detected by direct analysis, exert an appreciable effect. Hence the higher acidity of the oil boiled in contact with copper offers indirect but positive evidence that the concentration of metallic catalysts therein was higher than in the monel

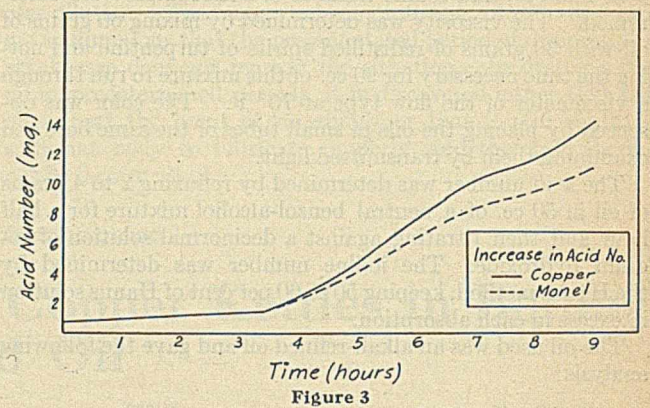


Figure 3

heated oil. Thus the acid number curves also tend to show that the relative darkness of oil bodied in the copper kettle is due to the presence of an excess of copper soaps, resulting from the relative solubility of copper in the free acids of linseed oil.

Conclusion

In the production of a kettle-bodied linseed oil, varnish kettles of monel metal have been found superior to copper kettles in two respects: (*a*) a much paler oil is produced; (*b*) a lower acid product is formed, because copper is more soluble in the acids of linseed oil than is monel metal.

[5] *J. Soc. Chem. Ind.*, **40**, 19 (1921).

Large-Scale Preparation of Sodium Amalgam in the Laboratory[1]

By R. R. Read and Carl Lucarini

University of Vermont, Burlington, Vt.

THE usual method of preparing sodium amalgams by the addition of sodium to mercury is a laborious one and requires the observance of caution.[2] In the preparation of small quantities of low-concentration amalgams the expedient[3] of melting the sodium under toluene or xylene and adding the mercury slowly suggested the method described herein for the preparation of amalgams of all concentrations in quantities of 15 kg. or less.

The top is cut from a steel mercury flask in a lathe and two holes are bored in it. One is tapped for a length of 6.4-mm. (1/4-inch) pipe, closed at the lower end, which serves as a thermometer well and stirring rod.

The required amount of sodium is placed in the flask, the top set in place, and 25 cc. of toluene are added through a funnel in the second hole in the top. The flask is then heated until the sodium is melted and the mercury added slowly. During the early stages of the addition there may be bursts of flame, or even slight explosions, but these do not lift the top off the flask. More toluene may be added to prevent oxidation. Some mercury vapor is undoubtedly thrown out of the flask, so that a well ventilated hood is necessary. The latter portions of the mercury may be added rapidly. When the amalgam is completely melted, it is stirred and poured into a round-bottom kettle to cool.

Amalgams up to 3 per cent of sodium may be granulated by vigorous stirring during cooling, the few remaining lumps being crushed with a pestle. This is particularly successful with 2 per cent amalgams. A useful modification is that of pouring the molten material into toluene,[4] but the writers have not found it adaptable to large quantities. To prevent ignition, amalgams of 15 to 25 per cent sodium are best poured after the addition of mineral oil. This can be washed off with toluene, care being taken to open up any oil pockets.

The solid amalgam may be crushed in a power-driven jaw crusher or in a large iron mortar by hand. In either case a moist gauze bandage should be worn over the face as the inhalation of the dust may cause pronounced symptoms of mercury poisoning. The crushed material heats rapidly on exposure and should be covered immediately. One melt, exclusive of crushing, may be completed per hour.

If it is desired to avoid the possible contamination from the iron vessels, smaller quantities of low concentration amalgam may be prepared in glass.[2] As much as 4 kg. of 2 per cent material may be prepared at once. The sodium is melted down under the toluene on an electric hot plate in a Pyrex beaker, chosen for its unusual thickness and the mercury added with caution. The material may solidify. In such a case, after all the mercury has been added the beaker is heated until the toluene has boiled away and the amalgam becomes liquid. The dross is removed and the melt cooled with stirring, the product being finely granular. The time required is about 3.5 hours.

[1] Received January 28, 1925.

[2] A complete melting point curve for sodium amalgams is given by Van Stone, *Chem. News*, **103**, 181 (1911).

[3] Nef, *Ann.*, **280**, 307 (1894).

[4] Hirschfelder and Hart, This Journal, **12**, 499 (1920).

Deterioration and Reclamation of Used Automobile Crank-Case Oil[1]

By Alan E. Flowers, Ford H. McBerty, and Ronald Reamer

De Laval Separator Co., Poughkeepsie, N. Y.

Automobile crank-case oil is in time rendered unfit for further use through the accumulation of removable impurities. Information is given on the nature and rate of accumulation of these contaminants. It is shown that eventually the dilution problem will be solved by the engine builder, but, for the present, excessive dilution and the still more harmful accumulation of solids should be dealt with through frequent change and recovery of the oil. A method and apparatus for reclaiming used oils are described and the characteristics of the recovered oils are compared with those of new oils.

A simple and rapid laboratory method is described for determining the degree of dilution of the used oil.

MANY attempts have been made in recent years to reduce the enormous waste now attendant upon the draining and discarding of used internal combustion engine lubricant. This paper presents the data obtained in the development of equipment for achieving this result. The work done has included the examination of numerous samples of new and used oils and the reclamation of the latter with a view to securing a product conforming to established standards.

The growth of interest in this subject among techincal men during the last few years has made available considerable information as to the nature and causes of the deterioration of crank-case oil.* It is well recognized that the oil is rendered unfit for use by an accumulation of removable impurities and not by actual breaking down into inferior and nonlubricating products.

Used oils differ from new oils in that (*a*) heavy ends of the motor fuel are dissolved in the oil, thereby reducing its viscosity; (*b*) solid particles of carbon, metal, and road dirt are suspended in the oil; and (*c*) the oil has a darker color, higher acidity, and higher Conradson carbon residue value.

Dilution has long been considered the most objectionable contaminant of the oil. Barnard[1],† states that engine wear at dilutions beyond 10 or 15 per cent increases at a much greater percentage rate than does the dilution. The writers' examination of used oils representing a very large number of cars (Table I) shows that dilutions in excess of these figures must be regarded as infrequent, at least for commercial vehicles. These operate under conditions approximating continuous running. Privately owned cars in winter represent the other extreme, since the high proportion of cold starts and short runs may result in dilutions as high as 30 per cent. (Samples 12 and 13, Table I)

The rate of increase of dilution with mileage is shown in Figure 1 for the three cars from which Samples 14 to 16 were taken. These curves show that maximum dilution, as indicated by reduced viscosity, is reached after from 100 to 250 miles (160 to 400 km.) of running. This observation is in fair agreement with that of Mac Coull,[2] who found the oil in five trucks reaching the point of minimum viscosity in from 25 to 250 miles (40 to 400 km.) and in each case the major part of the drop occurred in the first 25 miles (40 km.).

These facts give no justification for the generally recommended practice of changing crank-case oil after 400 to 1200 miles (640 to 1920 km.) of use. If dilution is to be regarded as the reason for changing oil, it would be necessary to recommend a change every 100 or 200 miles (160 to 320 km.). It is obvious that such a practice would be very difficult to establish. The universal use of oil reclamation apparatus would make it economically feasible to change oil frequently or even part of the oil daily,[20] but the lethargy of the average motorist makes it improbable that any such program would be carried out.

We are forced to conclude, then, that dilution alone is not the factor which, at present, determines the frequency of changing oil. It is logical to assume that engines are designed to operate satisfactorily with lubricants containing a reasonable amount of dilution. Where dilution is excessive, the solution of the problem is a matter of prevention through operating care or by engine design rather than reclamation. Mac Coull[2] has shown that by proper control of crank-case and cylinder jacket temperatures dilution can be reduced to an unimportant factor. The elimination of excessive dilution may therefore be considered a problem for the automobile manufacturer, but until it is thus solved it must be handled by the reclaimer of used oils and by the motorist himself. In winter the motorist can reduce dilution by using the radiator cover to maintain an engine temperature corresponding to summer operation. He should, of course, choose an oil such that a reasonable amount of dilution will not reduce its viscosity below the danger point, which is probably about 180 seconds Saybolt at 100° F. (38.7° C.)[3].

Inasmuch as these precautions are now very largely neglected, the reclaimer of used oils must be prepared to handle badly diluted lubricants. His problem is not the complete removal of this dilution, however, but only its reduction to a reasonable figure, since the dilution equilibrium will be reëstablished almost at once when the oil is put back into service.

The solids present in used oil present a problem of a radically different nature. Their complete removal is not only desirable, but imperative. Table I shows the percentage by weight of solids to vary from about 1 to 4 per cent. The volume percentages, as determined by centrifuging, are higher, usually in the neighborhood of 10 per cent. It is the opinion of the writers that these solids are the most harmful of all the contaminants of the oil, and it is fortunate that their removal is the easiest step in the reclamation of used oil.

Analysis of a typical sample of solids showed it to consist of:

	Per cent
Soft asphaltic material (benzene soluble)	5
Metals, chiefly iron (acid soluble)	20
Carbonaceous matter (by ignition)	50
Road dirt (acid-insoluble ash)	25

[1] Received March 3, 1925. Presented before the Division of Petroleum Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

* See bibliography at end of article.

† Numbers in text refer to bibliography.

Table I—Crank-Case Oil Properties

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Viscosity at 37.78° C.:																
New	400	205	205								355	342	165	240	240	240
Used	247	114	132	300	262	176	99	213	260	156	193	88	59	174	217	158
Reclaimed	350	192	191	484	456	405	347	420	442	378						
Lab. steam blown					491	540	337	423	453	398	325	408	313	308	297	270
Flash Point, ° C.:																
New	218.5	216	216								235	193	204.5	229	229	229
Used	127	85	105	105	107	79	60	85	110	82	102	66	57	88	113	91
Reclaimed	174	168	179	185	182	182	163	179	188	168						
Lab. steam blown					216	210	179	188	210	179	207	176	182	219	204.5	221
Fire Point, ° C.:																
New	249	243	243								274	221	235	260	260	260
Used	149	116	149	168	146	96	85	138	171	94	116	79	63	124	188	132
Reclaimed	221	224	235	252	240	213	201	216	238	204						
Lab. steam blown					257	238	213	221	235	219	249	210	216	252	227	244
Acidity, Mg. KOH/Gram:																
New	0.13	0.01	0.01								0.02	0.72	0.04	0.02	0.02	0.02
Used	0.30	0.21	0.19	0.40	0.30	0.91	0.58	0.20	0.31		0.33	0.88	0.27	0.17	0.11	0.08
Reclaimed	0.09	0.03	0.18	0.15	0.19	0.27	0.18	0.16	0.24	0.16						
Lab. steam blown																
Conradson Carbon, Per cent:																
New	0.56	0.04	0.04								0.37	0.08	0.04	0.15	0.15	0.15
Used				0.95	1.06	1.10	0.83	0.23	0.63	0.71	0.49	0.21	0.37	0.42	0.40	0.28
Reclaimed		0.19		1.08	1.06	0.93	0.84	0.44	0.70	0.71						
Lab. steam blown												0.26				
Specific Gravity at 15.55° C.:																
New	0.907	0.881	0.881									0.926	0.884	0.875	0.875	0.875
Used		0.877	0.876									0.906	0.878	0.876	0.881	0.876
Reclaimed	0.902	0.886	0.884													
Lab. steam blown																
Solids, Weight Per cent:																
Used				1.4	1.2		3.2	1	1			0.3	0.4	0.3	0.3	0.4
Dilution, Weight Per cent:																
Used				7	7	11	15	7	7	12	9	19	28	10	6	9

Samples 1 to 5, inclusive, and 8 and 9 were 189.5-liter lots of oil collected by operators of fleets of cars in commercial service, including both taxicabs and trucks. Characteristics are given for the new oil, which was said to have been used, in the first three cases.

Samples 6, 7, and 10 were 189.5-liter lots of oil from cars drained at service stations. The oils corresponding to Samples 1 to 10 were reclaimed by the process described in this paper, the recovered oil characteristics being given in the table.

Samples 11 to 13 were 3.78-liter lots from privately owned cars. Sample 12 was taken in early winter from a car that had run about 20,900 km. total, and about 1610 km. on this oil with the addition of 0.94 liter of make-up oil after 805 km. Sample 13 was taken in winter from a practically new car, which had used the oil for about 805 km.

Samples 14 to 16 were taken in summer from three taxicabs. The variation of viscosity with travel distance for these cars is shown in Figure 1.

This combination would undoubtedly make a very fair abrasive material. The analysis indicates that there is a possibility for preventive as well as curative measures in combating this evil. Although the metal particles come from the engine itself, the road dirt comes in as dust with the air supply, and the use of air cleaners, such as are provided on tractors, would seem to be a step in the right direction. However, the work of Barnard[1] indicates that some, at least, of the air cleaners now on the market are less efficient than might be hoped and play but little part in reducing engine wear. In any case, the use of air cleaners can hardly be expected to prevent the accumulation of metallic particles in the oil. This points to frequent change and reclamation as a logical solution of the problem.

The carbonaceous portion of the solids in used oil is probably not an appreciable factor in promoting engine wear directly. The asphaltic nature of this material, however, enables it to act as a binder in the formation of hard deposits on pistons and cylinder heads. It serves also to hold dirt and gritty particles where they will promote wear. Its removal is therefore an essential feature of any reclamation process.

Organic acidity, which is present to varying extents in new oils, increases during use. The question whether or not its presence is to be regarded as an evil is a much mooted one. In the absence of positive evidence of its serving a useful purpose, it may well be looked on with suspicion. The oil reclaimer can readily reduce the acidity to a value comparable with that in new oils.

Although a light color is considered an index of the amount of refining to which an oil has been subjected, there appears to be no evidence that color is in any way an indication of lubricating value. Having started with new oils of good quality, there is no reason to believe that the darkening which takes place in some oils more than others during use denotes a corresponding lowering of quality in the darker oil.

The Conradson carbon residue value is commonly regarded as an indication of the tendency of an oil to form carbon in an engine. There seems, however, to be a dearth of definite published evidence as to the interrelation of these properties. Since it is generally recognized that carbon deposits contain large amounts of road dirt and metallic particles, the carbon residue value is evidently by no means the only factor involved. Although it would naturally be expected that the use of an oil in an engine would tend to eliminate its less stable constituents, the carbon residue value of used oils is found to be invariably higher than that of new oils. Only drastic refining of the oil will reduce its carbon residue value, and this cannot be justified as a part of an oil reclamation procedure, until very definite evidence is forthcoming to show that it is necessary.

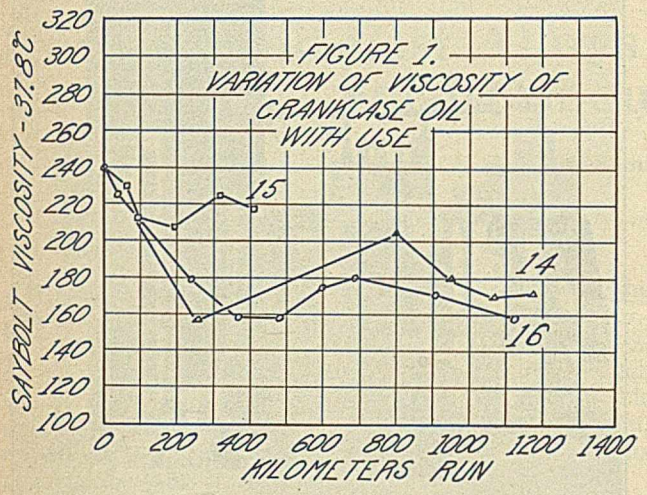
Laboratory Methods

The test methods used in the examination of the oils reported in this paper were the government test procedures, as given in *Bureau of Mines, Technical Paper* 323-A, with the single exception of the method for determining dilution which was formulated in this laboratory. It consists in weighing into a 500-cc., round-bottom, short-neck flask, 250 grams of the used oil. The flask is fitted with a 3-hole cork carrying a thermometer, which dips into the oil, a steam inlet tube reaching to the bottom of the flask, and a vapor outlet tube connected with a condenser. The oil is held at 330° F. (165° C.) and then steam is bubbled through it to drive off the light ends. The steam line should be insulated or else warmed to prevent slugs of water reaching the oil and causing bumping, but it is desirable not to give the steam any appreciable superheat.

Steam is passed through until a total of 200 cc. of condensed oil and water has collected in the receiving graduate. The volume of the oil layer is read, its gravity taken, and the per cent dilution by weight calculated. The volume per cent may be calculated if the gravity of the sample of used oil is known or

if it is measured instead of being weighed. The amount of oil distilled is only slightly dependent on the rate of steaming. The practice in this laboratory is to pass the steam at such a rate that the distillation is completed in about one hour.

This method has the advantages of simplicity and rapidity, and its accuracy is comparable with that of other methods, as is shown in Figure 2. The question of accuracy and interpretation of results depends to some extent on what portion of the used oil is to be considered as dilution. The lighter ends of used crank-case oil show a higher boiling point range than does gasoline. The diluent from Sample 13 was found to have an initial boiling point of 296° F. (147° C.), an end point of 503° F. (262° C.), and 90 per cent distilling below 437° F. (225° C.).



In the case of Sample 10, a 5-gallon (18.9-liter) batch of the oil was reduced in an experimental still, using open steam. From this batch 16.7 per cent by weight of the charge was taken off overhead in nine cuts. The first of these fractions had a boiling point range of 250° to 445° F. (120° to 230° C.) and the last had an initial boiling point of 480° F. (250° C.) and a Saybolt viscosity of 52 seconds at 100° F. (38.7° C.). This sample was collected at a garage, and was probably contaminated with kerosene, but it serves to show what may be encountered in oil reclamation work on a commercial scale. The flushing of crank-cases with kerosene is a discredited practice that is now seldom encountered, but even without this contamination it is impractical to remove the last traces of diluent from the oil.

The method given herein for determining dilution therefore furnishes a guide to commercial practice, rather than the exact amount of nonviscous oils present in the sample. This latter figure may be found, if desired, by continuing the distillation until two successive 100-cc. portions of condensed oil and water show equal quantities of oil present. This point will be reached when about 400 cc. of total oil and water have passed over and the dilution percentage will be about 2 per cent higher than when 200 cc. are collected.

Commercial Reclamation Equipment

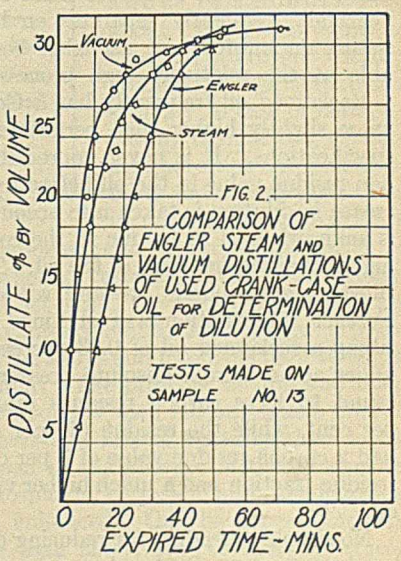
The principal difficulty encountered in attempting to introduce the idea of oil reclamation lies in the reaction of the average American to the word "reclaimed." Even although he may realize that the reclaimed oil passes all the tests new oil will pass, if you offer to sell him reclaimed oil for a third the price of new he will probably take the new oil just the same.

With this difficulty in mind, it was believed that the development of an oil-reclaiming unit adapted to the use of operators of large fleets of trucks or cars would be the logical method of attack. A unit capacity of about 50 gallons (189 liters) of reclaimed oil per day was therefore chosen. Electric operation seemed advisable for the standard equipment, although provision for heating by steam could readily be made.

In spite of the belief that complete removal of dilution is unnecessary and uneconomical, it seemed advisable in developing an oil-reclaiming unit to provide equipment which could turn out a lubricant conforming as closely as possible to the U. S. Government specifications for oil for internal combustion engines. The same equipment may be used to reclaim oil without completely removing the diluent, in which case the reclamation cost is reduced nearly 50 per cent and the capacity of the unit is more than doubled.

The original suggestion for the reclamation apparatus was made by P. F. Miller, of this company, and contemplated centrifugal purification followed by recirculation of the oil through an evaporating column, or tower, with a countercurrent of heated air for evaporation of the light ends.

Preliminary work quickly showed that centrifugal force alone could not be depended on for the complete removal of solids from the raw oil. Oils were encountered in which some of the "carbon" was so finely divided that it would go through even a dense filter paper. It is generally known that mild alkalies can be used to combine in a single step the neutralization of the oil and the coagulation of the "carbon." The use of Gold Dust for this purpose is common practice. After some preliminary work, it was decided that a hot solution of trisodium phosphate (1 pound of crystals per gallon or 120 grams per liter) was most satisfactory. Its use eliminates the possibility of introducing soaps into the oil, except, of course, those formed during neutralization. To insure complete reaction very thorough mixing was necessary. The method developed for doing this without forming tight emulsions has been made the subject of a patent application, and consists in continuously passing part of the mixture through a centrifugal separator during the mixing operation, the components returning separately to the main body of liquid. In this way a very large reaction surface is obtained without a correspondingly fine subdivision, since a single portion of phosphate solution reacts successively with several portions of oil. Trisodium phosphate solution so applied has proved a very satisfactory neutralizing and coagulating agent, permitting removal of all the solids, except the very small amount that may go into solution at the operating temperature and be slowly precipitated out again on cooling.



To permit the use of simple apparatus, the removal of dilution by a low-temperature evaporation assisted by a flow of gas or steam seemed to be the only feasible procedure. All gases except air were eliminated by their cost, and since but few garages have steam available throughout the year, its use could not be adopted as standard. It was found that for the circulation periods involved the oil characteristics are not appreciably modified by a contact with air, as long as the temperature does not exceed 300° F. (150° C.).

Tests using known mixtures of oil with gasoline showed the necessity of exposing a very large oil film to the action of the

air. Continuous recirculation of the oil, countercurrent to the air flow, through a tower filled with hollow tile rings, was finally selected as the best method of obtaining this result.

The equipment being placed on the market for carrying out these operations consists essentially of a receiving and treating tank, a centrifugal oil purifier, a pump for circulating and mixing, an oil heater, an evaporating tower, and a blower. (Figure 3) For convenience, the whole is mounted on a heavy wooden skid, all piping and wiring being installed at the factory. Standard equipment is used throughout, except that it was found necessary to design an oil heater which combined high velocity of oil flow with large heat transfer area, to obviate carbon deposition on the heating surfaces.

In processing a batch of oil, it is first heated to 180° F. (82° C.) by circulating through the heater. The hot phosphate solution is then added, and intimate contact with the oil established by circulation, a part of the stream being by-passed through the oil purifier. Much of the solid content deposits in the purifier bowl during this stage, necessitating cleaning once or twice. The phosphate solution is then removed by the oil purifier, and an equal quantity of hot water mixed with the oil for a short time. This in turn is separated off and the oil run to the evaporator, where it is circulated to remove as much of the diluent as desired. Practically complete removal can be effected in about 8 hours, the oil temperature finally reaching 300° F. (150° C.). In this case the total time required is about 12 hours for a 50-gallon (189-liter) batch. As a final precaution to insure absence of foreign matter, the oil may be run through the oil purifier to storage.

Reclaimed Oil Characteristics

Characteristics of a number of reclaimed crank-case oils are given in Table I. These conform to U. S. Government specifications for Class D oils, as given in *Bureau of Mines, Technical Paper* 323-A, as far as viscosity, flash point, fire point, and acidity are concerned. The reclaimed oils are clear, but dark in color. A small amount of finely divided "carbon" frequently separates on long standing, this consisting undoubtedly of asphaltic bodies which were oil-soluble at the relatively high processing temperature.

Reclaimed oil frequently has a Conradson carbon residue value slightly higher than permitted under the government specifications. It is never appreciably higher than the carbon residue value in the oil before reclamation, when the decrease in dilution is taken into account. The carbon residue is acknowledged to be due to the coking components of the highest boiling fractions of the oil. The diluents can be distilled at atmospheric pressure without appreciable residue. Further confirmation was obtained by the writers by distilling a reclaimed oil of 0.93 per cent carbon residue value under about 3 mm. absolute pressure. The distillates were found to have carbon residues ranging from 0.01 to 0.04 per cent, while the residue (30 per cent of the original oil) had a carbon residue value of 3 per cent. The 0.04 per cent residue fraction had a much higher viscosity than the original oil.

No simple procedure for reducing carbon residue value has yet been found. Both color and carbon residue can be improved to any desired degree by the use of decolorizing earths, but the amounts required are prohibitive. In practice, the use of a suitable oil for make-up would keep the carbon residue value inside any reasonable limit. It should be noted that work done on this subject by the writers indicates that the carbon residue value at first increases rather rapidly during use, but soon reaches a maximum value, little or no further increase occurring even after reclaiming and using the reclaimed oil without admixture with new oil.

Cost of Reclaiming Oil

The cost of processing used oil depends very largely on local conditions, especially the cost of electrical energy and the standards to which it is desired to work. When complete removal of dilution is desired, the power consumption will be about 2 kilowatt-hours per gallon (0.53 per liter) of reclaimed oil.

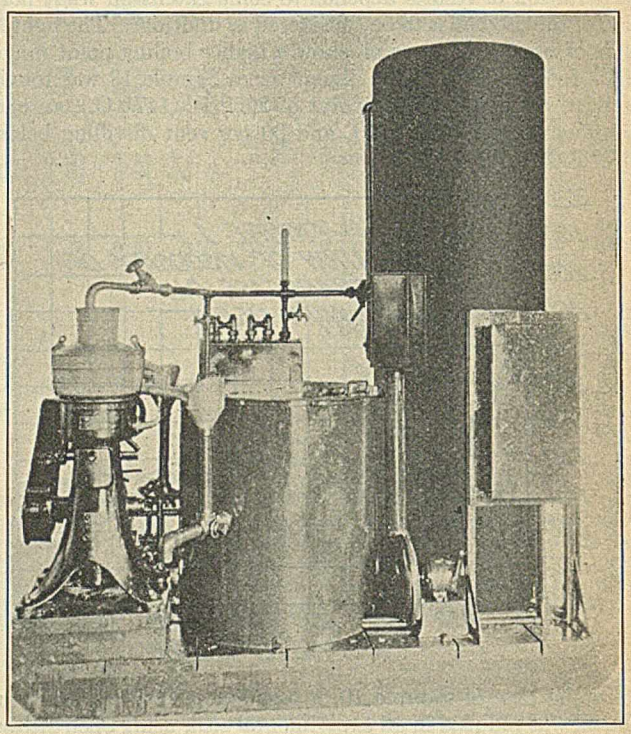


Figure 3

The yield of reclaimed oil will be 80 to 87 per cent of the weight of used oil processed, under these conditions. Users of reclaimed oil will undoubtedly soon realize that complete removal of dilution is not necessary, and will then be able to produce a satisfactory reclaimed oil with a power consumption of 1 kilowatt-hour, or less, per gallon (0.27 per liter). Similarly the labor cost may amount to 0.1 to 0.15 man-hour per gallon (0.027 to 0.04 per liter) of reclaimed oil at first, but this will be reduced as the solid content of the oil drops off under the influence of more frequent changes, since the solids determine duration of mixing periods and frequency of bowl cleaning. Even the cost of the trisodium phosphate, normally about one cent per gallon (0.27 cent per liter) of oil, can be reduced by cutting down the amount used as the quality of the used oil improves.

During the development of the process discussed in this paper, more than 1000 gallons (3780 liters) of reclaimed oil have been produced. Several hundred gallons of this were distributed to nearly a hundred individual car owners. Without exception, reports received indicate that this oil gives entirely satisfactory service.

Bibliography

1—Barnard, "The Effect of Crank-Case Dilution," *Ind. Eng. Chem.*, **17**, 278 (1925).

2—Mac Coull, "Consumption and Dilution of Automobile Engine Oils," *Lubrication* (*The Texas Co.*), **10**, No. 6, 66 (1924).

3—Parish, "Evils of Crank-Case Oil Dilution," read before Automotive Service Association at the Automobile Club of America, New York, November 11, 1923.

4—Herschel and Anderson, "Reclamation of Used Petroleum Lubricating Oils," *Bur. Standards, Tech. Paper* **223**.

5—Waters, "Carbonization of Lubricating Oils," *Bur. Standards, Circ.* **99**.

6—Garner, "The Carbonization of Lubricating Oils in Internal Combustion Engines," *J. Inst. Petroleum Tech.*, **7**, 98 (1921).
7—"Centrifugal Oil Cleaner," *Oil News*, **9**, No. 4, 21 (1921).
8—Parish, "Dilution of Crank-Case Oil," *J. Soc. Automotive Eng.*, **8**, No. 3, 231, 254 (1921).
9—Parish, "Reclamation of Used Motor Oils," *Sci. Lubrication*, **1**, No. 6, 5 (1921).
10—Parish, "Crank-Case Oil Dilution Problem and Its Solution," *Eng. World*, **20**, 307 (1922).
11—Larson, "Dilution of Crank-Case Oil," *Sci. Lubrication*, **1**, No. 10, 13 (1921).
12—Parish, "The Dilution of Lubricating Oil in the Present Automotive Engine," *Ibid.*, **2**, No. 1, 5, 21 (1922).
13—"Reconditioning of Crank-Case Lubricant by a New Method," *Automotive Ind.*, **46**, 910 (1922).
14—Clayden, "Effect of Dilution upon Viscosity and Oiliness of Lubricant," *Ibid.*, **47**, 1023 (1922).
15—Fenno, "Reclamation of Used Motor Oil," *Sci. Lubrication*, **1**, 11 (1921).
16—"The Dilution of Lubricating Oil," *Motor Transport* (*London*), **36**, No. 956, 771 (1923).
17—Clayden, "Dilution of Crank-Case Oil Is Serious Factor Even in Summer," *Automotive Ind.*, **49**, 415 (1923).
18—Knoch, Crosby, and Mathews, "Determination of Dilution of Crank-Case Oil," *Ind. Eng. Chem.*, **16**, 1153 (1924).
19—Parish, "New Plan Regenerates Motor Oil Continuously as Automobile Runs," *Nat. Petroleum News*, **14**, 49 (1922).
20—Van Brunt and Miller, "Reclamation of Automobile Crank-Case Oil," *Ind. Eng. Chem.*, **17**, 416 (1925).

Normal Sand-Cast Alloys of Aluminium Containing Small Amounts of Silicon[1]

By Samuel Daniels

War Department, Air Service, McCook Field, Dayton, Ohio

The 5 per cent silicon alloy of aluminium, at least, has attained importance as an engineering material. Small additions of silicon increase the strength and hardness of aluminium rather slowly, but decrease the percentage of elongation less rapidly than does any commonly added metal except zinc. Suitable heat treatment markedly improves the ductility of the alloys, without impairing their strength or hardness. The metallography of the series is described at length, and comment is made concerning the interpretation of present related equilibria diagrams.

SILICON is found in metallic aluminium as one of the principal impurities. Virgin aluminium ingot produced by electrolytic reduction is furnished to U. S. Air Service Specification 11, 010-B in three classes—Special, Grade A, and Grade B—in which the minimum allowable contents of aluminium are 99.5, 99.0, and 98.0 per cent, respectively. Chemical analysis of a number of shipments of metal in each of these grades has shown a silicon range of from 0.04 to 0.20 per cent in the ingot of special quality from 0.14 to 0.54 per cent in Grade A; and from 0.30 to 0.94 per cent in Grade B.

Silicon plays a more important role, however, as an *added* constituent in the binary and polynary sand-cast alloys of aluminium base. A true classification of the silicon-bearing alloys of aluminium necessitates making a distinction between the "normal" and the "modified" alloys. As differing from the "normal" alloys, which are prepared according to ordinary foundry practice, the "modified" alloys are those which are manufactured by adding to the molten aluminium-silicon mixture at the proper temperature a small amount either of a powder consisting essentially of an alkaline fluoride or of metallic alkali (with zinc). The modification treatment comminutes the particles of silicon, with beneficial alteration of tensile properties. The improvement in strength and ductility imposed upon the alloys by modification is lost wholly, or partly, on remelting.

Among the commercially useful binary alloys are the normal 5 per cent and the modified 13 per cent silicon alloy. Besides these simple alloys there are the proprietary 4.75 copper–0.75 silicon alloy, from which an ultimate strength of about 30,000 pounds per square inch and an elongation in 2 inches of about 6 per cent may be readily attained after suitable heat treatment, thus making it adaptable for moderately highly stressed parts; the 4 copper–3 silicon alloy having an ultimate strength of about 20,000 pounds per square inch and an elongation in 2 inches of about 2 per cent, very useful for intricate castings, where abrupt changes in section and thin walls would spell cracks and misruns in the alloys ordinarily employed in the foundry; and the proprietary and less well known 1 magnesium–1 silicon alloy, which requires heat treatment and develops tensile properties similar to those of the 4.75 copper–0.75 silicon alloy.

In general, the addition of silicon to aluminium-base alloys in amounts over about 1.0 per cent is felt in two directions. In the foundry, silicon contributes strongly to ease of manipulation, diminishing shrinkage, porosity, and susceptibility to hot shortness, and increasing the fluidity of the melt. These characteristics serve to cut down the number of wasters and to widen the field of castings which can be successfully poured. On the other hand, the alloys themselves acquire physically both advantageous and disadvantageous properties. Silicon hardens the alloys and improves their strength at the expense of ductility. The presence of iron and magnesium, which form compounds with silicon, causes greater intensification of hardness and loss of ductility than comes from the action of silicon in the absence of these elements. The resistance to atmospheric corrosion and the lightness of the alloys are also enhanced. On the other hand, the alloys containing more than about 1.5 per cent of silicon do not machine readily. This property is not particularly detrimental, however, as it engenders merely the adjustment of the machining practice to the peculiarities of the alloy.

In the binary series itself silicon hardens the metal and improves the ultimate strength quite rapidly for additions up to 5 per cent; then slowly to a maximum of about 22,000 pounds per square inch near the eutectic (about 11 per cent of silicon) point; beyond this point, up to 18 per cent of

[1] Received November 28, 1924. Published by permission of the Chief of Air Service, War Department.

silicon at least, the ultimate strength gradually declines.[2] At the same time, the percentage of elongation falls continuously, but at a much less rapid rate than is occasioned by additions of copper in the simple aluminium-copper alloys. These aluminium-silicon alloys, while possessing favorable foundry attributes especially in the hypo-eutectic range of silicon, moderately good tensile properties, relative soundness, and a high degree of resistance to corrosion, have a relatively low proportional limit and modulus of rupture

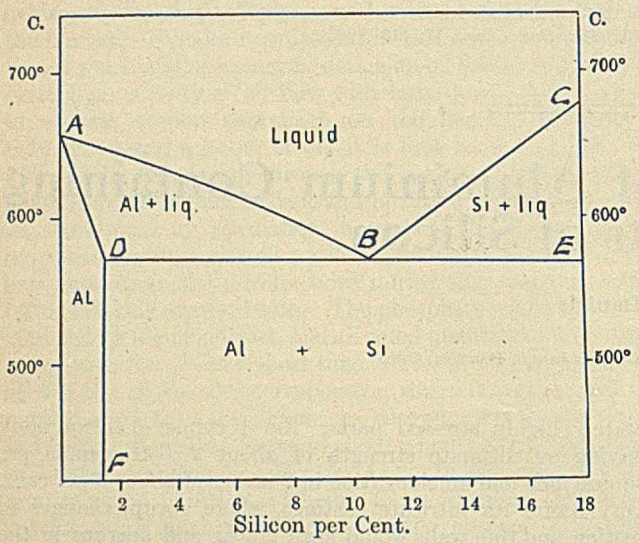


Figure 1—Partial Equilibrium Diagram for Aluminium-Silicon Alloys (Hanson and Gayler)

in bending—factors which must be carefully considered in designing. Again, there is the difficulty in machining, which may be overcome by proper attention to tools and cutting speeds.

The equilibrium diagram for the aluminium-silicon series is comparatively simple, although several points are in dispute. The first representation was constructed by Fraenkel,[3] who reported a simple eutectiferous series with the eutectic at 10 per cent of silicon and at a temperature of about 576° C. (1069° F.). Roberts[4] later confirmed Fraenkel's results, but placed the eutectic temperature at about 578° C. (1072° F.). Hanson and Gayler[5] published in 1921 the diagram shown in Figure 1. These investigators set the eutectic at 10.5 per cent of silicon and the eutectic temperature at 570° C. (1058° F.). They established the solubility of silicon in aluminium at 1.5 per cent at the eutectic temperature and found that this solubility appeared to be little, if any, less at lower temperatures. Edwards,[6] however, in 1923, placed the eutectic at 11.6 per cent of silicon and the eutectic temperature at approximately 577° C. (1071° F.), but he evidently made no determinations upon the solubility of silicon in aluminium. Other investigators have placed the eutectic at up to as high as 13.8 per cent of silicon.[7] Without attempting to discuss these discrepant results or the concomitant problem involved by the modification of the alloys, it is sufficient to note that the latest diagrams call for more accuracy.

The metallography of the system is not complex. The hypo-eutectic alloys show the aluminium-rich solid solution and the eutectic of this solution and silicon, whereas the hyper-eutectic alloys contain free (excess) silicon and the eutectic. Iron, an impurity, occurs possibly in two forms—as the iron (aluminium) silicide, and as the iron aluminide ($FeAl_3$). What copper there is in the aluminium ingot or the hardner is retained as copper aluminide ($CuAl_2$) in solid solution in the aluminium. Still another unidentified impurity is observable in the series.

The present paper is the second of a number of investigations into the properties of the sand-cast alloys of the aluminium-magnesium-silicon system, undertaken by the Material Section, Engineering Division, Air Service, U. S. A. In this article are discussed the normal alloys of aluminium containing not over 5 per cent of silicon, and hence falling within the lower hypo-eutectic field (Figure 1).

Methods of Alloying

Five melts of aluminium-silicon alloys were cast in the form of test specimens to the calculated silicon contents of 0.25, 0.5, 1.0, 3.0, and 5.0 per cent. These melts were numbered 2796, 2798, 2797, 2794, and 2795, respectively.

Table I indicates the composition of the aluminium ingot and the aluminium-silicon hardener used in the alloying. The aluminium conformed to the requirements of "Special" under Air Service Specification 11,010-B, the content of aluminium by difference being 99.54 per cent and the actual silicon content 0.14 per cent. The hardener contained 18.45 per cent of silicon and was made by dissolving 25 pounds of metallic silicon in an equal amount of aluminium at 1800° F. Seventy-five pounds of aluminium were melted in another furnace and added, at a temperature of about 1350° F., to the first molten mixture. After the melt had been thoroughly stirred, it was pigged into thin ingots to prevent segregation.

Table I—Composition of Raw Materials
(Per cent)

Melt	Material	Copper	Silicon	Iron	Aluminium (Diff.)
2063	Al ingot	0.02	0.14	0.28	99.54
2415	Al-Si hardener	...	18.45	0.48	...

Table II—Foundry Practice
Furnace, Monarch; fuel, oil; weight of charge, 10 pounds

Melt	Time in furnace Minutes	Temperature, ° F. Max. furnace	Pouring
2796	10	1370	1300
2798	10	1365	1300
2797	10	1380	1300
2794	15	1400	1300
2795	15	1380	1300

The several alloys were made in 10-pound lots by charging the necessary amounts of aluminium ingot and hardener together in a plumbago crucible and melting rapidly in an oil-fired furnace. The maximum furnace temperature ranged from 1365° to 1400° F. Just before pouring the alloys were thoroughly stirred and skimmed. The pouring temperature was uniformly 1300° F. A detailed schedule of the melting procedure is given in Table II.

Method of Casting Test Specimens

Temperature measurements were made with a bare chromel-alumel thermocouple and a potentiometer.

The tension test specimens were cast to size (0.505 inch diameter), three to the mold, with individual risers and a common pouring sprue, in green Sandusky sand. A photograph of the Air Service standard TB-1 test bar has been shown in a previous article.[8]

Methods of Testing

Chemical Analysis—All the melts were analyzed for total and combined silicon (graphitic by difference) by the partial oxidation method devised at McCook Field, with the results given in Table III. The values for total silicon only were accepted; for, at the time, the temperature and period of

[2] Daniels and Zimmerman, "Properties of Some Silicon Alloys of Aluminium," *Air Service, Serial* **1728** (1921), War Department Report.
[3] *Z. anorg. Chem.*, **58**, 154 (1908).
[4] *J. Chem. Soc. (London)*, **105**, 1383 (1914).
[5] *J. Inst. Metals*, **26**, 323 (1921).
[6] *Chem. Met. Eng.* **28**, 167 (1923).
[7] Rassow, *Z. Metallkunde*, **15**, 106 (1923).
[8] Daniels, This Journal, **16**, 1243 (1924).

ignition of the mixture of iron and aluminium hydroxides, silicic acid, and of graphitic silicon were not observed, so that undoubtedly the reported percentages of the two forms of silicon were incorrect. It has since been found that the rationale of analysis is quite important; and the preliminary conclusions do not entirely agree with those of Gat,[9] who believes that silicon is present only in the graphitic form. It seems as though the so-called *X* constituent, the compound which many investigators have described as containing iron, silicon, and possibly aluminium, should yield combined silicon.

Table III—Analyses of Melts Investigated

(Per cent)

Melt	Silicon: Calcd. total	Silicon: Actual total	Iron
2796	0.25	0.50	0.31
2798	0.50	0.67	..
2797	1.00	1.20	0.32
2794	3.00	2.80	..
2795	5.00	4.80	..

MECHANICAL TESTING—Tensile, Brinell hardness (500-kg. load, 10-mm. ball), and specific gravity tests were made according to standard methods, with the results shown in Table IV. Each value in the table is the average for three bars, except in the case of Brinell hardness, where only one impression was made for a given condition in the alloy.

Table IV—Physical Properties of Al-Si Alloys

Melt	Total silicon	Ultimate strength Lb./sq. in.	Elongation in 2 in. Per cent	Brinell hardness	Specific gravity
		As sand-cast			
2063[a]	0.14	11,050	29.2	20	2.68
2796	0.50	12,240	18.0	23	2.66
2798	0.64	12,270	12.8	24	2.67
2797	1.20	13,830	12.5	28	2.66
2794	2.80	16,370	10.2	31	2.64
2795	4.80	18,310	7.8	34	2.62
		As quenched and aged (1025—96 CW-300—8)			
2796	...	12,850	25.3	22	2.67
2798	...	13,690	19.7	24	2.67
2997	...	16,270	17.2	29	2.66
2794	...	18,160	13.8	30	2.64
2795	...	19,990	17.0	32	2.63
		As annealed (1025—96F)			
2796	...	11,630	26.0	19	2.67
2798	...	11,210	19.2	23	2.67
2797	...	11,120	19.5	21	2.68
2794	...	11,180	9.8	22	2.59
2795	...	10,800	6.0	22	2.62

[a] Data from Melt 2137, a remelt of Melt 2063, and from Melt 1660, of practically identical analysis.

The specimens as sand-cast were tested within 2 days after being cast, and the heat-treated specimens 7 days after the completion of treatment.

Several of the annealed (furnace-cooled) bars were badly warped during heat treatment. These were straightened before testing.

Methods of Heat Treatment

The purpose of the heat treatments was to compare the mechanical and hardness properties of the alloy as quenched and aged or as annealed to those of the material as sand-cast. The heat treatments approximated equilibrium conditions at the quenching temperature and for slow cooling.

Six test specimens from each melt were wrapped three to the bundle (and to each treatment) in iron wire and then heated for 96 hours at 1025° F., just below the melting point, 1058° F.,[5] of the aluminium-silicon eutectic, in an electric furnace automatically controlled to within ±10° F. One set of these bars of each alloy was then quenched into cold water (at about 75° F.) and directly aged in an electric oven at 300° F. for 8 hours; the other set was very slowly cooled in the furnace over a period of 7 days down to room temperature. After the completion of heat treatment the specimens were aged at room temperature for 7 days and then subjected to tensile and hardness tests.

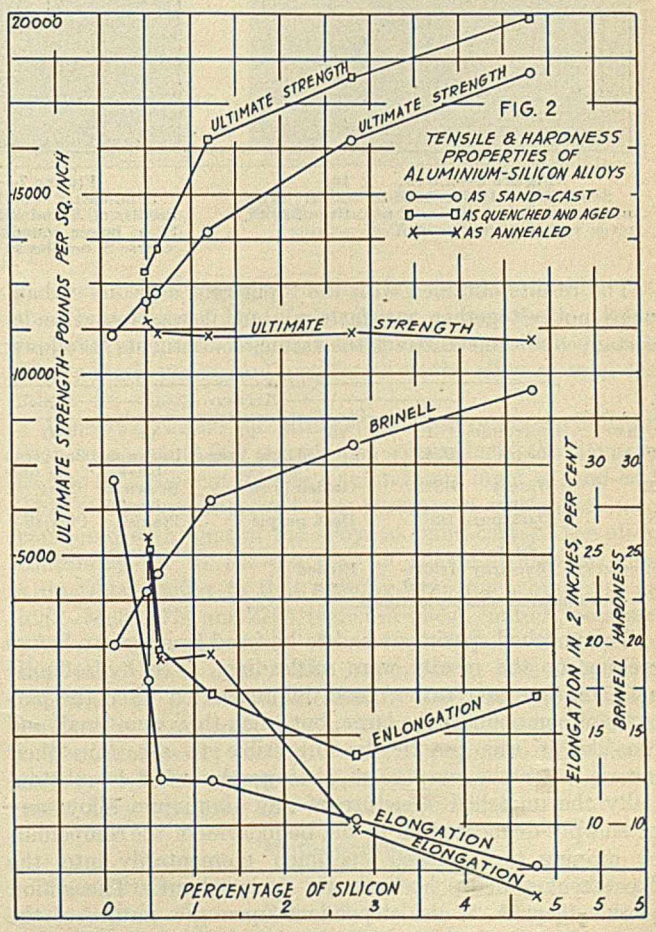
[9] THIS JOURNAL, **16**, 959 (1924).

Preparation and Examination of Metallographic Specimens

Metallographic examination was conducted at low and at high (oil immersion) magnification on specimens from the aluminium ingot and on 0.5-inch transverse sections from the riser end of the middle bar in the mold of the cast and of the heat-treated alloys containing 0.5, 1.2, 2.8, and 4.8 per cent of (total) silicon (Melts 2796, 2797, 2794, and 2795, respectively). These specimens were polished according to the procedure which has already been outlined.[8]

For the purpose of comparison the metallographs of three other melts are included. Melt 2982 was a remelted and sand-cast aluminium ingot originally (as cast in permanent mold) containing 0.04 per cent of silicon, 0.07 per cent of iron, and 0.07 per cent of copper. This original ingot (Melt 2690) is the purest aluminium (99.82 per cent, by difference) which the Material Section has purchased for research work. Photographs of this aluminium as sand-cast were substituted for those of Melt 2063, the more impure ingot utilized for the alloying of the aluminium-silicon alloys discussed in this article. The structure of Melt 2107, a sand-cast alloy with 1.5 per cent of silicon and 0.38 per cent of iron, is also shown, as is that of Melt 2415, the hardener used.

The alloys were examined both as unetched and as etched for 10 seconds in a 2 per cent aqueous solution of hydrofluoric acid. This reagent was selected after experimentation



with aqueous solutions containing 1 and 2 per cent of acid, and with alcoholic solutions containing 1, 4, and 8 per cent of acid. The specimens must be moved about in the hydrofluoric acid solutions to prevent hydrogen bubbles from protecting the surface from action. The alcoholic reagents acted too slowly, whereas, in the concentrations tried, the aqueous reagents were perhaps too rapid.

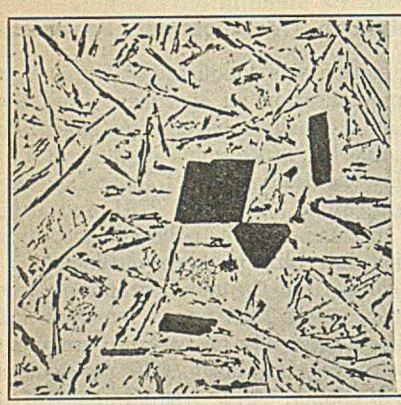


Figure 3—18.4 Si. ×100
Al-Si hardener. Primary Si in eutectic Al-Si matrix. Note areas of finely divided Si. Large dark needles are eutectic Si

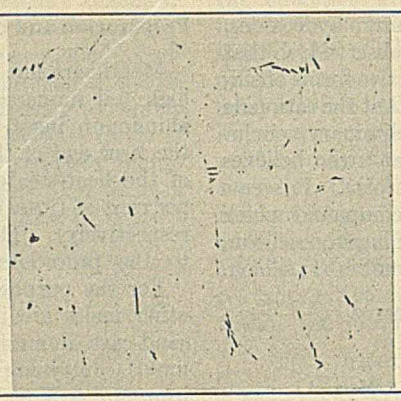


Figure 4—0.5 Si. × 100
Sand-cast. 12,240–18.0–23. Note very small Fe-bearing needles. No Al-Si present

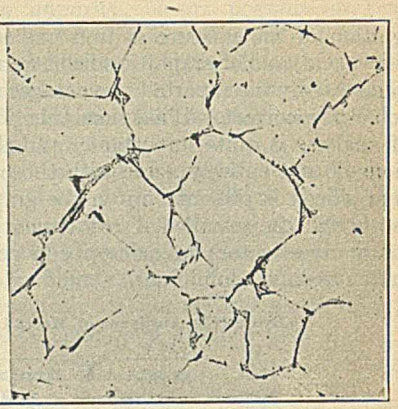


Figure 5—1.2 Si. × 100
Sand-cast. 13,830–12.5–28. Larger needles of *X* cut through Al-Si areas

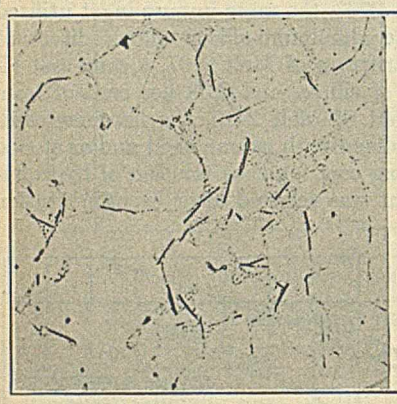


Figure 6—2.8 Si. × 100
Sand-cast. 16,370–10.2–31. Still larger needles of *X* and increased quantity of Al-Si, often with fine needles of *X*

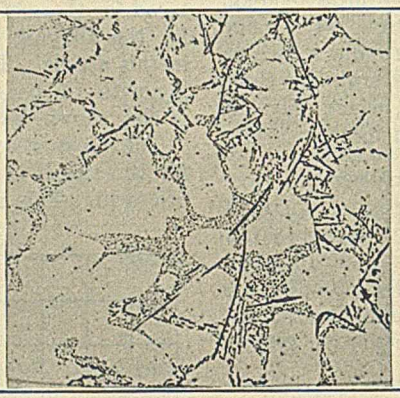


Figure 7—4.8 Si. × 100
Sand-cast. 18,310–7.8–34. Very large needles of *X* and still greater quantity of Al-Si in larger rounded particles. Note also coarse Si needles to right

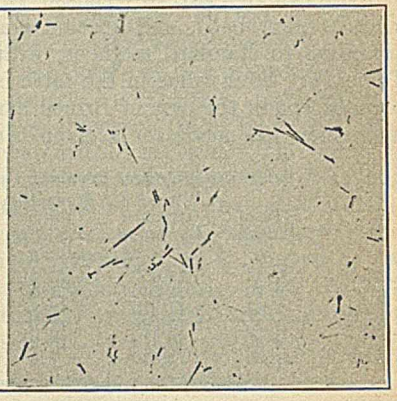


Figure 8—1.2 Si. × 100
Quenched and aged. 16,270–17.2–29. Compare with Figure 5 and observe that particles of Si have gone into solution

The results obtained with the 2 per cent aqueous etchant were not altogether satisfactory, but it was found under certain conditions to attack the various constituents as follows:

Constituent	Color: Unetched	Color: Etched — Period of Immersion, seconds: 1	5	10	30	60
$FeAl_3$	Purple	BSO[a]	Purple or light brown		Brown or black	Sea-green or blue
X	Watery blue	BSO	Golden brown		Brown or black	Olive
Si	Dark purple (slate)	BSO	Dark purple		Pinkish	Pinkish
Blue-gray	Blue-gray	Iridescent	Etched out			

[a] Boundaries sharply outlined.

The polished specimens had to be freed from grease before etching or the results were misleading. The hydrofluoric acid solution gave rather good differentiation when the particles of compound were large, but when they were small and film-like it was practically impossible to ascertain their nature. For the purpose of photography what is substantially the unetched structure of any aluminium alloy may be sharply delineated as to the boundaries of the compounds by dipping the polished specimen momentarily into the 2 per cent aqueous hydrofluoric acid etchant. The action of this reagent is also dependent upon the nature of the alloy. It seems valueless, for instance, with copper-bearing aluminiums, because it reveals latent scratches and tarnishes the matrix.

The several alloys were also examined after etching with Dix's nitric acid quench,[10] which, while it sharpened the boundaries of the various hard particles, did not establish definitely the presence of two iron-bearing compounds in the series.

[10] *Trans. Am. Inst. Mining Met. Eng.*, **69**, 965 (1923).

Foundry, Mechanical, and General Properties

Cast Alloys—Although only a few experimental castings were made from the alloys, which were easily prepared, it was observed from the molds of standard (TB-1) tension test specimens poured from 1300° F. that the tendency to pipe for the alloys containing up to about 2.8 per cent of silicon was approximately the same as that for pure aluminium. The soundness of the alloys within this range of composition was fairly satisfactory. Those melts which had 2.8 and 4.8 per cent, especially, of silicon piped appreciably less and were more sound than the melts with lower content of silicon.

It was found possible to cast the series to within ±0.2 per cent of the total silicon content desired, but it might be possible, with careful weighing and homogeneous ingot and hardener, to melt to a tolerance of ±0.15 per cent of silicon. By using high-grade aluminium ingot and good melting practice the iron content can be maintained below 0.35 per cent.

The ultimate strength of these alloys as sand-cast increased with the silicon content from about 11,000 pounds per square inch for the purest aluminium ingot to about 18,000 pounds per square inch for the material with about 5 per cent of silicon. The Brinell hardness increased correspondingly from 20 to 34. The elongation in 2 inches, however, decreased with increase in silicon content, from about 29 per cent to about 8 per cent, as did the specific gravity, from 2.68 to 2.62 (Table IV and Figure 2). As the silicon content increased the fracture became increasingly gray.

For small percentages, say up to 5 per cent of the added element, silicon increases the ultimate strength and hard-

Figure 9—1.2 Si. × 100
Annealed. 11,120–19.5–21. Compare with Figures 5 and 8. Si particles have reappeared in much larger particles than existed in the cast alloy

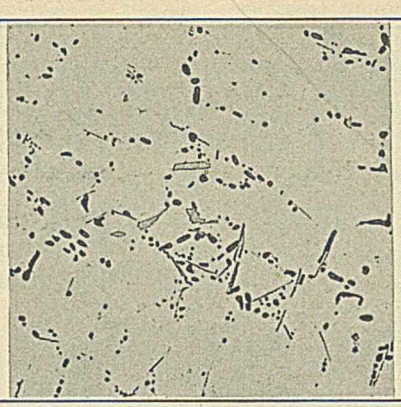


Figure 10—4.8 Si. × 100
Quenched and aged. 19,990–17.0–32. Compare with Figure 7. Much of the Si (dark) has gone into solution, while the excess has coagulated. Network largely obliterated

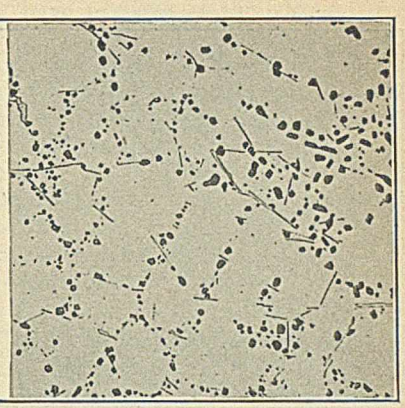


Figure 11—4.8 Si. × 100
Annealed. 10,800–6.0–22. Compare with Figures 7 and 10. Precipitation of Si heavy and in coagulated form

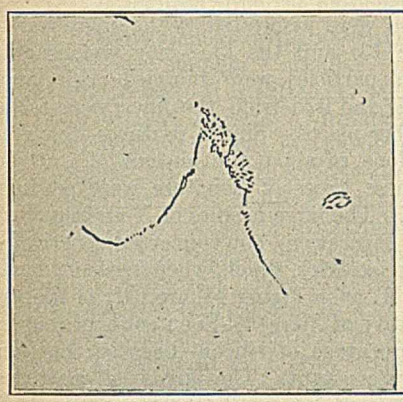


Figure 12—0.04 Si, 0.07. × 100
Sand-cast. Typical skeleton of Fe-bearing compound ($FeAl_3$?)

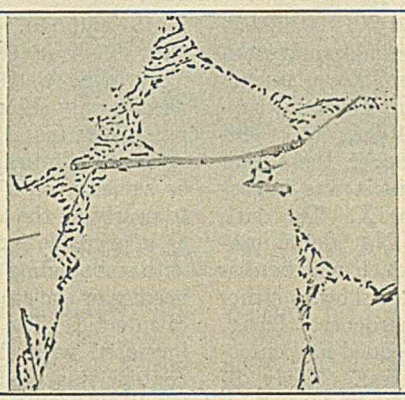


Figure 13—1.2 Si. × 500
Sand-cast. Large needles of *X* (gray) with Al-Si (black) eutectic in some places mixed with small needles of *X*

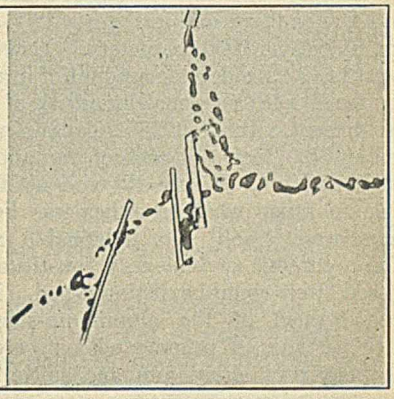


Figure 14—1.2 Si. × 1000
Sand-cast. Large needles of *X* and Al-Si eutectic free from small needles of *X*

ness of the aluminium-base alloy less rapidly than do copper and magnesium and more rapidly than does zinc. Silicon causes the percentages of elongation to drop off less rapidly than any commonly added metal except zinc.

CAST AND HEAT-TREATED ALLOYS—In Figure 2 the results from heat treatment are compared graphically with the properties of the alloy as cast. During heat treatment the quenched specimens did not suffer distortion, but some of the annealed samples were adversely affected. In Melt 2798 (0.64 per cent of silicon) there was one slightly warped test specimen; in Melt 2794 (2.8 per cent of silicon) all three were badly bent; and in Melt 2795 (4.80 per cent of silicon) one was satisfactory, another badly warped, and the third partially melted. Melt 2796, containing 0.5 per cent of silicon, withstood the heat treatment successfully.

Quenching and aging effected but little improvement in the ultimate strength and hardness of each alloy. The specific gravity was not changed. The percentage of elongation, however, was markedly enhanced, as is shown in Figure 2 and in following table:

Melt	Total silicon Per cent	Percentage of Elongation— As cast	As quenched and aged
2796	0.50	18.0	25.3
2798	0.64	12.8	19.7
2797	1.20	12.5	17.2
2794	2.80	10.2	13.8
2795	4.80	7.8	17.0

The alloy containing 4.80 per cent of silicon was therefore most responsive to this treatment, with a resulting ultimate strength of 19,910 pounds per square inch, an elongation of 17.0 per cent, and a Brinell hardness of 32. This is an interesting point, because it demonstrates that the 5 per cent silicon alloy of aluminium, which is a commercial product, may be made considerably more ductile by heat treatment without loss of strength or of hardness.[11] It also suggests the possibility that the proportional limit of about 3000 pounds per square inch found in the alloy as sand-cast might be raised.

Annealing caused the ultimate strength of all the alloys to drop to about 11,000 pounds per square inch, the figure for 99.0 to 99.5 per cent (Grade A) aluminium ingot as sand-cast. This treatment improved the percentage of elongation, as compared with that of the alloys as sand-cast, of the alloys containing up to 1.2 per cent of silicon, which acquired a ductility similar to that ensuing from quenching and aging. Melts 2794 and 2795, higher in silicon content, possessed after annealing practically the same percentage of elongation that they did as cast. The increment in Brinell hardness conferred on the cast materials by the addition of silicon was lost by annealing. The specific gravity was not affected.

The fractures of the heat-treated specimens were silvery and amorphous, except in Melts 2794 and 2795, annealed, where they were gray and coarsely crystalline.

Metallography

The metallography of these aluminium-silicon alloys is portrayed in Figures 3 to 22, inclusive. With the exception of Figures 8 and 18, as etched for 10 seconds in 2 per cent aqueous hydrofluoric acid, and of Figures 14 and 15, as etched for 30 seconds in the nitric acid quench, these are of structures as unetched.

As sand-cast the aluminium-silicon hardener and the various alloys are represented in Figures 3 to 7, inclusive,

[11] This work, though nearly two years old, is apparently anticipated, at least in part, by U. S. Patent 1,508,556 (September 16, 1924).

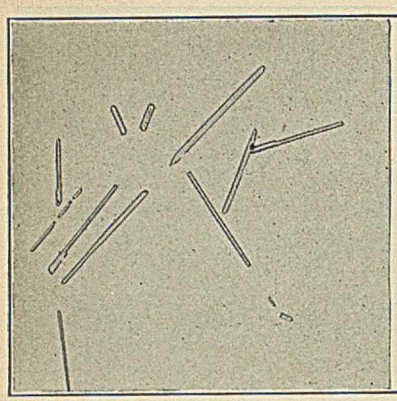


Figure 15—1.2 Si. × 500
Quenched and aged. Needles of *X*. Si particles are in solution. Compare with Figure 13

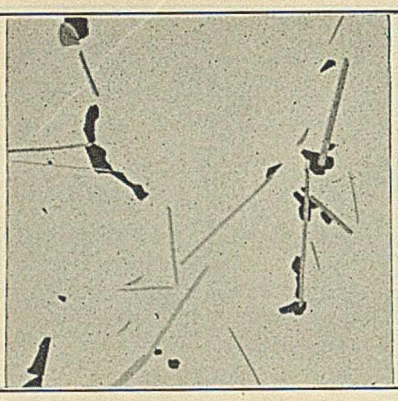


Figure 16—1.2 Si. × 500
Annealed. Needles of *X* (gray) and re-precipitated and coagulated Si (black). Compare with Figures 13 and 15

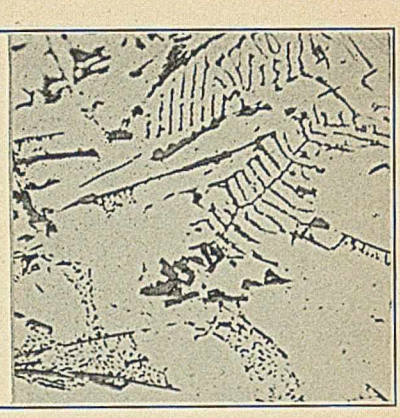


Figure 17—1.5 Si. × 500
Sand-cast. Needles and skeletons of *X* with Al-Si eutectic, all closely associated

at 100 diameters, and in Figures 12 to 14 and 17 to 20, inclusive, at 500 or 1000 diameters. Very high-grade aluminium ingot has a considerable amount of intergranular constituents compared with the small quantity of silicon, iron, and copper present. In Melt 2892, containing 0.04 per cent of silicon and 0.07 per cent each of iron and of copper, there were small skeletons (Figure 12) and needles, but it was impossible to judge whether either was $FeAl_3$ or *X*. The dark films were small and indefinable also. No aluminium-silicon eutectic or blue-gray constituent (which will be discussed later) could be distinguished. Figure 3 shows a structure typical of the aluminium-silicon hardener. Large, dark particles of primary silicon were imbedded in a eutectic matrix of aluminium and silicon (needles). Finely divided silicon was present too, often associated with tiny skeletons. Needles of the iron-bearing constituent were plentiful and the blue-gray constituent occurred in moderate amount.

In Melt 2796 (Si 0.50, Fe 0.31), however, the iron-bearing needles were quite distinct though small (Figure 4). A few ill-formed skeletons and particles of blue-gray constituent were noticed, but despite the added silicon there was no evidence of silicon in particles sufficiently large to be identified, except in a segregated zone near a small pipe, where iron-bearing needles and perfectly formed skeletons and the blue-gray compound were especially abundant. Such perfectly formed skeletons as these were seldom encountered in any of the alloys except in segregated areas.

In the average structure of Melt 2797 (Si 1.20, Fe 0.32), Figure 5, there was a moderate quantity of large and small needles of *X*, both tending to be curvilinear in habit (Figures 7, 18, and 20). These were associated with small particles of silicon (Figure 13) and the blue-gray constituent. Very often the silicon particles were mingled with large needles only (Figure 14) and free from the finer, needle-like precipitate found in other places. Silicon particles were also arranged elliptically, alone, or about the nucleus of a needle or skeleton of *X*. These types of structure were peculiar to nearly all the alloys. The large needles of *X* are regarded as a primary (excess) separation, not connected genetically with surrounding silicon particles, which, when free from small needles or skeletons of *X*, as in Figure 14, are part of the Al-Si eutectic. The quantity of *X*-free Al-Si eutectic, of course, increased with the percentage of silicon, because the iron content was practically constant. The areas of particles of silicon which are crossed by small, short needles of *X* (Figure 20) are what have been denominated by the British investigators[12] as the ternary-eutectic of aluminium-silicon-*X*.

As the silicon content increased the size of the needles of *X* increased, though the quantity appeared to remain the same (the iron content being constant), and with the increase in the amount of the Al-Si eutectic the character of the silicon particles changed. Whereas the particles of silicon in the eutectic were small and generally rounded in the cast alloys with silicon content up to about 1.2 per cent (Figure 14), they became elongated (Figure 18), then irregularly skeleton-like (Figure 20) before they passed, with increase of silicon, into the form of coarse needles (Figures 3, 7, and 19). Undoubtedly, the forms in which the silicon particles

[12] Institute Mechanical Engineers, Eleventh Report to the Alloy Research Committee, 1921, p. 213.

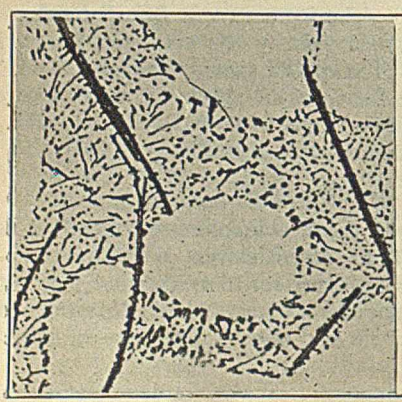


Figure 18—2.5 Si. × 500
Sand-cast. Large needles of *X* cutting through Al-Si eutectic which contains fine needles of *X*. Note elongated Si particles

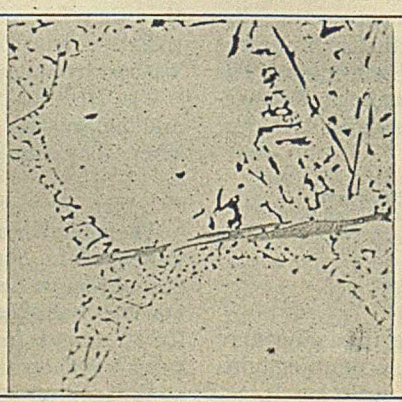


Figure 19—4.8 Si. × 500
Sand-cast. Transition zone from fine, rounded particles of Si to the coarse, acicular (black) form

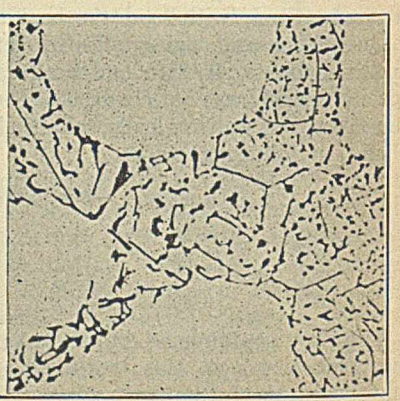


Figure 20—4.8 Si. × 500
Sand-cast. Skeletonic particles of Si with interspersed small needles of *X*

occur markedly affect the machining properties of the alloy. In Melt 2795 (Si 4.80) areas of finely divided Al-Si eutectic were often found with the coarse variety, either unconnected or merging (Figure 19). The size of the iron-bearing needles in Melts 2794 and 2795 (2.80 and 4.80 per cent, respectively, of silicon) was sufficient, after etching in both hydrofluoric and nitric acid reagents, to leave the impression that they and the small skeletons noticed in the alloys of higher silicon were of the *X* constituent. In Melt 2107 (Si 1.5, Fe 0.38) needles and skeletons of *X* and coarse and fine silicon particles were found together (Figure 17). A few small skeletons were observed in Melt 2795 but not in Melts 2797 or 2794, as sand-cast. The blue-gray compound (Figure 22), first described by Dix,[10] was present in all the sand-cast alloys but not in the aluminium ingot. Since this compound is not present in remelted aluminium ingot, it must be introduced from the hardener.

This blue-gray constituent appeared in hexagonal, rectangular, acicular, or rhomboidal form. It is extremely soluble in 2 per cent aqueous hydrofluoric acid but apparently not in the nitric acid quench. It is fairly soft, as hard compounds go. Its melting point is higher than that of the *X* constituent and of the Al-Si eutectic, for particles were found wedged in between sections both of the iron-bearing needles and of silicon needles. Its solubility in aluminium, at least at 1025° F., is very low, if of any magnitude at all. It is thought to be not silicon carbide, because of its solubility in hydrofluoric acid, but rather silicon dioxide (SiO_2), introduced from the silicon used in making the hardener. The composition of the silicon (Melt 1578) was:

	Per cent		Per cent
Carbon	0.02	Iron	1.02
Copper	0.33	Manganese	0.07
Calcium	Nil	Silicon	Remainder

Heat treatment resulted in the typical structural changes exhibited by Figures 8 to 11, 15, 16, 21, and 22.

Quenching caused the retention of dissolved silicon in solution (Figures 8 and 15) up to near the limit of solubility of about 1.5 per cent. In the alloys with a higher percentage of silicon or in equivalent segregated areas of alloys less rich in average silicon content (Melt 2797), heating before quenching caused most of the particles of excess silicon to become rounded and to coagulate, as in Melt 2795 (Si 4.80 per cent), into larger particles (Figures 10 and 21) than were present in the alloy as cast (Figures 7, 19, and 20). Although the quenching operation might improve the machining properties of the alloys containing less than about 1.5 per cent of silicon, because of coagulation it would probably decrease the machinability of these alloys of higher silicon content. The slight increase in ultimate strength and the gain in elongation secured for all the alloys in the series by quenching is attributable to the aluminium-rich matrix hardened by dissolved silicon and to the elimination of the network structure. The same effect might be produced by a much shorter soaking period at the quenching temperature. It is believed that the aging operation did not disturb the constitution or properties of the alloys.

Annealing (furnace cooling) was also productive of rounding and coagulation of the particles of silicon in excess of the solubility limit; but the slow cooling threw the dissolved silicon out of solution, so that even in Melt 2796 (Si 0.50 per cent) many fairly large particles of this element were discernible in the average structure, as in Melt 2797, containing 1.20 per cent of silicon (Figures 9 and 16). In the alloys with higher content of silicon, the coagulated particles increased in size (Figures 11 and 22), comparable to the condition of the particles of excess silicon in the quenched and aged alloy (Melt 2795, Figure 21). The reversion of the alloy after annealing to practically the ultimate strength of Grade A aluminium ingot is ascribable to the total expulsion of dissolved silicon from the grains of the aluminium-rich solid solution. The destruction of the network structure accounts for the high percentage of elongation in the alloy containing up to about 1.2 per cent of silicon, but the low percentage in the alloys richer in silicon is probably caused by a network partially restored when the dissolved silicon was rejected on slow cooling.

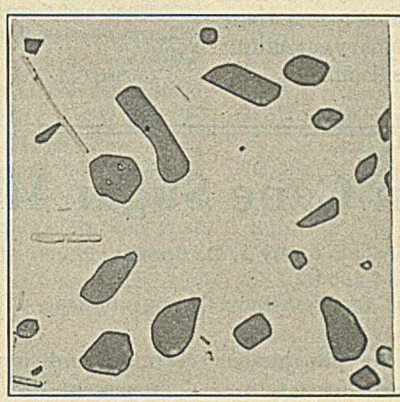


Figure 21—4.8 Si. × 500
Quenched and aged. Large coagulated particles of excess Si about a grain, with needles of *X*. Compare with Figures 19 and 20

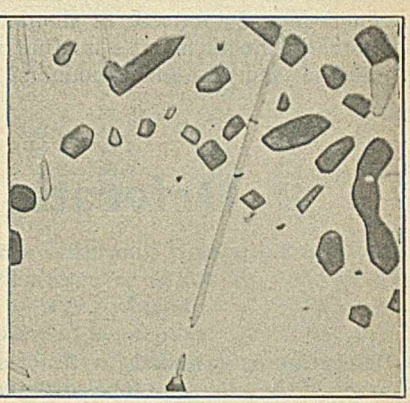


Figure 22—4.8 Si. × 500
Annealed. Si (dark), needles of *X* (gray), and hexagons of blue-gray constituent (halftone)

Heat treatment did not affect the form or solubility of the needles of *X*, of the blue-gray constituent or of the iron-bearing skeletons, except in Melt 2796. In this alloy the skeletons were composed of rounded particles after heat treatment. It was not possible to determine in the cast alloys whether these particular skeletons might have been $FeAl_3$ which reacted with the aluminium-(silicon) rich matrix to form the *X* (Fe-Si-Al?) compound.

The findings of this investigation are not in entire accord with the equilibria diagrams of the aluminium-silicon series (Figure 1) by Hanson and Gayler and of the aluminium-iron-silicon series advanced in the Eleventh Report to the Alloys Research Committee.[11]

In regard to the aluminium-silicon diagram two questions revolve about the solubility of silicon in aluminium. According to the Eleventh Report, the presence of iron in the alloys is initially a guarantee that invariably at least some of the *X* constituent will be formed when $FeAl_3$ reacts at lower temperature with the liquid. Inasmuch as this difficultly soluble compound *X* is reputed to contain silicon, the true solubility of silicon in aluminium in the absence of iron is probably less than 1.5 per cent. It will be noted that the aluminium used by Hanson and Gayler averaged 0.19 per cent of silicon, 0.17 per cent of iron, with no copper reported.

The same diagram and the accompanying text indicate constant solubility of silicon at 1.5 per cent from the eutectic temperature, 1058° F. (570° C.), down to atmospheric temperature (Figure 1, line *DF*). Melts 2796 and 2797 (0.50 Si and 1.20 Si, respectively) when annealed (furnace-cooled) both showed unmistakable precipitation of silicon (Figure 16); yet when quenched no silicon was distinguished (Figure 15) except in a segregated area near a pipe. This

condition would postulate for silicon a curve of diminishing solubility with decrease in temperature.

As for the aluminium-iron-silicon diagrams given in the Eleventh Report, a point is raised in regard to the so-called ternary eutectic of aluminium-silicon-*X*. In this publication (page 216) the ternary eutectic temperature is given as 570° C., which is the temperature noted by Hanson and Gayler as the eutectic temperature for the binary aluminium-silicon eutectic itself. If there is a ternary eutectic of aluminium, silicon, and *X*, its melting point cannot be the same as that of the binary eutectic of aluminium and silicon. It seems as though the structural components are primary (reaction product) *X* and a eutectic of aluminium and *X*; and that the ternary eutectic is but a mixture of two binary eutectics: aluminium and *X*, and aluminium and silicon.

Acknowledgment

Grateful acknowledgment is herewith made to Clifford F. McMahon and to John L. Hester for their assistance in this experimentation.

General Additional References

Dix and Lyon, "Physical Properties of Some Copper-Silicon-Aluminium Alloys when Sand Cast," *Am. Soc. Testing Materials*, June, **1922**, preprint.

Jeffries, "Aluminium-Silicon Alloys," *Chem. Met. Eng.*, **26**, 750 (1922).

Edwards, "Properties and Manufacture of Aluminium-Silicon Alloys," *Ibid.*, **27**, 654 (1922).

Edwards and Archer, "The New Aluminium-Silicon Alloys," *Ibid.*, **31**, 504 (1924).

Basch and Sayre, "Foundry Treatment and Physical Properties of Silicon-Aluminium Sand Castings," *Am. Foundrymen's Assoc., Preprint* **428** (1924).

Guillet, "A New Aluminium Alloy—Alpax," *Ibid.*, **418** (1924).

Defecation in Cane Sugar Manufacture[1]

By J. D. Bond

EWA PLANTATION CO., EWA, HAWAII

Defecation is primarily a function of the phosphate content of the juice and is essentially a process for removing coarse dispersoids from the juice by the formation of a flocculent precipitate within the juice. This precipitate not only adsorbs coloring and colloidal matter, but, enmeshing the suspended matter, carries it down in settling. Sufficient phosphate must be present in the juice to insure a precipitate large enough to function efficiently. This precipitate is a solid solution of lime in the secondary calcium phosphate.

The volume of settlings depends upon the phosphate content of the juice and upon the reaction carried, the reaction affecting the relation of CaO to P_2O_5. Under certain conditions the CaO content of the juice may decrease on liming, though above a reaction of about pH 8 in the cold the CaO content increases rapidly.

Gums are unaffected by defecation, though about 25 per cent of the colloids present (as hydrosol) is removed. Organic matter is present in the precipitates, though this is of secondary importance to inorganic matter.

Heat is of particular value in preventing enzymic action and is of significance in assisting precipitation and settling. In the range pH 6.8 to 7.1, boiling juice shows much more pronounced buffer effect than the cold juice, and the weight of precipitate in the boiling juice is considerably greater in this range.

IN SPITE of the long-continued use of lime in defecation, there is still considerable confusion in the literature and among technical men as to the actual mechanism of the process. Thus, Deerr[2] reports a precipitate consisting of coagulated colloids, phosphates, aluminium and ferric oxides, albuminoids, chlorophyl, cane wax, and some of the coloring matter of the juice; whereas Geerligs[3] states that gums are not precipitated in slightly alkaline liquids, and Horne[4] believes the added lime precipitates more and more of the gummy constituents of sap before the juice finally becomes alkaline to phenolphthalein. Geerligs[5] further states that the degree of dispersion of the colloidal constituents of the juice is the most important factor in defecation. Farnell[6] has shown that under optimum conditions the removal of nitrogenous substances, presumably albumin, will increase the purity 0.2 to 0.3 point.

There seems to be some misunderstanding in the use of the term "albuminoids." These are classed under the simple proteins as insoluble in water, salt solutions, acids, or alkalies, and as far as is known no representatives of this class are found in plants.[7] It is probable that albumin is understood and recent literature has shown this to be true.

There is also confusion in the use of the term "colloids." Deerr evidently uses it as including all dispersed matter in cane juices passing through glass wool. This is certainly a very broad use including, as it does, coarse dispersoids readily visible under the low power of the microscope. We must carefully distinguish between coarse dispersoids and the particles in a true hydrosol and to this end must define limits that may readily be applied in practice. The use of Filter-Cel, filtering under pressure or vacuum, suggests itself as a convenient limit and is quite comparable with filtration through filter paper, which is so exceedingly slow as to be prohibitive.

Dialysis

The work here reported was carried out under the specific conditions obtaining at a single plantation factory. In all dialysis work sacks made from a 5 per cent solution of collodion in a 3 to 1 by volume ether-alcohol mixture were used. Sacks were made by coating the inside of 500-cc. Erlenmeyer flasks, draining, inverting for 8 minutes, followed by immersion in water and removal of the sack; 200 cc. of juice were always used in each sack, at least four sacks to a determination. To each sack were also added 5 cc. of toluene. The dialysis was continued for 24 hours in running tap water, followed by 48 hours in distilled water with four changes. The contents of the sacks were then washed out into evaporating dishes, evaporated on the steam bath, transferred to platinum dishes, and dried to constant weight at 105° C. Table I gives a comparison of the nondialyzing matter obtained under various treatments of juice, the average of two sets of tests being reported. The filtrate from the paper-filtered juice was collected after 24 hours, formalin in the proportion of 1:1000 being used as a preservative.

[1] Received September 2, 1924.

[2] "Cane Sugar," p. 266.

[3] Prinsen-Geerligs, "Cane Sugar and Its Manufacture," p. 145.

[4] THIS JOURNAL, 16, 732 (1924).

[5] *Intern. Sugar J.*, 26, 151 (1924).

[6] *Ibid.*, **26**, 361 (1924).

[7] Thatcher, "Chemistry of Plant Life," p. 176.

Table I

Filter	Juice ° Brix	Nondialyzing matter Grams/liter
Paper	12.65	0.140
Filter-Cel	12.75	0.163
Glass wool	12.70	2.724

Ultra-filtration, in a sense, can perhaps be demonstrated in the filtering of mixed juice through paper or Filter-Cel, but it is not likely that adsorptive effects play a determining part. Work reported later in this paper will further justify this selection of a dividing point between coarse dispersoids and colloids. Following this procedure, it may easily be demonstrated that any well-dialyzed sol from mixed juice, free from molecularly dispersed matter, will show not the slightest agglomeration through very wide ranges of reaction. When alkali-precipitable minerals are present, however, colloids are removed to some extent, owing to the adsorptive effects of precipitates of large surface areas. Furthermore, settlings from mixed juice, treated in the Kopke laboratory centrifugal separator,[8] yielded a turbid run-off, which settled only extremely slowly though the reaction was varied over a wide range. Inspection under the microscope showed that the turbidity was due to coarse dispersoids, characteristic of mixed juice. Addition of a small amount of phosphoric acid was very effective in obtaining a satisfactory settling, the reaction of the liquid remaining alkaline.

Factors Governing Defecation

The precipitation of matter from juices is characteristic of all alkalies, whether inorganic, organic, or produced locally by electrolysis. The increase in purity attendant upon this precipitation has not exceeded a maximum value of three points in the writer's work, and the purity increase is in no way related to the purity of the juice. This conclusion can be drawn by inspection of any comprehensive data in the literature.[9] However, the weight of material precipitated must certainly be related to some property of the juice, and since the literature constantly refers to gums and organic nonsugars their influence has been noted in Table II. In these tests the reaction was varied by the use of a calcium saccharate solution. The first series was limed so as to show a reaction of about pH 9 after heating to 90° C. and filtering; Series 2, about pH 9 in the cold; Series 3, about pH 7.5 in the cold. Gums were determined by the method of Ruff and Withrow;[10] colloids as already described. The weight of precipitated matter was run on 3-liter lots, filtering through a tough grade of paper, washing with water once only. The precipitate was removed from the filter paper by the careful use of a rubber policeman and a wash bottle, the suspension evaporated down on the steam bath, transferred to platinum dishes, and dried to constant weight. This was then ashed at a low red heat in the ash muffle.

Table II

Series	Gravity purity	Glucose Grams	Ash Grams	Organic nonsugars Grams	Ash-Free Gums Grams	Ash-Free Colloids Grams	Precipitate As weighed Grams	Precipitate Ash-free Gram
1	84.7	5.0	3.3	6.8	0.32	0.62	1.38	0.54
	85.7	4.7	2.6	7.0	0.47	0.85	1.47	0.57
	86.9	5.0	2.7	5.4	0.40	0.87	1.34	0.47
	87.4	4.8	2.1	5.7	0.34	0.38	1.28	0.51
Av.	86.18	4.9	2.7	6.2	0.38	0.68	1.37	0.52
2	81.9	6.9	4.3	6.9	0.50	0.43	1.30	0.59
	85.7	4.3	3.4	6.6	0.49	0.43	1.38	0.74
	86.2	3.8	2.8	7.2	0.67	0.56	1.13	0.45
	86.9	4.6	3.1	5.4	0.41	0.31	1.22	0.73
	87.7	4.6	2.6	5.1	0.36	0.53	1.48	0.89
Av.	85.68	4.8	3.2	6.2	0.49	0.45	1.30	0.68
3	80.7	7.6	4.1	7.6	0.37	0.40	0.84	0.35
	84.7	7.1	2.0	6.2	0.47	0.61	0.79	0.55
	85.2	8.1	2.0	4.7	0.36	0.51	0.60	0.37
	87.7	3.9	3.0	5.4	0.28	0.39	1.04	0.76
	89.4	3.0	2.5	5.2	0.35	0.54	0.82	0.51
Av.	85.54	5.9	2.7	5.8	0.37	0.49	0.82	0.51

[8] Report of the Committee on Manufacturing Machinery, J. N. S. Williams, Chairman, *Hawaiian Planters' Record*, **18**, 125 (1918).

[9] McAllep, *Ibid.*, **28**, 162 (1924).

[10] This Journal, **14**, 1131 (1922).

All figures except those on precipitate are based on 100 gravity solids and refer to Filter-Cel filtered raw mixed juice. It is evident that the weight of precipitate obtained from mixed juice on clarification bears no relation to purity, organic nonsugars, gums, or colloids.

Table III gives data on colloids. The juices were treated with the alkali specified so as to show a reaction of about pH 9 after heating to 90° C. and filtering. The whole juice was then filtered through Filter-Cel.

Table III

Alkali Used	Filtered Through	Purities Apparent	Purities Gravity	Per 100 Gravity Solids Colloids Grams	Per 100 Gravity Solids Ash Grams	No. of tests averaged
$Ca(OH)_2$	Cotton wool	83.5	84.3	2.53	3.4	3
	Filter-Cel	84.3	85.3	0.64	3.3	
	Clarified	84.8	85.0	0.39	3.9	
NaOH	Cotton wool	83.4	84.4	3.75	3.1	4
	Filter-Cel	83.9	84.8	0.78	3.0	
	Clarified	84.4	85.3	0.67	3.8	
NH_4OH	Cotton wool	82.8	83.7	3.13	4.1	3
	Filter-Cel	82.9	83.8	1.10	4.0	
	Clarified	85.1	85.6	0.77	3.5	

If we consider all the dispersoids passing through cotton wool, about 74 per cent is removed on filtering through Filter-Cel. Of the colloids as true hydrosols in Filter-Cel filtered juice, only about 25 per cent is removed. It is evident that coarse dispersoids and colloids are of importance in defecation only as a result of the precipitation produced by the action of alkalies on juices and are not of themselves responsible for this action.

Table IV shows the relation of gums to the defecation process.

Table IV

Juice	No. of tests averaged	Gravity purity	Per 100 Gravity Solids Alcohol ppt. Grams	Gums Gram
Raw, filtered	21	85.68	0.94	0.52
Clarified	21	86.18	1.21	0.48

It is evident that the defecation process has very little effect on gums. There was no apparent relation between gravity purity and gums, nor was there any relation between the ash of the alcohol precipitate and the ash of the juice. The alcohol precipitate from clarified juice showed uniformly a higher ash content than that from raw juice.

It has been shown how the precipitate weight varies with added alkali and that ash constitutes a large part of the precipitate. The character of this ash is shown in Table V, the procedure for carbonated ash being followed in every case. Mixed juice was filtered through Filter-Cel, evaporated to a sirup on the steam bath, and ashed. Sirup and waste molasses were ashed as sampled and contained all the suspended matter usually present in these products. Precipitates were obtained from filtered juice by the addition of the alkali specified to a reaction of about pH 9 in the cold followed by heating as usual. The precipitates were filtered off, washed on the filter, and ashed directly. The various analyses have no direct relation to each other and are not in sequence, but they do show general relations. No attempt was made to determine the alkalies in these analyses.

Table V

(Figures in per cent)

	Ash			Ash of Precipitates from:		
	Mixed juice	Sirup	Molasses	$Ca(OH)_2$	NH_4OH	NaOH
SiO_2	3.67	5.49	7.42	2.87	0.42	0.50
SO_3	20.21	18.66	21.37	0.19	0.15	0.20
P_2O_5	26.90	4.72	2.36	38.65	60.90	47.65
Cl	19.73	16.21	16.33	2.64	0.43	1.79
Al_2O_3, Fe_2O_3	0.40	0.46	0.38	7.66	0.10	0.12
CaO	5.62	24.80	10.30	38.53	10.98	29.96
MgO	12.31	13.24	9.89	6.23	26.16	16.03
Deduct O = Cl	4.45	3.66	3.68	0.60	0.10	0.40
Unburned C, CO_2, alkalies	25.61	20.28	35.63	3.83	0.96	1.84

Inspection of the precipitate ash analysis shows that it is composed chiefly of CaO, P_2O_5, and MgO, and that P_2O_5 as phosphate plays the most important part. Magnesium, as will develop, is of only secondary importance so that calcium and phosphates present are of primary importance. Table VI gives data on CaO–P_2O_5 relations in the precipitate. CaO was determined by precipitating as the oxalate directly in the juice, making acid with citric acid, and igniting to CaO. P_2O_5 was determined by precipitating directly, after removal of CaO, as magnesium ammonium phosphate and igniting to the pyrophosphate.

Table VI

(Per 100 gravity solids)

Total CaO Grams	Juice CaO Grams	Precipitate CaO Gram	Precipitate P_2O_5 Gram
0.309	0.159	0.150	0.158
0.507	0.247	0.260	0.212
0.754	0.434	0.320	0.222
1.401	0.915	0.486	0.234
1.841	1.281	0.560	0.235
2.156	1.491	0.665	0.236

It is particularly interesting to note the increasing CaO content of the precipitate with P_2O_5 virtually constant. These data represent extremely alkaline conditions such as never obtain in the defecation process.

If phosphates are removed from the juice, a marked change will be noted (Table VII). This may be accomplished in acid solution by the application of the basic acetate separation principle, and by the use of uranium salts. It is extremely difficult, however, under these conditions, to avoid the use of an excess of reagents, and since they precipitate on making the solution alkaline, some precipitation from them may be expected. Filtered juice was used.

Table VII

Treatment	Weight of Precipitate: Untreated juice Gram/liter	Treated juice Gram/liter
Basic acetate, filter alkaline with NaOH	0.442	0.063
Uranyl nitrate, filter, alkaline with NaOH	0.442	0.049

The importance of phosphates in the formation of a precipitate is evident. Of seventy-three laboratory reagents tested as to their effect on boiling juice, those resulting in satisfactory precipitates were barium hydroxide, ferric salts, lead acetates, and uranium salts, all of which precipitate with phosphoric acid under conditions obtaining in boiling juice. Alkali carbonates did not give satisfactory results.

It has been shown that phosphates are the determining factor in defecation in so far as mineral matter is concerned; it remains to show the amount and influence of organic matter. Precipitates were obtained from filtered mixed and last mill juices, using C. P. milk of lime. These precipitates were carefully washed with dilute limewater until the washings gave no test with alpha-naphthol. Organic matter was then estimated by the wet oxidation method, using chromic acid. The results of this test are given in Table VIII.

Table VIII

Juice	Per cent ash-free	Carbon Expressed as: C	CO	$C_6H_{12}O_6$
Mixed	28.7	5.70	20.9	14.3
Last mill	56.2	14.23	52.2	35.6

There is considerable organic matter in these precipitates, but its effect is evidently secondary to that of inorganic matter.

If defecation is essentially an inorganic reaction, or reactions, it should be possible to devise a laboratory scheme of clarification which will be superior to the usual methods. To this end filtered mixed juices were treated with barium hydroxide (to precipitate sulfates and phosphates and increase pH values), and with freshly precipitated silver oxide (to precipitate chlorides), followed by a second filtration through Filter-Cel after heating (Table IX).

Table IX

Juice	° Brix	Polarization	Apparent purity
Mixed	13.70	11.87	86.64
Clarified	9.55	8.86	92.77

An excellent clarification was obtained, showing that the part played in defecation by inorganic reactions is at least of considerable importance.

The actual amount of precipitate in defecation is of great importance; if too small, inefficient defecation results, if too great, the filter presses are overburdened by the large volume of material which must be treated. Defecation, as the writer knows it, is essentially a process for removing coarse dispersoids from juices by the formation of a flocculent precipitate within the juice. This precipitate not only adsorbs coloring and colloid matter, but enmeshing the suspended matter carries it down in settling. This is clearly demonstrated under the microscope. Since the formation of this precipitate is dependent upon the phosphate content of the juice, a low content will, prima facie, result in poor defecation. After sufficient precipitate has been formed, very little is gained by additional precipitation, and for this reason the addition of phosphates to juices cannot be justified unless the phosphate content is too low. McAllep and Bomonti[11] have shown that for efficient clarification the P_2O_5 content of the juice should not fall below 0.30 to 0.35 gram per liter.

In Table X are shown relations between liming and volume of settlings, and between liming and CaO: P_2O_5 ratios. Calculated ratios are taken from Table XI.

Table X

No.	CaO : P_2O_5 Ratios A	B	C	D	E	F	Volume of Settlings, Per cent A′	B′	C′
1	1.189	1.087	0.986	1.172	1.053	1.050	8	6	3.6
2	1.065	0.967	0.925	1.110	1.067	1.032	11	11	11.6
3	0.889	0.911	0.825	0.992	0.983	0.878[a]	16	13	18.9
4	0.876	0.802	0.706	0.947	0.931	0.961	17	19	19.8
5	...	0.806	0.666	...	0.921	0.958	22	25	28.8
6	...	...	...	...	...	...	30	26	32.7

[a] Error.

Magnesium in the precipitate shows no relation to volume changes—a fact which direct tests have substantiated. The increasing volume of settlings must be due to changes taking place in the CaO–P_2O_5 relations, as the data in Table X distinctly show.

In Tables XI and XII are given data on the relation of CaO and P_2O_5 in juice and precipitate. In Table XI, six tests are reported; in Table XII, two tests. pH values were estimated by the method of Gillespie.[12]

Table XI

(Figures in grams per liter)

pH	Juice CaO	Precipitate CaO	Precipitate P_2O_5	Precipitate MgO	pH	Juice CaO	Precipitate CaO	Precipitate P_2O_5	Precipitate MgO
6.5	0.291	...	...	...	6.9	0.228	0.097	0.081	0.042
7.0	0.241	0.169	0.201	...	7.8	0.179	0.298	0.324	0.058
7.2	0.216	0.340	0.362	...	8.5	0.241	0.396	0.383	0.087
8.0	0.211	0.450	0.400	...	9.2	0.347	0.426	0.388	0.142
8.8	0.280	0.460	0.403	...	9.8	0.441	0.500	0.401	0.175
					10.5	0.695	0.521	0.420	0.219
6.9	0.384	...	...	...	7.2	0.283	...	...	...
7.4	0.259	0.295	0.291	0.070	7.5	0.205	0.128	0.150	0.031
7.9	0.237	0.361	0.334	0.080	7.8	0.170	0.200	0.222	0.045
8.4	0.272	0.423	0.349	0.108	8.1	0.194	0.241	0.239	0.058
9.0	0.343	0.511	0.361	0.114	8.4	0.226	0.277	0.260	0.061
10.0	0.455	0.560	0.373	0.150	8.8	0.254	0.282	0.267	0.069
7.2	0.320	...	...	...	7.0	0.356	...	...	...
7.7	0.190	0.226	0.238	0.058	7.0	0.265	0.100	0.105	0.019
7.9	0.190	0.238	0.254	0.052	7.1	0.247	0.124	0.128	0.024
8.2	0.144	0.302	0.297	0.078	7.2	0.241	0.197	0.173	0.032
8.8	0.257	0.332	0.309	0.085	7.5	0.240	0.206	0.198	0.035
9.2	0.300	0.340	0.313	0.087	7.8	0.245	0.240	0.230	0.046

Table XII shows the analysis of clarified juices and precipitates for CaO, P_2O_5, and MgO.

The remarkable fact shown in these tables is that, though lime is added to the juice, its CaO content may actually decrease up to a reaction of about pH 8 in the cold. Above

[11] *Hawaiian Planters' Record*, **26**, 139 (1922).

[12] Clarke, "The Determination of Hydrogen Ions," p. 129.

this point the CaO content increases rapidly. Thus it is entirely possible to clarify juices with lime and obtain a clear juice of lower CaO content than originally present.

Table XII
(Figures in grams per liter)

	Juice			Precipitate		
pH	CaO	P_2O_5	MgO	CaO	P_2O_5	MgO
Raw	0.154	0.384	0.406	...	...	...
7.2	0.249	0.191	0.356	0.185	0.193	0.050
8.85	0.251	0.093	0.325	0.289	0.292	0.081
9.1	0.259	0.087	0.318	0.316	0.297	0.088
9.25	0.311	0.084	0.314	0.317	0.301	0.091
Raw	0.219	0.388	0.388	...	...	...
7.3	0.223	0.252	0.357	0.141	0.136	0.031
8.0	0.263	0.198	0.348	0.238	0.190	0.040
8.3	0.258	0.132	0.338	0.260	0.256	0.049
8.8	0.241	0.113	0.330	0.292	0.276	0.058

Table XIII gives data on a juice whose reaction was increased in small steps.

Table XIII
(Figures in grams per liter)

	Juice				Juice		
pH	CaO	P_2O_5	MgO	pH	CaO	P_2O_5	MgO
Raw	0.180	0.357	0.392	7.6	0.241	0.099	0.346
7.0	0.252	0.188	0.355	7.7	0.241	0.099	0.341
7.1	0.249	0.180	0.360	7.8	0.258	0.089	0.341
7.2	0.239	0.125	0.355	8.0	0.259	0.062	0.339
7.3	0.230	0.115	0.348	8.2	0.267	0.060	0.341

Table XIV shows data on cold juices, clarified without heating.

Table XIV
(Figures in grams per liter)

	Juice		Precipitate			Juice Only	
pH	CaO	P_2O_5	CaO	P_2O_5	pH	CaO	P_2O_5
Raw	0.225	0.427	...	...	Raw	0.187	0.339
6.9	0.322	0.381	0.031	0.038	7.2	0.277	0.276
7.0	0.333	0.356	0.060	0.083	8.0	0.261	0.102
7.1	0.349	0.328	0.067	0.099	8.8	0.271	0.013
7.4	0.291	0.211	0.221	0.198	9.2	0.310	0.006
7.8	0.239	0.102	0.351	0.325	9.4	0.417	0.001
8.4	0.219	0.019	0.428	0.390	9.7	0.420	0.001
9.0	0.259	0.008	0.522	0.416	...	...	...

With these data at hand, it remains to correlate them to existing laws of equilibrium. This, after a comprehensive review, the writer has been unable to do. It is evident that there are disturbing influences. The ratio of CaO to P_2O_5 in the precipitates is not constant, but increases as the reaction is increased as shown in Table X. From Table VI the ratios are in the order, 1.06, 0.86, 0.66, 0.48, 0.42, 0.35. This ratio for the secondary calcium phosphate is 1.127 and for the tertiary salt, 0.83. Uncombined CaO can exist, then, only in solid solution in the precipitate. These relations of CaO to P_2O_5 in dilute solutions have been noted in the literature.[13]

The influence of organic acids is shown in Table XV. Solutions of monosodium phosphate containing 0.74 gram P_2O_5 per liter and acid as indicated were brought up to a reaction of pH 8.0, while boiling, with a normal solution of calcium saccharate. The analyses refer to the filtrate.

Table XV
(Figures in grams per liter)

Citric		Tartaric		Hydrochloric	
Acid	CaO	Acid	CaO	Cc. *N*	CaO
0.70	0.057	0.00	0.000	4	0
1.40	0.169	0.75	0.020	8	0
2.10	0.320	1.50	0.211	12	0
...	...	2.25	0.372	...	...

The influence of organic acids is thus quite evident and the contrast with mineral acid sharp. It has long been known that the precipitation of salts soluble with moderate difficulty, such as phosphates, is rendered more difficult by complex ions of organic oxygen derivatives.[14]

Data on the buffer action of juice are given in Table XVI. The boiling juice shows marked buffer action in the range 6.8 to 7.1, though distinct buffer action is shown over the entire range. This buffer action is due primarily to phosphates, influenced, however, by organic acids and especially by adsorbed substances.

Table XVI

Cc. *N* saccharate per liter	pH Values			
	Juice 1		Juice 2	
	Cold	Hot	Cold	Hot
1	6.0	...	6.0	6.0
2	6.4	6.2	6.2	6.2
3	6.5	6.4	6.4	6.4
4	6.6	6.6	6.6	6.6
5	6.9	6.7	6.9	6.7
6	7.0	6.8	7.0	6.8
7	7.1	6.8	7.1	6.9
8	7.3	6.8	7.2	7.0
9	7.4	6.9	7.3	7.0
10	7.5	6.9	7.5	7.0
11	7.7	7.1	7.6	7.1
12	7.9	7.2	7.8	7.2
13	8.0	7.4	7.9	7.3
14	8.1	7.8	8.1	7.5
15	8.3	8.0	8.3	7.8
16	8.6	8.2	8.4	8.1
17	9.0	8.6	8.6	8.3

Table XVII shows the relation of pH values in the various steps in clarification in the factory. The data cover a period of 10 hours, sampling every 15 minutes. Excellent clarification was obtained.

Table XVII

	Raw-limed juice	Clarified juice	Sirup
No. tests averaged	40	79	40
pH values	8.42	7.99	7.82

It is thus evident that the actions taking place in defecation are influenced by so many varying factors that their formulation will be difficult, indeed, if not precluded.

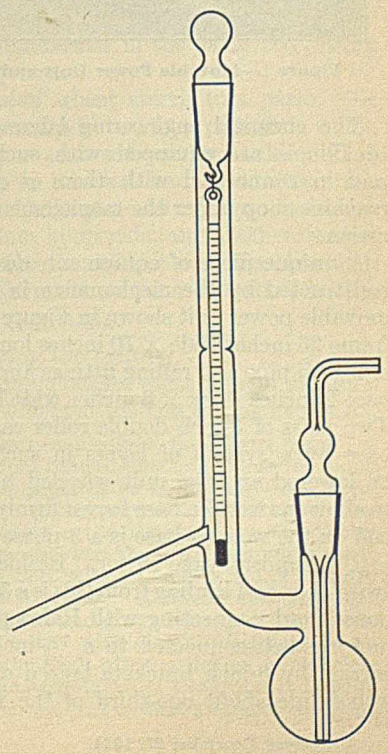
[13] Roscoe and Schlorlemmer, "Treatise on Chemistry," Vol. II, p. 557.
[14] Stieglitz, "Qualitative Chemical Analysis," Vol. I, p. 239.

A Distilling Flask for Corrosive Liquids[1]

By Louis Sattler and Bernard R. Mortimer

Kent Chemical Laboratories, University of Chicago, Chicago, Ill.

THE distilling flask is of the Claissen type, but it is so modified that a short thermometer can be hung from a hook in the ground stopper by means of a platinum wire. In order to allow the thermometer to hang vertically without touching the glass, three sharp depressions are made. The other stopper is hollow, and 0.5-mm. tubing is sealed to each end. In this way an inert gas may slowly be bubbled into the flask while the distillation is in progress. The side arm is put on with an inner seal to prevent mechanical contamination. Short-range thermometers which come in sets of six or seven, about 15 cm. long, are found to be excellent for use with the distilling flask.



[1] Received February 24, 1925.

Chemical Engineering Equipment for University Laboratories[1]

By M. J. Bradley

University of Illinois, Urbana, Ill.

THE science of chemical engineering has now advanced to the point where it is possible to plan a laboratory course in which the student is required to make direct application of his theoretical knowledge to problems of the type with which he will be often confronted in industry. Any chemical process may be resolved into a coördinate series of what may be termed "unit operations," such as distillation, evaporation, filtering, etc., etc. The number of these basic unit operations is not large and relatively few of them are involved in any one particular plant. The university chemical engineering laboratory, if equipped with representative units of these basic operations, can demonstrate by suitable flexibility in installation any chemical process carried on in the industry.

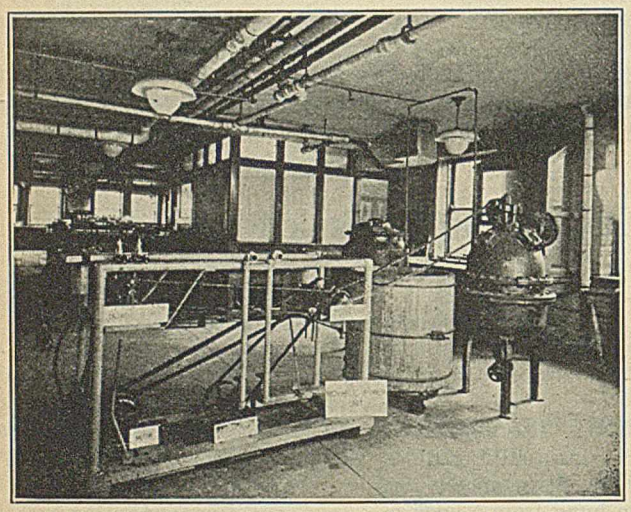


Figure 1—Movable Power Unit and Movable Wooden Tub

The chemical engineering laboratories at the University of Illinois are equipped with such semicommercial units, and in connection with them is a well-equipped student machine shop under the management of a competent mechanician.

A unique piece of equipment, designed by the writer and constructed by the mechanician in the student shop, is the movable power unit shown in Figure 1. It consists of an iron frame 26 inches wide × 70 inches long × 40 inches high, made of 2-inch pipe and railing fittings and attached to a hardwood base 2 inches thick × 6 inches wide by means of floor flanges. Two pairs of 3-inch double roller casters are attached to the base by a system of levers in such a way that they may be lowered and the unit wheeled to any location, or raised to allow the wooden base to rest firmly on the floor. At the one end on the wooden base is a 3-phase, 220-volt, 60-cycle, 1160 r. p. m. squirrel-cage motor. Beside the motor is mounted a switch box and leading from this is a 30-foot section of packing-house cord connecting with Ralco plug to receptacles. The motor is belt-connected to a $^{7}/_{8}$-inch countershaft, which is carried by 8-inch brackets bolted directly to the end of the iron frame about one-third of the way from the top. The shafting carries one 4-section cone pulley and four separate pulleys, varying in diameter from 3 to 12 inches, thus allowing variable speeds when driving agitators in kettles, etc. In front of the motor, installed on the base, is a rotary pump, with 1-inch openings, the pipes from which end with unions flush with the top of the iron frame. Installed on brackets directly above the motor and opposite the countershaft is a Crowell blower with $^{1}/_{2}$-inch opening. Both of these pumps can be belt-driven from the countershaft. This unit eliminates several motors and belts and installation of long overhead shafting.

Figure 1 also shows a 200-gallon wooden tub, mounted on a triangular base, carried by three 4-inch double wheels. One man can easily wheel it full of solution from the filter presses in one room to the evaporator in another section of the laboratory. Sheet steel tanks of 200-gallon capacity are similarly mounted. A portable agitator with monel metal shaft, which is capable of being set at various lengths, and a propeller-shaped agitator are easily clamped on the top of these tanks to provide agitation. The agitator is motor-driven and can be connected with any 110-volt, a. c. light socket.

A movable crane having a capacity of 2 tons is very useful. The base is equipped with heavy iron casters so arranged that the crane can turn in its own width. The front casters and handle work on an eccentric which automatically locks the wheels when the handle is released. This unit is especially convenient when equipment such as a 50-gallon cast-iron kettle has to be moved, and in lifting a barrel of solution or other heavy object onto the scales for weighing.

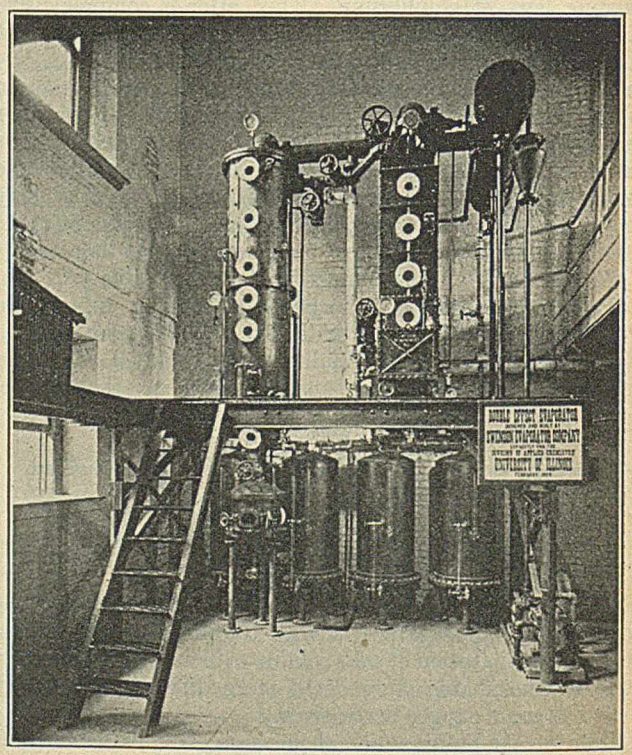


Figure 2—Double-Effect Evaporator

[1] Received December 27, 1924.

Figure 2 shows a double-effect evaporator of special design. The vertical effect is of the patented basket type, 24 inches inside diameter by 8 feet high. The heating surface is an internal drum made throughout of 1/4-inch steel plate and fitted with an auxiliary cylinder and umbrella deflector. The tubular surface consists of twenty-four 2 inch × 13 gage × 30 inch charcoal iron tubes expanded in the head of the drum. The horizontal effect is 19 × 27 inches and 7 feet 6 inches high, and is heated with a steam chest containing one hundred 3/4 inch × 27 inch × 18 gage cold-drawn copper tubes, so arranged that any number may be blocked off.

The unit is provided with vacuum pump, water-cooled surface condenser, four 200-gallon condensate receivers, vapor lines, by-passes, etc. It is so installed that either unit may be used as the first effect or they may be used separately.

The laboratory floor is constructed with positive drainage, sloping to large screened openings connecting directly to the trunk sewer. Leading from the trunk sewer at definite intervals under the concrete are smaller drain pipes, with openings at the walls and in the higher sections of the floor, for the discharge of cooling water or condensate. The elimination of exhaust steam pipes leading from the kettles to the floor openings greatly increases the convenience of the laboratory and improves its appearance.

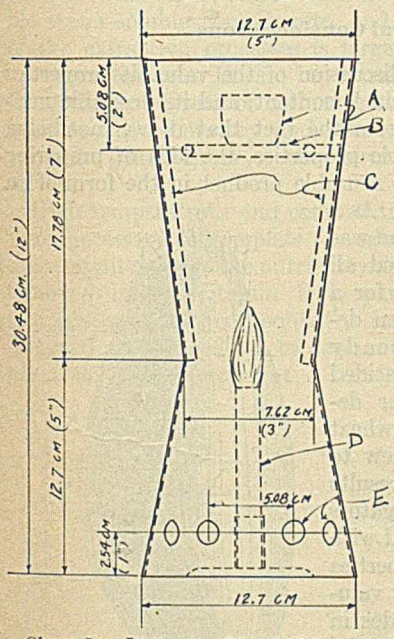
A Process for Sulfur in Coal[1]

Lead Oxide-Reduced Iron-Iodate Method

By W. J. G. Meade

ZENITH FURNACE CO., WEST DULUTH, MINN.

GRIND well in a mortar 5 grams of pig iron low in sulfur and mixed well with 6 grams of lead oxide. Weigh 0.5 gram of coal low in sulfur, or 0.25 gram if high. Transfer to the mortar containing the mixture and mix well with a pestle. Brush into a small porcelain crucible that has been lined with approximately 2 grams of zinc oxide. Clean out the mortar with a little lead oxide, using this as a cover and put on a tight-fitting porcelain lid.



Sheet Iron Asbestos-Lined Chimney
A—Porcelain crucible
B—Iron holder
C—Asbestos lining
D—Standard Bunsen burner
E—Air holes (1.27 cm. diameter)

The heating apparatus is best described as a sheet iron chimney lined with asbestos (see figure). In the first stages heat the mixture in the chimney for 15 minutes, with the flame at least 2.5 cm. from the bottom of the crucible. Using this low flame at the beginning will eliminate any errors caused through the sulfur passing off with the volatile matter. There should be no visible fumes. Gradually increase the heating, letting the flame touch the crucible for 10 minutes, then apply extra heat for five minutes, but not enough to cause reddening of the whole crucible. Although all coal gas contains small quantities of sulfur, this does not seem to affect the results, especially when a good-fitting porcelain lid is used. The success of the process depends upon this heating, and therefore great care must be used here.

Cool the crucible in a desiccator for 10 minutes, and then empty the contents into an agate mortar. The mixture now looks like a compressed lead and coal button, which drops out easily from the crucible. The lining also will come out on tapping the crucible against the mortar. Crush button and lining with a pestle and brush into a sulfur flask through a funnel. Mix the contents with a little distilled water. Connect with a rubber cork, funnel tube, and delivery tube. Place the delivery tube in a 100-cc. beaker or tumbler containing 150 cc. of distilled water and 8 cc. of cadmium chloride solution. Pour through the funnel tube 100 cc. of 1:1 hydrochloric acid. Heat a little at first to start the action, but then discontinue the heat until action has almost ceased. Resume heating very gently until the delivery tube gets hot. Disconnect and wash contents into a 800-cc. titrating jar containing 250 cc. of distilled water. Add 1 cc. of starch solution, 100 cc. of 1:1 hydrochloric acid, and titrate immediately with a standard solution of iodate, stirring well to a deep blue color.

Solutions

STANDARD IODATE—Weigh 0.56 gram potassium iodate, 6.0 grams potassium iodide, and 0.5 gram potassium hydroxide. Dissolve the salts in distilled water and make up to 1 liter. Each cubic centimeter equals approximately 0.0056 per cent sulfur. Standardize in the usual way, using 5 grams of standard pig iron.

STARCH—Mix 6.0 grams of wheat starch to a paste with a little cold distilled water and add to 1 liter of boiling water containing 15 cc. of 10 per cent sodium hydroxide. This solution must be made up in advance and used when cold.

AMMONIUM CADMIUM CHLORIDE—50 grams cadmium chloride, 1500 cc. ammonium hydroxide, and 1000 cc. water. Add the water to the cadmium chloride and dissolve with ammonium hydroxide. Keep the solution in a dark bottle.

Precautions

Care must be taken during the heating.

The solution in the absorbing beaker must be kept alkaline.

The solution must not be heated too fast during evolution.

Notes—The iodate solution is made up on the 5-gram basis. A blank determination is run from time to time and the sulfur found is subtracted from results obtained from each sample analyzed.

The use of the zinc oxide lining prevents the mixture from having the direct heat, especially at the first stages, and also helps to absorb any sulfides which otherwise the crucible would absorb.

The grade of iron used is best selected from a No. 2 foundry iron heat and should be low in sulfur. It should also be cooled carefully so that it can be drilled and ground easily. A quantity of this could be stored in a bottle with a tight-fitting cork.

The residue remaining in the flask after evolution is complete is soft and light. During the first stages of evolution it is helpful to shake the flask a little, giving the acid a chance to act on all the sulfides.

[1] Received April 4, 1924.

Production and Nutritional Value of Commercial Wheat Germ Extract[1]

By Charles Hoffman

WARD BAKING CO., NEW YORK, N. Y.

Wheat germ, a by-product of the flour mills, has been converted into an extract that may be used for human nutrition. The valuable properties of the germ—its high vitamin B content, its proteins of high nutritional value, and its content of the unidentified factor *X*, necessary for reproduction—have been preserved in the extract. The preparation of this extract has been briefly reviewed and feeding experiments conducted to show its valuable properties have been described. The toxic properties of the oil of wheat germ have been confirmed, and extensive biological experiments have shown that the removal of this oil results in a product more nutritious than the original germ. The high nutritive value of the proteins contained in the wheat germ extract has been shown by further feeding tests. Charts of growth curves of test animals under various conditions are given, as well as the analysis of the extract. Attention has been called to the value of the extract of wheat germ in food for infants and invalids.

WHEAT berries are made up of approximately 83.5 per cent endosperm containing the greater part of the starch, 15 per cent bran constituting the outer seed coats, and 1.5 per cent germ containing the embryo of a new plant. In spite of the small amount of germ present it contains a large portion of the vitamin B of the wheat berry and some very valuable proteins. It is with these constituents of the germ and their partial isolation on a commercial scale that the present paper deals.

Composition of Wheat Germ

Commercial wheat germ (moisture-free) was found by Osborne and Mendel[2] to have the following composition:

	Per cent		Per cent
Sugar	7.71	Fiber	2.35
Dextrin	7.50	Fat	10.44
Starch	18.21	Ash	4.91
Pentosans, etc.	8.29	Undetermined	5.59
Protein (N × 6.25)	31.00		

The material with which they worked and upon which this analysis is based was found to contain approximately 23.5 per cent endosperm, 23.7 per cent bran, and 52.8 per cent pure wheat germ. Frankfurt[3] made a careful investigation of the wheat embryo and reports the following analysis of the pure germ:

	Per cent		Per cent
Carbohydrates soluble in water, including sucrose and raffinose (6.89%)	24.34	Crude fat	13.51
"Crude protein" [N(6.44%) × 6.25]	40.25	Ash	4.82
Fiber	1.71	Undetermined (chiefly insoluble carbohydrates)	15.37

Complete discussions of wheat embryo and of the nutritional value of its proteins have been published by Osborne and Mendel,[2] McCollum,[4] and by McCollum, Simmonds, and Pitz.[5] Briefly summarized, the results of these investigators tend to show that the proteins existing in the germ of wheat are of very high nutritional value compared with the proteins of milk and eggs, and are apparently much more nutritive than those contained in the other parts of the wheat berry. This high nutritional value of the germ is further enhanced by the fact that it contains a very large proportion of the vitamin B content of the whole berry. Discussions of the vitamin distribution in the whole berry and of the character of the vitamin present are found in papers by McCollum, Simmonds, and Pitz,[5,6] by Bell and Mendel,[7] by Voegtlin, Lake, and Myers,[8] by Osborne and Mendel,[2] by McCollum,[4] and by Chick, Hume, and Cooper.[9] These discussions cover the subject thoroughly and show the great value of wheat germ as a source of this indispensable vitamin.

In spite of these valuable qualities the germ of the wheat has only recently been utilized for human food by the addition of a prepared extract to white bread,[10] and the pronounced tendency to rancidity possessed by the germ has prevented its extensive use as animal fodder.

General Considerations

From the wealth of discussion of the valuable properties of its proteins, its vitamin B content, and its desirable mineral constituents, and from the fact that it was not being utilized for these valuable properties, the idea of preparing from the germ of wheat a usable product in the form of an extract was worked out. As a result a loaf of white bread was prepared which contained all the elements necessary for a complete diet, as has been described in articles already cited.[10] Later it was decided to investigate in greater detail the properties of this wheat germ extract with a view to comparing it with the results obtained by other investigators on wheat germ itself and with the idea that its properties might make it extremely valuable for other uses besides in bread. The results of careful investigation fully justified these expectations.

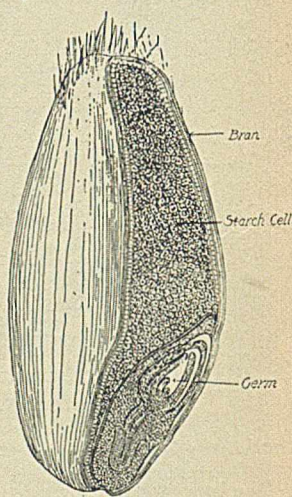


Figure 1—Longitudinal Section through a Grain of Wheat Showing the Main Component Parts (after Jago)

The commercial production of such an extract as would contain the valuable constituents of the original germ unimpaired presented many unexpected problems of engineering and manipulation, but these have been successfully solved and commercial production of the product is now a reality.

[1] Received August 6, 1924.
[2] *J. Biol. Chem.*, **37**, 557 (1919).
[3] *Landw. Vers.-Sta.*, **47**, 449 (1896).
[4] "The Newer Knowledge of Nutrition," 2nd ed., **1922**, p. 124. The Macmillan Company.
[5] *J. Biol. Chem.*, **25**, 108 (1916).
[6] *J. Biol. Chem.*, **28**, 1916 (1916).
[7] *Am. J. Physiol.*, **62**, 145 (1922).
[8] *Public Health Rept.* **33**, 647 (1918).
[9] *Med. Research Com. London, Spec. Rept.* **38**.
[10] Hale, THIS JOURNAL, **15**, 122 (1923); Hoffman, *Ibid.*, **15**, 1225 (1923).

Commercial Problems

Few flour mills were separating the germ from the shorts (feed) at the time these investigations were started, and those that made any kind of a separation made a very incomplete one. The best product obtainable at that time was a mixture containing mostly bran and endosperm with a small proportion of germ. It was therefore necessary to interest the millers in separating the germ completely from other products so that the raw material for extraction would contain a minimum proportion of unnecessary bran and endosperm. A satisfactory germ was finally obtained.

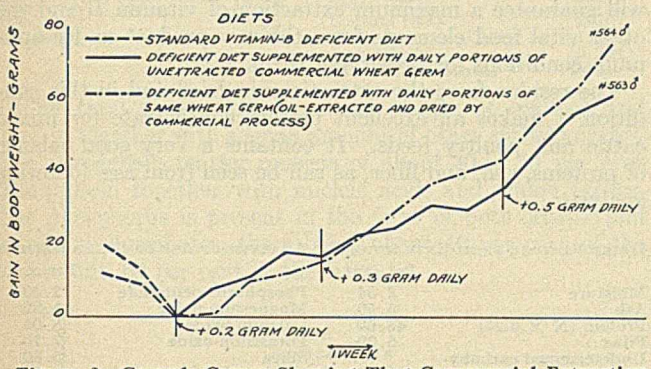


Figure 2—Growth Curves Showing That Commercial Extraction of Oil from Wheat Germ Does Not Injure nor Remove Any of Vital Elements of Germ

The commercial germ contains about 10 per cent of an oil which has a bitter, disagreeable taste and odor and is not very stable. This oil interfered with the extraction of the valuable water-soluble constituents, and the commercial success of the extraction processes is largely attributed to the removal of the oil. It can be extracted commercially from the germ by benzene or carbon tetrachloride, and tests made both in this laboratory and others show that none of the valuable constituents of the germ are removed by either solvent.

High temperatures and comparatively long periods of time were necessary to complete the extraction, and it was feared these might damage the nutrient constituents that were to be removed later. Vitamin B is particularly susceptible to temperature, and consequently feeding experiments were designed and carried out to determine the effect of the operation on this constituent. Test animals were fed a diet deficient in vitamin B to the point where they were declining in weight rapidly, and were then given supplementary rations consisting of oil-free and unextracted wheat germ to make up for this deficiency. Immediate response was obtained in both cases, as shown by typical examples in Figure 2. The animals on extracted germ gave a slightly better response than those on the original. This difference became more pronounced in longer tests than that shown in the figure. Certainly this proved that the value of the germ was not being injured by the treatment, but that it was actually being improved.

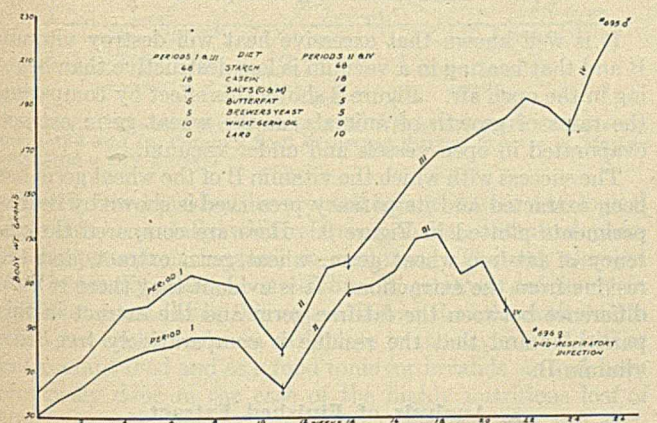


Figure 3—Toxic Effect of Wheat Germ Oil

The crude oil obtained from the extraction of the germ in commercial manufacture is heavy and very dark brown in color. It has a pronounced bitter, astringent taste which is characteristic of this oil. It has unusual emulsifying properties and froths easily with agitation.

Toxicity of Wheat Germ Oil

Besides the difficulty of extracting the valuable parts of the germ, the oil, by its bitter taste, would more or less seriously affect the taste of any food product containing it. Furthermore, McCollum and his co-workers[11] showed that the ether-soluble extract of wheat germ and the oil which it contained were somewhat toxic to albino rats. The additional observation was made by these investigators that swine were seriously affected by the inclusion of large amounts of wheat in their diet, even though the diet was complete in other particulars. Osborne and Mendel[2] and Voegtlin and Meyers[12] disagreed with this and found no evidence of toxic effect produced by this oil. To resolve the difficulty feeding experiments were carried out by the present writers, and three sets of these have been plotted in Figures 3, 4, and 5.

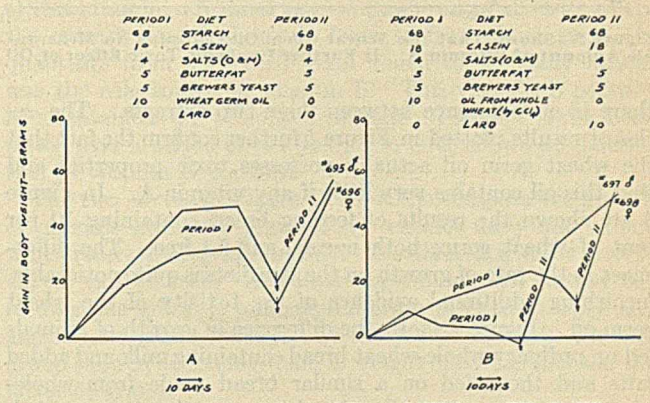


Figure 4—Comparison of Toxic Effect of Oil from Whole Wheat and from Germ of Wheat

The growth curves of a pair of animals fed alternately on two different diets are plotted in Figure 3. The basic diet used throughout this experiment was a standard synthetic one complete in all the vital factors. During Period I this diet was supplemented by ten parts of wheat germ oil and both animals showed a pronounced decline in weight between the eighth and the eleventh weeks. This was evidently caused by the toxicity of the oil. For the next three weeks, Period II, an equal weight of lard was substituted for the wheat germ oil, in order that the animals might receive the same number of calories from the diet in each case, and both animals showed surprising gains in weight as soon as the oil was removed from the diet. During Period III the oil was again included in the diet as in Period I. The male again began to lose weight after the eighth week of this period, while the female began to lose weight after the fourth week. During Period IV, lard was again substituted for the oil and the male again began to gain weight while the female did not, presumably because her condition had become too weakened to permit recovery.

For further confirmation of these results, samples of oil extracted from the germ and from whole wheat flour with

[11] Wisconsin Agr. Expt. Sta., *Bull.* **17** (1911); *J. Biol. Chem.*, **19**, 373 (1914); **25**, 105 (1916); **25**, 249 (1916); **28**, 211 (1916).

[12] *Public Health Rept.* **33**, 843 (1918).

carbon tetrachloride were fed to animals for comparison purposes. Special precautions were taken in every case to remove all trace of solvent from the extract used. The results of these feedings are shown in Figure 4, where Curves *A* show the effect of the oil from germ and Curves *B* of extract from the whole wheat. These tests indicate that

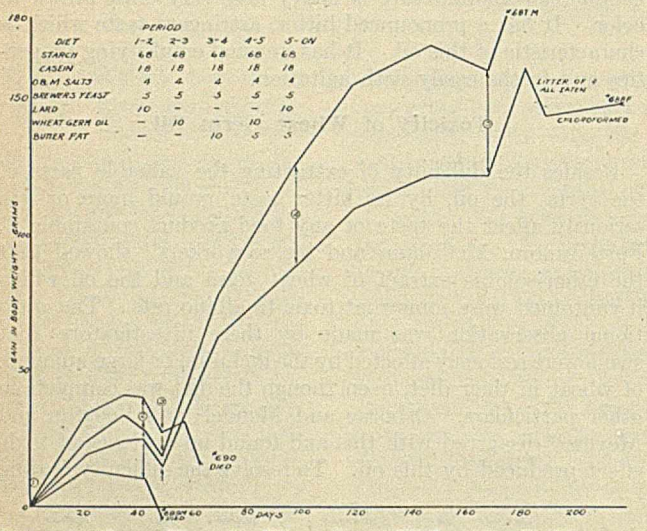


Figure 5—Shows That the Wheat Germ Oil Contains No Measurable Amount of Vitamin A. It Further Confirms Toxic Effect of Oil

there is no difference between these two extracts. The series of results plotted in Figure 5 further confirm the fact that the wheat germ oil actually possesses toxic properties and that this oil contains very little if any vitamin A. In Figure 6 are shown the results of feeding bread containing 10 per cent of wheat germ, both normal and fat-free. The differences in the rate of growth on the two diets is quite noticeable, furnishing additional evidence of the toxicity of the wheat germ oil. Figure 7 shows the difference in growth of animals fed on ordinary whole-wheat bread containing milk and added salts and those fed on a similar bread made from whole-wheat flour from which the oil had been previously extracted. These results show conclusively that the wheat germ oil is

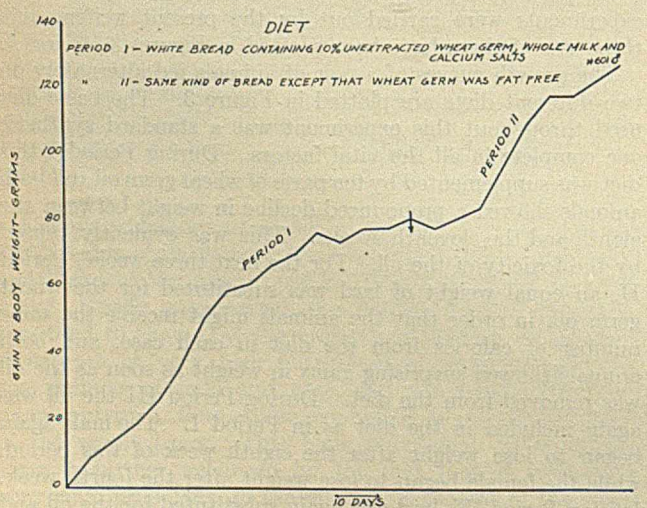


Figure 6—Biological Difference between the Extracted and Unextracted Wheat Germ

deleterious and exerts its toxic action even though the diet is otherwise complete.

Malting and Extracting Oil-Free Germ

The germ freed from its oil is cooked and malted under conditions which preserve the important nutritive elements of the germ. Special methods are necessary for the extraction of the solubles. These are then concentrated in vacuum evaporators to a 50 Baumé sirup. Vacuum driers then completely dry the sirup. The dried product is afterward finely ground. Great care is necessary throughout to use equipment that will guarantee a maximum extraction of vitamin *B* and the other vital food elements form the raw product under optimum conditions for preserving them.

The residue from the extractions is dried and in this condition it makes an excellent protein concentrate for mixed cattle and poultry feeds. It contains a very good balance of proteins, ash, and fiber, as can be seen from the following analysis:

Dried Residue from Extractions	Per cent	Analysis of Ash of Dried Residue	Per cent
Moisture	3.54	Phosphorus pentoxide	62.40
Ash	5.50	Magnesium oxide	11.80
Protein (N × 6.25)	45.60	Calcium oxide	8.06
Fiber	6.99	Potassium oxide	7.10
Undetermined carbohydrates, pentosans, etc.	38.37	Silica	5.80
		Ferric oxide	4.04

The protein content is practically insoluble in water and is of quite a different character from that of the soluble proteins that appear in the dry extract. The entire output of this by-product is in much demand as the basic ingredient in cattle feeds. Close observations have been made of cows fed on rations including this product, and not only was it tolerated remarkably well but actual increases in the yield of milk were noted.

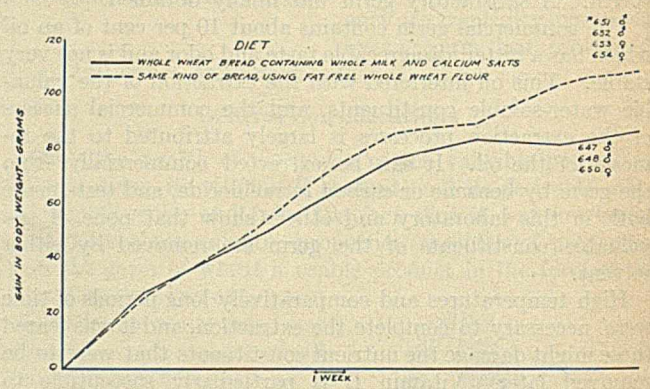


Figure 7—Extracting the Oil from Whole Wheat Flour Improves Its Nutritive Qualities

Manufacturing Conditions

It is well known that excessive heat will destroy vitamin B and that heating in a vacuum is less destructive than heating in the open air. Figure 8 shows this effect by comparing the rates of growth of animals on the wheat germ extract evaporated in open vessels and under vacuum.

The success with which the vitamin B of the wheat germ has been extracted and its potency preserved is shown by the experiments plotted in Figure 9. Here are compared the potency of fat-free wheat germ, wheat germ extract, and the residue from the extraction. It is evident that there is little difference between the fat-free germ and the extract in this particular and that the residue is comparatively free from vitamin B.

Analysis of Finished Extract

The final product manufactured under these conditions is a fine, sugary powder, golden yellow in color and possessing an agreeable, malty taste. It is very hygroscopic and readily soluble in water. It further possesses the property of "beating up" when whipped, similar to that of other albuminous products. The composition of the product is approximately as follows:

ANALYSIS OF DRY EXTRACT

	Per cent
Total soluble carbohydrates:	76.09
Maltose 47.70	
Dextrin 21.10	
Other carbohydrates (by difference) 7.29	
Protein (N × 6.25)	15.36
Ash	5.05
Moisture	3.50

ANALYSIS OF ASH

	Per cent
Potassium oxide (K_2O)	39.36
Phosphorus pentoxide (P_2O_5)	37.40
Sulfuric anhydride (SO_3)	7.34
Magnesium oxide (MgO)	4.80
Chlorine (Cl)	3.80
Silica (SiO_2)	2.74
Sodium (Na)	2.50
Calcium oxide (CaO)	1.28
Iron (Fe_2O_3)	0.294
Manganese (MnO_2)	Trace

The total sugars are composed chiefly of maltose and dextrin together with a small amount of other carbohydrates. The nitrogenous matter consists of about 30 to 40 per cent true protein together with nucleic acids and amino bodies. The phosphorus is present in the form of both organic and inorganic phosphates, there being about 40 per cent of the former and 60 per cent of the latter.

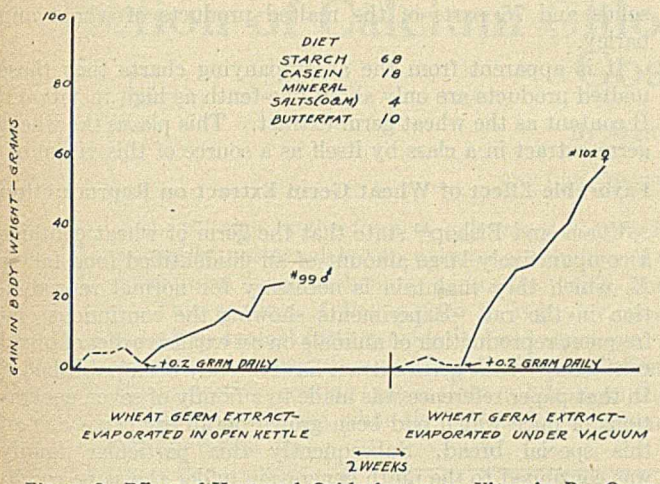


Figure 8—Effect of Heat and Oxidation upon Vitamin B. Open Kettle Evaporation of Wheat Germ Liquor Is Quite Destructive to Vitamin B

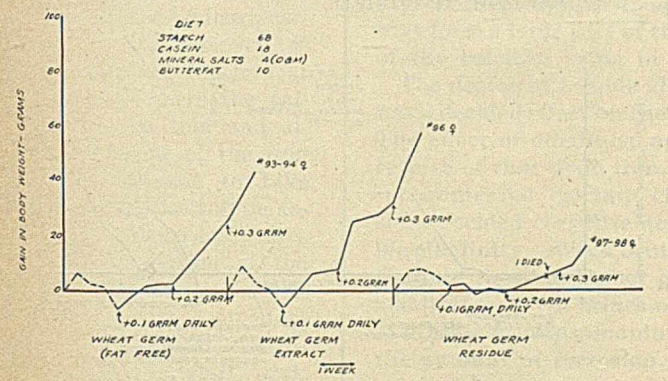


Figure 9—Shows that Vitamin B in Wheat Germ Is Completely Extracted and Its Potency Well Preserved during Process of Manufacturing a Dry Extract

The finished product is very well balanced from a biological viewpoint, especially with reference to its content of phosphates, potassium, magnesium, and iron. The only element that is greatly deficient is calcium, a common deficiency in cereal products. For this reason it was thought desirable to add 1 per cent of calcium carbonate to the dry extract for use as an infant food and as a food tonic for invalids, as had been previously done in the case of the highly nutritious loaf of bread prepared by its use.[10] This increases the ash content of the extract to 5.4 to 5.8 per cent and gives it the following representative composition:

ANALYSIS OF ASH OF FINISHED (FORTIFIED) EXTRACT

	Per cent		Per cent
Phosphorus pentoxide (P_2O_5)	32.50	Magnesium oxide (MgO)	4.65
Potassium oxide (K_2O)	30.50	Sodium (Na)	3.40
Calcium oxide (CaO)	12.10	Silica (SiO_2)	1.20
Sulfuric anhydride (SO_3)	10.51	Iron (Fe_2O_3)	0.18
Chlorine (Cl)	5.20	Manganese (MnO_2)	Trace

Vitamin B Content of Wheat Germ Extract

The high concentration of vitamin B in the finished product is shown by means of the standard feeding method of Osborne and Mendel. Figures 10 and 11 show charts based on a large number of tests carried out to demonstrate the efficiency of the extract as a source of vitamin B. The extract compares favorably with good, dry brewer's yeast as a source of this vitamin. Normal gains were shown in all cases where the extract described, made from oil-free wheat germ, in quantities from 0.1 to 0.3 gram added to the daily ration, was the sole source of vitamin B. This vitamin B potency is maintained on prolonged storage. Samples have been tested over a period of two years and have shown no diminution in vitamin B potency.

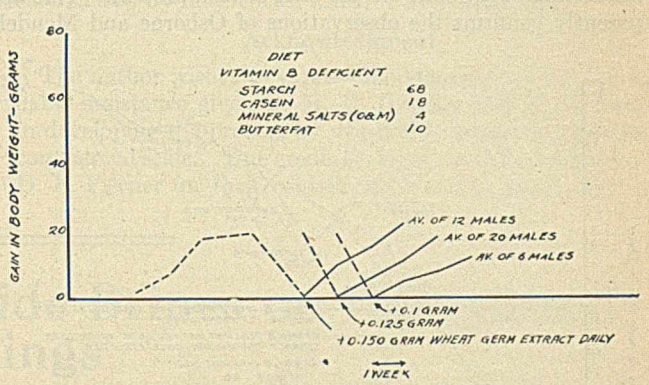


Figure 10—Curves Showing High Potency of the Dry Wheat Germ Extract in Vitamin B. A Large Number of Animals Were Used so as to Get Good Average Results

The two curves in Figure 12 show the comparative growth of animals given 0.3 gram of the extract daily and others which received 2.0 grams weekly. No difference in the growth curves can be seen. A similar experiment was carried out feeding one group of animals 0.2 gram of extract daily and another 1.4 grams weekly. At the end of 10 weeks the first group showed an average gain in weight of 35.5 grams and the latter 51 grams.

Biological Value of Protein in Wheat Germ Extract

Analyses of the extract showed it to contain from 2.3 to 2.7 per cent of nitrogen, which is equivalent to from 15.0 to 16.5 per cent of protein (N × 6.25). The true protein content, however, is only 4.5 to 6.5 per cent. The remainder of the nitrogen is present as nucleic acids and amino bodies. Figure

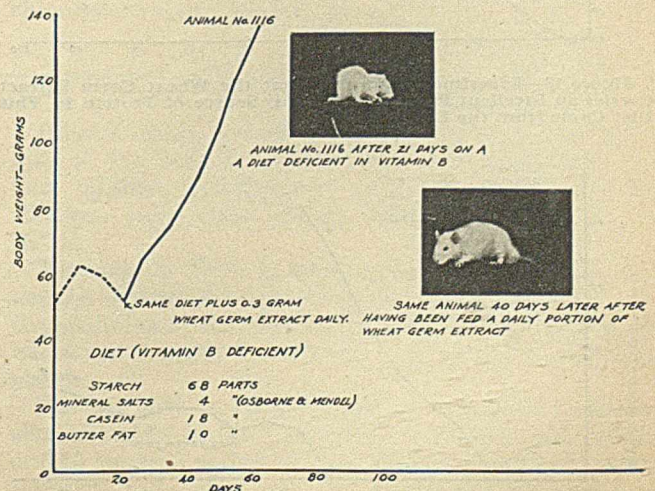


Figure 11—Upper Picture Shows the Typical Condition of an Animal Suffering from a Lack of Vitamin B in the Diet. Lower Picture Shows the Same Animal 40 Days Later after Receiving a Daily Portion of Wheat Germ Extract. Growth Curve Shows the High Potency of the Extract in Vitamin B

13 shows a feeding test in which the animals received no other protein than that contained in the extract. The animals made a fair growth considering the fact that the diet contained only 83 per cent of extract, of which only about 4.5 was true protein. The animals grew, therefore, on a diet containing only about 4.1 per cent of true protein. This apparently confirms the observations of Osborne and Mendel[2]

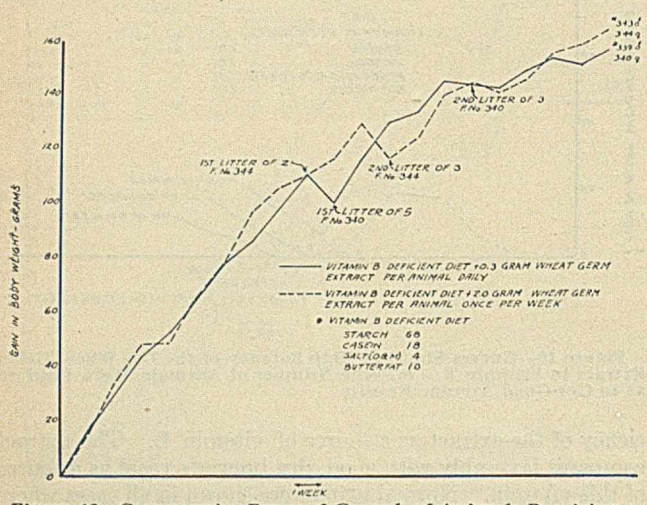


Figure 12—Comparative Rates of Growth of Animals Receiving a Daily and Weekly Ration of Vitamin B

and of McCollum,[4,5] who found that these particular proteins had very high biological value.

Comparison with Other Malted Cereal Products

In order to determine the real merit of this wheat germ product with respect to vitamin B, comparisons were made with malted cereal products and with malted cereal and milk combinations. The cooking, malting, evaporating, and drying of these products were carried out under the same conditions as those adopted for the preparation of the wheat germ

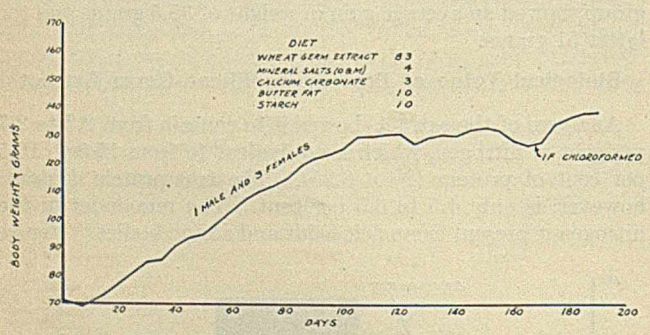


Figure 13—Experiment Showing That the Wheat Germ Extract Carries an Excellent Protein. The Only Source of Protein in This Diet Came from the Extract

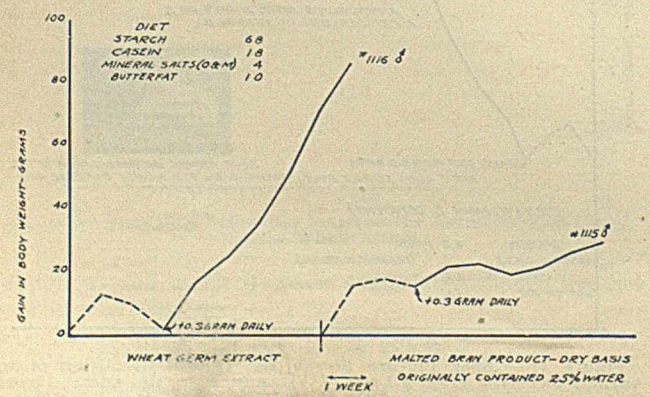


Figure 14—Comparison in Vitamin B Content of Wheat Germ Extract with a Malted Bran and Corn Product

product. Three series of comparative feeding tests were conducted. In the first, wheat germ extract was compared with an extract made from a product prepared by cooking 40 parts of bran with 40 parts of whole corn and then malting with 20 parts of ground malt. The growth curves of this series are seen in Figure 14. In the second series the wheat germ extract was compared with malt extract (Figure 15, *A*), and with an extract prepared from a diastatic fungus growth on a mixture of approximately 40 parts of bran and 60 parts of corn grits (Figure 15, *B*). In the third series the wheat germ extract was compared with a dry extract prepared by malting 70 parts of wheat with 30 parts of malt (Figure 16, *B*), and with an extract prepared by adding milk to the wheat-malt mixture, proceeding with the malting and later making a dry extract of the resulting product (Figure 16, *A*), so that the final dry extract contained 25 parts of whole milk solids and 75 parts of the malted products of wheat and barley.

It is apparent from the accompanying charts that these malted products are only about one-tenth as high in vitamin B content as the wheat germ extract. This places the wheat germ extract in a class by itself as a source of this vitamin.

Favorable Effect of Wheat Germ Extract on Reproduction

Evans and Bishop[13] state that the germ of wheat contains a comparatively large amount of an unidentified food factor *X*, which they maintain is necessary for normal reproduction in the rat. Experiments showing the continuous and frequent reproduction of animals on an exclusive diet of bread containing wheat germ extract have already been published.[10] In that paper reference was made to a family of seven generations of mice which had been grown on an exclusive diet of this special bread. Subsequently this particular family was continued to the ninth generation under the same conditions, and there was every reason to believe that the experi-

[13] *J. Biol. Chem.*, **44**, 132 (1920).

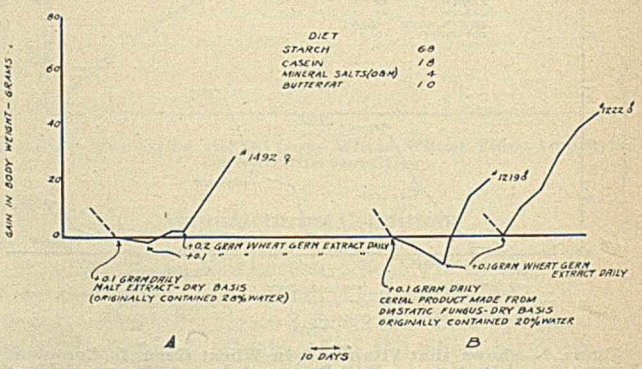


Figure 15—Wheat Germ Extract Compared in Vitamin B Content with *A*, Malt Extract, and *B* an Extract Prepared from a Fungus Growth on Bran and Corn

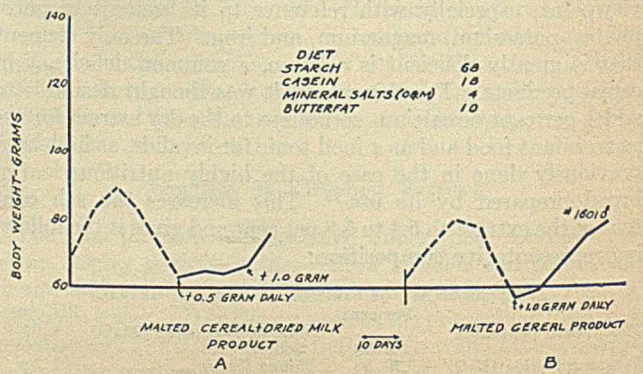


Figure 16—Vitamin B Content of a Malted Wheat and Milk Product (*A*) and a Malted Wheat Product (*B*)

ment could have been continued indefinitely. A sixth generation of albino rats was similarly reared before the experiment was discontinued.

Conclusions

It is apparent that wheat germ extract so prepared possesses valuable nutritive properties and should find a considerable use in human nutrition. A waste product of the flour mills, which has previously been used only as a cattle feed within a rather narrow area near the flour mills, may by this method be converted into a valuable, concentrated food for human beings and particularly for infants and invalids. It may be used in many ways as a supplement to the ordinary diet incorporated in food products of various kinds or it may even be used as a partial substitute for table sugar. In limited numbers of experiments made with human subjects the results so far obtained lead to the conclusion that this extract may be extremely valuable as a modifier of milk for infants. The readiness with which it is assimilated and its ease of toleration add further to its possible usefulness in any disease caused by deficiencies which it may make up.

Acknowledgment

The author wishes to express his appreciation for the valuable assistance given by H. D. Grigsby and N. M. Cregor in developing the process by which this extract is made on a commercial scale. Due credit is also given to Laura Ashe and D. P. Fischer for their contributions to this paper.

Action of Calcium Chloride Brines on Galvanized Coatings[1]

By Arthur C. White

The Dow Chemical Co., Midland, Mich.

METALLIC zinc in the form of galvanized coating is generally protected by an extremely thin film of a mixture of basic carbonate, carbonate, oxide, and hydroxide. This coating, if the surface is kept dry, is a decided protection against further oxidation and corrosion.

In water, or in brines containing carbon dioxide in solution, part of this protective coating passes into solution as the sparingly soluble bicarbonate, while the bulk of it, in suspension, gives the milky appearance so often noticed in brine systems.

As the original coating of zinc is slowly oxidized, carbonated, and removed, it finally exposes the iron at some point where the galvanizing was thin and allows corrosion of the iron by air oxidation to take place. The electrolytic action then set up accelerates the decomposition of the zinc metal. After the galvanizing has completely disappeared, local electrolytic actions start work upon the iron itself.

Considerable attention has been given, papers have been read, and numerous articles written on the subject of corrosion of iron and steel in refrigerating plants,[2,3,4] but very little mention seems to have been made of the action of calcium chloride brines on galvanized coatings as differentiated from iron itself. The tendency in the past has been to lay stress only on the corrosion of the iron and to neglect all other metals that may be present in commercial plants.

A large part of the metal surface exposed to the action of the refrigerating brine in the modern ice plant consists of the outside walls of the galvanized ice cans. This, in conjunction with the smaller proportion of black iron surfaces used in piping, shell coolers, agitators, and the usual steel plate tank filled with brine of any sort, makes an ideal situation for both chemical and electrolytic corrosion.

The old practice of allowing the zinc coating to disappear as rapidly as it cared to—which was often very rapid indeed—without making any attempt to conserve it, was an economic waste. The fact that galvanizing acts only as a protective coating and not as a corrosion-resisting metal, and will eventually disappear, offers no excuse for the neglect to preserve it as long as possible. Every month or year of retention of this coating adds that quota to the life of the comparatively expensive cans and cuts depreciation costs.

Metallic zinc when used as a coating for iron forms a protective coating upon itself. Galvanized coatings may form a large part of the metal exposed to the action of the calcium brine in a refrigeration installation.

The degree of soluble alkalinity present in the brine has a decided effect on the corrosion of the galvanizing. The effect of alkalinity on galvanized coatings is the reverse of that upon iron.

Commercial calcium chlorides now on the market show decided corrosive action due to their high soluble alkalinity. Weak brines show more corrosive action than do those of higher gravity for the same degree of alkalinity. With brines of low alkalinity the presence of ammonia or ammonium chlorides tend to increase the amount of corrosion.

Corrosion by Different Brands of Commercial Calcium Chloride

That nearly all brands of commercial calcium chloride do attack zinc and galvanized coatings rapidly is shown by the following experiment:

Plate I shows the effect of the action on galvanized iron of five samples of commercial calcium chloride from four different manufacturers and each with a different alkalinity when made up into brines of 1.20 gravity at 20° C.

The strip in Tube 1, after approximately 70 days' immersion in neutral brine, shows no corrosion whatever (although owing to the effect of lighting when the photograph was taken it appears as though slight corrosion had taken place).

The test strip in Tube 2 immersed in a brine having an alkalinity of 1.5 cc. 0.1 *N* per 100 cc. (0.004 per cent $Ca(OH)_2$ or 0.15 per cent normality) had small isolated areas where corrosion had taken place, these showing the customary white deposit and evidently occurring where the zinc coating was thin.

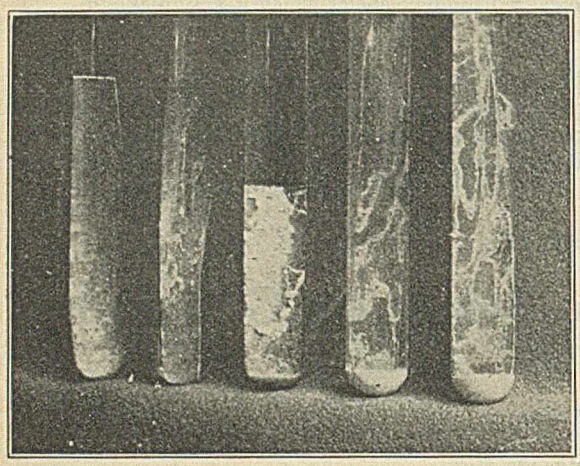
[1] Received November 19, 1924.

[2] Poste and Donauer, *Milk Dealer*, February, 1923.

[3] Hull, *Ice and Refrigeration*, March, 1923.

[4] Speller, *J. Am. Soc. Refrig. Eng.*, **8**, 216 (1921).

Strip 3 showed a very heavy coating of the white zinc hydroxide after even a few days' immersion. The product from which this solution was made contained a soluble alkalinity of 8.40 cc. 0.1 *N* per 100 cc., equivalent to 0.0854 per cent $Ca(OH)_2$ or 0.8 per cent normality. The deposit



Tube....	1	2	3	4	5
Mfgr....	*A*	*A*	*B*	*C*	*D*
Days....	70	30	3	50	50

Plate I

due to corrosion was thick and slimy and adhered to the test strip. Strips 4 and 5, with alkalinities, respectively, of 9.7 and 10.8 cc. 0.1 *N* per 100 cc., after 50 days, had lost practically all of the original coating of zinc, which can be noticed in the form of a sludge occurring in the bottom of both tubes. Tube 3, after about 30 days, showed approximately the same volume of precipitate.

Aside from the corrosion of the zinc and loss of the galvanizing from the cans, the presence of the insoluble sludge resulting from such corrosion is detrimental to high efficiency in the brine tank. This is particularly true in fixed can systems, where excessive sludge deposits may easily lead to slow and poor freezing at the bottom of the cans.

It will be noted that neutral brine has a much less corrosive effect on galvanized iron than any of those having a decided alkaline reaction.

This fact was not in agreement with the generally accepted assumption, based on work done on iron surfaces, which showed that, in general, alkaline brines are less corrosive than those having neutral or acid reactions.[2]

Following this lead, calcium chloride brines of varying alkalinities were used to determine the effect produced on galvanized surfaces. It was found that with an immersion of completely galvanized strips for 30 days in 1.20 gravity solutions of calcium chloride whose alkalinities varied from neutrality to saturation, decided differences were very apparent.

Effect of Soluble Alkalinity

Carefully weighed strips of galvanized iron were dipped once each day into a solution of calcium chloride of 1.20 specific gravity having the alkalinities shown, and allowed to hang exposed to the air for the remainder of the 24 hours. This was to get the corrosive effect due to the air exposure. The strips were held in a hard rubber frame, which effectually kept them from contact with each other. At the end of 90 days the strips were cleaned with distilled water and a stiff bristle brush until all deposits were removed that it was possible to get off without actual scraping (Table I and Plate II).

Table I—Effect of Soluble Alkalinity

Alkalinity Sp. gr. 1.20 at 18.3° C. (65° F.) Cc. 0.1 *N*/100 cc.	$Ca(OH)_2$ Per cent	Normality Per cent	Loss in 90 days Mg./sq. cm.
19.0	0.060	1.90	2.66
5.6	0.017	0.56	0.41
0.0	Neutral	0.00	0.53[a]

[a] Gain.

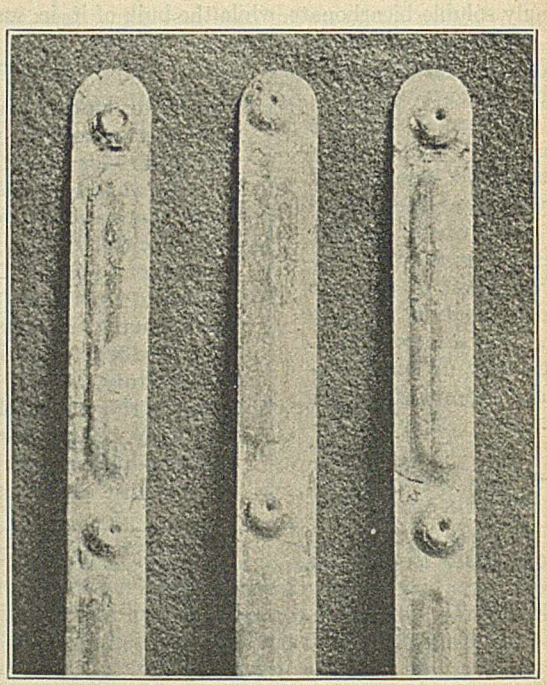
The results showed:

1—In a solution neutral to phenolphthalein there was practically no corrosion. This strip had been somewhat oxidized, but the corrosion losses were not sufficiently large to offset the slight gain due to the formation of hard oxide and carbonate not removed by cleaning the test strips.

2—A solution with an alkalinity corresponding to 5 cc. 0.1 *N* per 100 cc. (0.015 per cent $Ca(OH)_2$ or 0.5 per cent normality) showed that the galvanizing in irregular patches was somewhat darkened and slightly corroded, although approximately 75 per cent of the immersed strip showed the original bright surface.

3—With alkalinities of 15.9 cc. 0.1 *N* per 100 cc. (0.048 per cent $Ca(OH)_2$ or 1.59 per cent normality) and of 16.7 cc. 0.1 *N* per 100 cc. (0.051 per cent $Ca(OH)_2$ or 1.67 per cent normality), the zinc of the test pieces was practically eliminated, with the exception of the zinc-iron alloy[5] and small patches of zinc oxide. A heavy grayish white precipitate was deposited in the bottom of the test tubes.

4—With an alkalinity of 58 cc. 0.1 *N* per 100 cc., corresponding to nearly the saturation point for the OH ion in calcium chloride solutions of 1.20 gravity at approximately 20° to 25° C., containing 0.1765 per cent $Ca(OH)_2$, 5.8 per cent normality, a very much worse corrosive action resulted than with any of the other three solutions for an equal time period. Not only was all the galvanizing and the underlying zinc-iron alloy entirely removed, but the strip was practically coated with a slimy deposit of zinc carbonate and hydrated zinc oxide, while more of the same precipitate could be found in the bottom portion of the glass container.



A *B* *C*

A—0.060 per cent $Ca(OH)_2$
B—0.017 per cent $Ca(OH)_2$
C—Neutral

Plate II

From these results it may be seen that the effect of calcium brines of high alkalinity on galvanizing is exactly the reverse of their action upon iron as found by Poste and Donauer[2] and that neutral solutions have a much less corrosive action upon zinc or zinc-coated surfaces than do those of higher alkalinity.

[5] *Bur. Standards, Circ.* **80**, 14, 2nd ed. (1922).

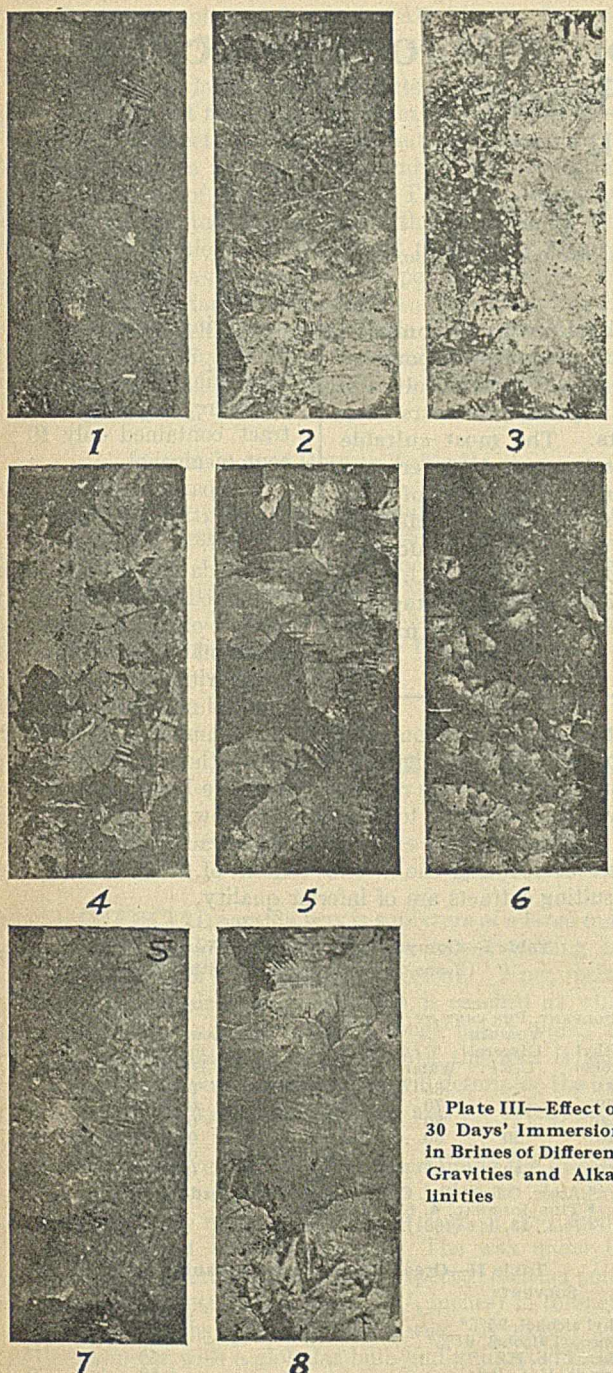


Plate III—Effect of 30 Days' Immersion in Brines of Different Gravities and Alkalinities

Comparison of the Corrosion Losses in Brines of Different Gravities

In order to determine the effect of a difference in gravity of brines upon their corrosive action, a series of tests was run using brines of 1.10 and 1.20 gravities with varying degrees of alkalinity (Table II and Plate III).

This series of tests showed that corrosion was increased by dilution only on brines of high alkalinity. The increase in corrosion due to dilution is in agreement with earlier work by Poste and Donauer,[2] who found the same effect on black iron plate.

Effect of Ammonia and Ammonium Chloride in Brine Solutions

Realizing that calcium chloride when used as brine in a refrigerating plant is liable at any time to become contaminated with ammonia, it was deemed important to obtain data on the corrosion of such a brine. In the presence of magnesium chloride, sometimes present as an impurity or as a bona fide constituent of refrigerating brines, the addition of ammonia results in the formation of the rather insoluble magnesium hydroxide, together with an equal molecular quantity of ammonium chloride. The latter salt is very corrosive to iron and its effect of increasing the corrosion in the case of galvanizing, particularly in the presence of free ammonia, is shown in Table III.

Table II—Corrosion Losses in 1.10 and 1.20 Sp. Gr. $CaCl_2$ Brines of Different Alkalinities

Fig.[a]	Alkalinity using phenolphthalein Cc. 0.1 N/100 cc.	$Ca(OH)_2$ Per cent	Normality Per cent	Loss in mg./sq. cm. 30 days	60 days
	1.10 specific gravity at 18.3 ° C. (65° F.)				
1	Neutral	0.000	0.000	0.465	2.171
2	1.75	0.005	0.175	0.670	2.535
3	4.40	0.013	0.440	0.828	2.328
4	11.00	0.033	1.100	7.650	10.740
	1.20 specific gravity at 18.3° C. (65° F.)				
5	Neutral	0.000	0.000	1.254	3.275
6	2.20	0.006	0.220	0.913	2.070
7	6.70	0.020	0.670	1.516	3.275
8	10.50	0.032	1.050	2.273	8.240

[a] See Plate III.

Table III—Effect of Presence of Ammonia and Ammonium Chloride

Brine Sp. gr. 1.20 at 18.3° C. (65° F.)	Alkalinity Cc. 0.1 N/100 cc.	Normality Per cent	Loss in mg./sq. cm. 30 days	60 days
$CaCl_2$	0.8	0.08	1.375	4.03
$CaCl_2$ + 10% (by wt.) NH_4OH	26.6	2.66	2.31	6.44
$CaCl_2$ + 1% NH_4Cl	1.4	0.14	2.97	6.92
$CaCl_2$ + 1% NH_4Cl + 10% NH_4OH	40.2	4.02	3.66	7.25

The results in Table III show that calcium chloride brines of low alkalinity are much more corrosive when they are contaminated with ammonia and that the presence of even a small percentage of ammonium chloride will increase the corrosive effect on galvanizing just as it does on iron.

Acknowledgment

The writer wishes to acknowledge helpful criticisms and suggestions from Ivan F. Harlow and Kelvin Smith.

Committee Advisory to the Chemical Warfare Service Meets

On April 3 and 4 the following members of the Committee Advisory to the Chemical Warfare Service met at Edgewood Arsenal: E. P. Kohler, of the subcommittee on research; W. K. Lewis and L. T. Sutherland, of the subcommittee on development; L. C. Jones, C. L. Reese, and W. H. Walker, of the subcommittee on production; R. Hunt, A. S. Loevenhart, and J. Stieglitz, of the subcommittee on physiological chemistry; and H. E. Howe, chairman.

Friday and Saturday morning the subcommittees discussed lists of problems with the men at the head of the various special departments. The meeting was one of the most successful in the history of the committee and much satisfaction was expressed not only with the work in progress but particularly with the attitude of the men who were engaged upon this research.

The difficulty at Edgewood continues to be the inadequacy of appropriations for research. A number of problems important in national defense are receiving less attention than is desirable and minor questions must be held in abeyance until money is available to make increases in the staff and provide necessary facilities and material. The fact that in the last few years war supplies have been drawn upon for research is often overlooked and the time has about arrived when purchases must be made to replenish exhausted stocks. Misunderstandings regarding the treaty situation have made it difficult to obtain for chemical warfare the appropriations that it should have, and we cannot expect to keep abreast of developments unless largely augmented appropriations can be had in the immediate future.

It is expected that the subcommittee will be called together more frequently in the future, that the list of consultants to the Chemical Warfare Service will be increased, and that steps will be taken to maintain an even closer contact between the research men at the arsenal and chemists in the laboratories of our educational institutions and industries.

Suitability of Various Solvents for Extracting Vanilla Beans[1]

Part III

By J. B. Wilson and J. W. Sale

WATER AND BEVERAGE LABORATORY, BUREAU OF CHEMISTRY, WASHINGTON, D. C.

Parts I and II of this series dealt with the composition of vanilla and tonka extracts made from oleoresins that had been prepared by the use of various solvents. This paper deals chiefly with organoleptic tests conducted on the vanilla extracts. The most suitable solvent for the vanilla extracts is neutral 65 per cent ethyl alcohol. The other solvents, in the order of their suitability, placing the most suitable first, are alkaline 65 per cent ethyl alcohol, 95 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. acetone, U. S. P. ether, and carbon tetrachloride. No advantage is gained by the preliminary removal of oily matter from the beans.

THE preparation and analysis of a series of extracts made from Mexican, Bourbon, and Tahiti vanilla beans and from Tonka beans by extraction with 65 per cent ethyl alcohol, 95 per cent ethyl alcohol, alkaline 65 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. ether, U. S. P. acetone, and 99.5 per cent carbon tetrachloride, have been described in Parts I[2] and II.[3]

Experiments Using Carbon Tetrachloride for Preliminary Treatment

It is recognized in the trade that it is not practicable to extract vanilla beans with alcohol weaker than about 45 per cent, on account of the difficulty of percolation. As the previous experiments had shown that carbon tetrachloride removes the flavorless, oily material from vanilla beans and extracts very little of the real flavoring constituents, it seemed that if the beans were first treated with carbon tetrachloride to remove the oily matter, they might later be extracted successfully by means of alcohol of lower strength than 45 per cent. Accordingly, 500 grams of Bourbon vanilla beans were macerated for 48 hours with 1 liter of carbon tetrachloride, with frequent shaking. The solvent was separated by decantation, and evaporated under diminished pressure. When only traces of carbon tetrachloride remained, the residue was transferred to a weighed flask and left near the steam bath. After standing some time it was weighed, and it was found that 31.5 grams, corresponding to 6.3 per cent, of oily matter had been extracted. As a slight odor of carbon tetrachloride still remained, the flask was left near the steam bath overnight. A direct determination of the vanillin in the oily matter was not made, since some of it may have been lost. From the amount of vanillin in the original beans and that found in the extract richest in vanillin, it is estimated that from 0.1 to 0.2 gram of vanillin (corresponding to 0.02 to 0.04 per cent in the extract) was removed from the beans with oily matter. Vanillin can be readily recovered from the oily matter by sublimation and returned to the extracts.

After extraction with carbon tetrachloride the beans were dried in air until the odor of the solvent was no longer perceptible. Such quantities (41.2 grams) of these dried beans as were equivalent in solid matter to 50 grams of the Bourbon beans used in the experiments described in Part I were then placed in Erlenmeyer flasks and extracted with three successive portions of solvent and made up to 500 cc. each. The solvents used were mixtures of alcohol, glycerol, and water in varying proportions. No trouble was experienced in separating the solvent from the marc, even when the extract contained only 10 per cent of alcohol.

The partial composition of these extracts is set forth in Table I.

The data in Table I, when compared with the data in Table I of Part II, show that preliminary extraction of the beans with carbon tetrachloride did not materially affect either the vanillin content or the lead number. However, the apparent high quality, as judged by the analytical data, of some of the extracts referred to in Table I was not confirmed by the organoleptic tests described below, so that, although it is practicable to employ carbon tetrachloride for the purpose of reducing the alcohol content of the menstruum, the resulting extracts are of inferior quality.

Table I—Composition of Bourbon Vanilla Extracts
(Beans previously extracted with CCl_4)

Solvent, Per cent by Volume			Ethyl alcohol found per cent by volume	Vanillin		Lead Number	
Ethyl alcohol	Glycerol U.S.P.	Water		A.O.A.C.[a]	Folin-Denis[b]	Winton	Wichmann[c]
65		35	60.9	0.23	0.21	0.59	0.78
30		70	28.6	0.20	0.18	0.55	0.86
20		80	20.4	0.18	0.17	0.52	1.05
20	20	60	18.2	0.18	0.18	0.58	0.75
20	10	70	18.8	0.18	0.18	0.55	0.79
10	10	80	10.3	Lost	0.16	0.55	0.89

[a] Assoc. Official Agr. Chem., Methods, Revised to November 1, 1919.
[b] THIS JOURNAL, **4**, 670 (1912).
[c] *Ibid.*, **13**, 414 (1921).

Table II—Organoleptic Tests on Vanilla Extracts

Solvents	Aroma	Flavor
Mexican		
Ethyl alcohol, 95%[a]	75	90
Isopropyl alcohol, 91%[a]	75	90
Ether, U. S. P.[a]	50	70
Acetone, U. S. P.[a]	50	90
Carbon tetrachloride, 99.5%[a]	25	Off flavor
Ethyl alcohol, 65%	100	100
Alkaline 65% ethyl alcohol	75	110
Bourbon		
Ethyl alcohol, 95%[a]	75	90
Isopropyl alcohol, 91%[a]	75	70
Ether, U. S. P.[a]	50	50
Acetone, U. S. P.[a]	50	80
Carbon tetrachloride, 99.5%[a]	25	Off flavor
Ethyl aclohol, 65%	100	100
Alkaline 65% ethyl alcohol	75	110
Tahiti		
Ethyl alcohol, 95%[a]	75	60
Isopropyl alcohol, 91%[a]	75	40
Ether, U. S. P.[a]	50	30
Acetone, U. S. P.[a]	50	40
Carbon tetrachloride, 99.5%[a]	50	Off flavor
Ethyl alcohol, 65%	100	80
Alkaline 65% ethyl alcohol	75	60
Bourbon (double extraction)[b]		
2nd solvent 65% ethyl alcohol	75	70
2nd solvent 30% ethyl alcohol	50	60
2nd solvent 20% ethyl alcohol	25	50
2nd solvent 20% ethyl alcohol and 20% glycerol	50	40
2nd solvent 20% ethyl alcohol and 10% glycerol	50	50
2nd solvent 10% ethyl alcohol and 10% glycerol	50	33

[a] Beans extracted with the solvents as listed, solvents evaporated off and extractive matter dissolved in 65 per cent ethyl alcohol.
[b] First solvent was carbon tetrachloride which eliminated oily matter.

[1] Received April 1, 1925. Presented before the Divison of Agricultural and Food Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] THIS JOURNAL, **15**, 782 (1923).

[3] *Ibid.*, **16**, 301 (1924).

Results of Organoleptic Tests on All Vanilla Extracts Described in Parts I, II, and III

Two sets of experiments were conducted to test the quality of the extracts. At first, 1 cc. of extract was added to 50-cc. portions of milk sweetened with sugar, but these tests were not so delicate as those carried out by adding 3 cc. of extract to 50-cc. portions of distilled water. This latter procedure was therefore adopted, the results of the organoleptic tests being given in Table II. The extract made from Mexican vanilla beans with a menstruum of 65 per cent alcohol was employed as a standard of comparison and was given a rating of 100. The numerical ratings in Table II indicate the relative flavoring quality of other extracts as compared with the standard. Three people tasted the extracts, the averages only being reported.

Discussion of Data in Table II

These data show that, from the standpoint of aroma and flavor, the most desirable solvent of those tested is neutral 65 per cent alcohol. It is of interest to note that the Research Committee of the Flavoring Extract Manufacturers' Association found 47 to 50 per cent of alcohol (corrected by the addition of alcohol for moisture in the bean) to be the best menstruum for extracting vanilla beans.[4] The addition of alkali increased the strength, as judged by the flavoring, of the Mexican and Bourbon beans, but made the aroma less pleasant. Also, it affected both the aroma and flavor of the Tahiti beans unfavorably. The extracts made from the oleoresins prepared with carbon tetrachloride possessed an objectionable foreign flavor, which it is believed would render them unmarketable. From the standpoint of flavor the suitability of the other solvents is as follows, the most suitable being given first: 95 per cent ethyl alcohol, 91 per cent isopropyl alcohol, U. S. P. acetone, and U. S. P. ether. For the manufacture of vanilla oleoresins 95 per cent ethyl alcohol would probably be preferable to neutral 65 per cent ethyl alcohol because it could be more easily removed. Neutral 65 per cent ethyl alcohol is, of course, more desirable than 95 per cent ethyl alcohol when the product to be manufactured is an extract.

None of the extracts made from the beans after they had been subjected to a preliminary extraction with carbon tetrachloride equaled the standard in aroma and flavor. Therefore, the preliminary removal of the oily matter from the beans is not recommended. The extracts made with a low-alcohol content were decidedly inferior to the standard.

[4] *Tea Coffee Trade J.*, **47**, 121 (1924).

Crystallizing Point of Paraffin Wax[1]

By A. P. Bjerregaard

EMPIRE REFINERIES, INC., OKMULGEE, OKLA.

COMMERCIAL paraffin wax is a mixture of a large number of homologous hydrocarbons whose melting and boiling points are not widely different. When melted oil-free wax is cooled, a temperature is reached at which crystals separate and over a short range below which the process of crystallization continues until the wax is solid. Obviously, the composition of the wax will determine the temperature at which crystallization starts and the extent of the solidification range.

Two methods have been used for determining the so-called melting point of paraffin wax. The older or American method consists in reading the temperature of the melted wax when the first crystals separate. The wax under the test is heated to about 5° C. above the expected melting point. A hemispherical metal cup 9.5 cm. ($3^3/_4$ inches) in diameter is filled three-fourths full with melted wax. A special wax-test thermometer with a globular bulb and graduated in half degrees Centigrade or quarter degrees Fahrenheit is used to take the temperature. The thermometer bulb is two-thirds immersed in the melted wax. The surface of the liquid is closely watched and when the crystals of solid paraffin first appear on the surface and extend to the bulb of the thermometer, the thermometer is read and this temperature recorded as the melting point of the wax. It is a common practice to read the thermometer when three crystals of wax have formed.

The English method, now adopted as a standard by the American Society for Testing Materials, is based on determining the cooling curve, and, by observation of the slope of this curve, finding the mean temperature of the wax during the solidification of the main bulk of the wax. This method has been fully described under the designation D87-22.[2]

[1] Received February 20, 1925. Presented before the Division of Petroleum Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] A. S. T. M. Standards, **1924**, p. 882.

These two methods not only give different figures, but the relationship between the melting points varies according to the composition of the wax under investigation. A sample of wax, the melting points of whose components lie close together, will naturally show a smaller difference between the crystallizing temperature of the first portions and the crystallizing temperature of the main mass. On the other hand, a wax composed of substances covering a wide range of melting points will show a larger difference between the crystallizing point of the first portion and the crystallizing point of the main mass.

The accompanying tables present the American and English melting points of paraffin waxes made from two varieties of crude oil. All these waxes came from two independent refineries, one using Kansas crude and the other Oklahoma crude.

Table I—Paraffin Waxes from a High-Sulfur Crude Petroleum Oil from Butler County, Kansas

(21 determinations)

	American		A. S. T. M.		Difference	
	° C.	° F.	° C.	° F.	° C.	° F.
Max.	56.4	133.5	54.9	130.9	1.5	2.6
Min.	53.6	128.5	52.8	127.0	0.4	0.7
Av.	54.9	130.8	53.9	129.1	0.9	1.6

Table II—Paraffin Waxes from Low-Sulfur Crude Petroleum Oil from Okfuskee County, Oklahoma

(24 determinations)

	American		A. S. T. M.		Difference	
	° C.	° F.	° C.	° F.	° C.	° F.
Max.	54.7	130.4	53.9	129.1	2.2	3.9
Min.	37.8	100.0	36.4	97.5	0.1	0.2
Av.	50.6	123.0	49.9	121.7	0.8	1.4

There is no consistent difference between the melting points as determined by the two methods. The variations are due to the differences in the composition of the waxes with regard to the relative amounts of higher melting homologs and intermediate melting homologs, and with regard to the spread between the melting points of the higher melting point waxes and of the medium melting point waxes actually present.

The Oxidation of Chinese Wood Oil[1]

By F. H. Rhodes and T. T. Ling

CORNELL UNIVERSITY, ITHACA, N. Y.

The drying of Chinese wood oil, like the drying of linseed oil, is due to an oxidation reaction which is autocatalytic in character. Raw tung oil absorbs about 44 per cent of oxygen in 500 hours. Bodied tung oil takes up oxygen much more slowly and in much smaller amounts. Compounds of lead, cobalt, or manganese act as catalysts for the oxidation reaction but differ markedly in their exact effects upon the progress of the oxidation. Blending Chinese wood oil with resins has a very great effect upon the progress of the oxidation reaction.

THE value of Chinese wood oil in the manufacture of paints and varnishes depends upon the fact that this oil absorbs oxygen from the air to form a solid oxidation product. This property was observed by Cloez[2] when he first examined tung oil. The amount of oxygen taken up by Chinese wood oil in drying has been determined by a number of investigators. Weger[3] found that when films of tung oil are exposed to the air they show an increase in weight of about 21 per cent in 14 days. He pointed out that the oil becomes dry to the touch before the maximum increase in weight is attained. Boughton[4] found that Chinese wood oil absorbs oxygen more slowly than linseed oil. Meister[5] says that tung oil absorbs from 12 to 15.8 per cent of oxygen. He further states that tung oil that has been thickened or bodied by heat takes up only slightly less oxygen than the raw oil. Fahrion[6] found that the increase in weight of tung oil on oxidation was about 11.5 per cent of the original weight of the oil.

In all this previous work the rate of oxidation of the oil and the amount of oxygen absorbed by the oil during drying have been determined by measuring the increase in weight of samples of tung oil exposed to the air. In no case, apparently, have the investigators contemplated the possibility that the formation of volatile products during the drying may render the mere increase in weight a very inaccurate measure of the actual amount of oxygen absorbed by the oil. It is known that such volatile products are formed when linseed oil is oxidized by exposure to air, and it is reasonable to suppose that the oxidation of Chinese wood oil might similarly be accompanied by a formation of volatile substances. If such substances are formed, the net change in weight would not be an accurate, or even an approximate, criterion of the actual weight of oxygen involved in the drying reactions.

Furthermore, these previous investigators have not studied carefully the effect of the heat treatment of the oil upon the rate of oxidation. In very few cases is raw Chinese wood oil used in paints or varnishes—in practically every case the oil is cooked or bodied by heating to a rather high temperature, either before or during the manufacture of the paint or varnish. In studying the drying of Chinese wood oil, therefore, it is desirable to determine the rate of oxidation of both the raw or unheated oil and the bodied or heated oil. Moreover, when the oil is bodied in making varnish it is not usually heated alone but is first mixed with some other oil or with a resin in order to prevent gelatinization, and the presence of this other oil or resin may have a very marked effect upon the rate of oxidation of the bodied oil. Finally, in actual paints or varnishes the oxidation of tung oil is not allowed to proceed spontaneously, but is accelerated by incorporating in the oil a small amount of catalyst or drier. The driers that are commonly used are soaps of lead, cobalt, or manganese. A comprehensive study of the drying of Chinese wood oil should include an investigation of the effects of these driers upon the rate of oxidation of the oil.

[1] Received October 30, 1924.

[2] *Compt. rend.*, **81**, 469 (1875).

[3] *Jahresber. chem. Tech.*, **44**, 1163 (1898).

[4] *7th Intern. Cong. Appl. Chem.*, **1**, 89 (1909).

[5] *Chem. Rev. Fett-Harz-Ind.*, **17**, 150 (1910).

[6] *Farben-Ztg.*, **17**, 2689 (1912).

Experimental

The oil used in this work was pure raw Chinese wood oil pressed in this country from imported Chinese grown nuts. It showed the following analysis:

Specific gravity at 15.5° C.	0.9401
Iodine number (Hübl)	168.6
Saponification value	193.4
Acid number	2.27
Refractive index	1.5162
Browne heat test	9 minutes 53 seconds

The driers used were paste linoleate driers, containing the following amounts of the active elements:

Lead drier	17.88 per cent lead
Cobalt drier	5.20 per cent cobalt
Manganese drier	4.76 per cent manganese

In bodying the oil and in incorporating the driers into the oil the following procedure was used: Two hundred grams of raw oil were placed in a copper beaker which was surrounded by a heavy, thick-walled iron cylinder in order to secure uniform heating. The beaker was closed with a top of asbestos board, through which was inserted the thermometer for indicating the temperature of the oil. The oil, or mixture of oil and drier, was heated to 220° C., maintained at that temperature for 45 minutes, cooled to 190° C., and kept at that temperature until the oil became very viscous and began to "string" when allowed to drip from a stirring rod. The bodied oil was then cooled and placed in a bottle which was sealed to exclude air. In a few cases the oil did not become very viscous even on long heating. In these cases the heating was discontinued after the temperature had been maintained for 3 hours at 190° C.

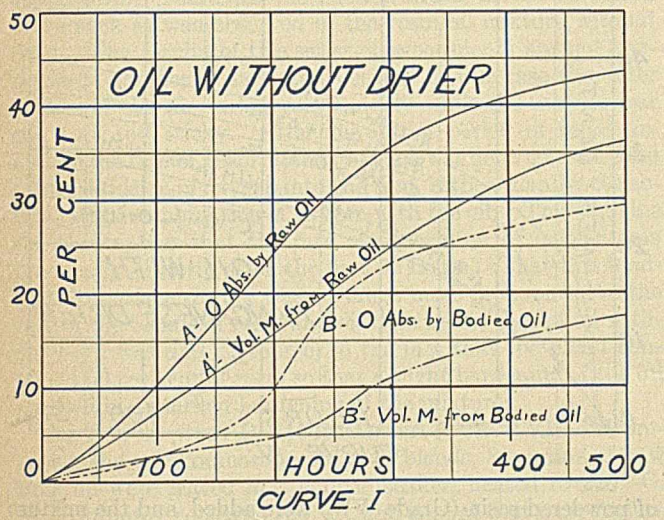
The apparatus and the procedure used for determining the actual rate of absorption of oxygen and the actual rate of evolution of volatile matter were substantially identical with the apparatus and procedure described by Rhodes and Van Wirt.[7] Weighed samples of the raw or the treated oils were spread on strips of cloth and exposed in an atmosphere of pure oxygen at constant temperature (30° C.) and practically constant pressure, and the actual rate of absorption of oxygen and the rate of evolution of volatile matter were measured. In each case at least two determinations were made with each sample. The duplicate determinations gave results which agree closely with each other.

Results

The results are shown graphically by the accompanying curves, in which the amounts of oxygen absorbed and the amounts of volatile matter evolved (each expressed in terms of percentage by weight of the tung oil in the sample taken) are plotted against the lengths of time of exposure.

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

RAW OIL (CURVE I)—Raw Chinese wood oil absorbed oxygen rather rapidly during the first 300 hours' exposure. At the end of this time the rate of oxidation began to decrease, and after about 500 hours the reaction practically stopped. The total amount of oxygen absorbed in 500 hours was about 44 per cent. It will be noted that previous investigators have reported that Chinese wood oil, in drying, absorbs from 8 to 21 per cent of oxygen. These previous results, based on the increase in weight of the oil during drying, are incorrect because no allowance was made for the evolution of volatile matter during the drying.



CURVE I

The maximum gain in weight of the samples—i. e., the maximum difference between the weight of oxygen absorbed and the weight of the volatile matter given off—was at the end of about 250 hours' exposure. This maximum difference was about 10.5 per cent of the weight of the original sample, which agrees very well with results given by other investigators as to the net change in weight on drying. After 250 hours the rate of absorption of oxygen becomes somewhat less than the rate of evolution of volatile matter, so that there is a slight decrease in net weight. This phenomenon has been reported by other observers.

The form of the oxidation curve indicates that the drying of raw Chinese wood oil, like the drying of linseed oil, is an autocatalytic reaction. The initial period of induction, however, is not so pronounced as in the case of linseed oil.

BODIED TUNG OIL (CURVE I)—Tung oil that was bodied by heating alone, without drier or resin, behaved very differently from the raw oil. The bodied oil absorbed much less oxygen than the raw oil. This difference is due, presumably, to the fact that during the heating of the oil a certain amount of polymerization takes place and the degree of unsaturation is markedly reduced. The initial period of induction for the oxidation reaction was also much more pronounced in the case of the bodied oil; in fact, during the first 100 hours the weight of oxygen absorbed was even less than the weight of volatile matter given off, so that there was a decrease in the actual weight of the sample. The bodied oil not only absorbed less oxygen but also gave off less volatile matter. The decrease in the amount of volatile matter evolved was almost equal to the decrease in the weight of oxygen absorbed, so that the net change in weight was about the same for the bodied oil as for raw oil. This fact was observed by Meister[5] and led him to the very incorrect conclusion that raw oil and bodied oil absorb substantially the same weights of oxygen.

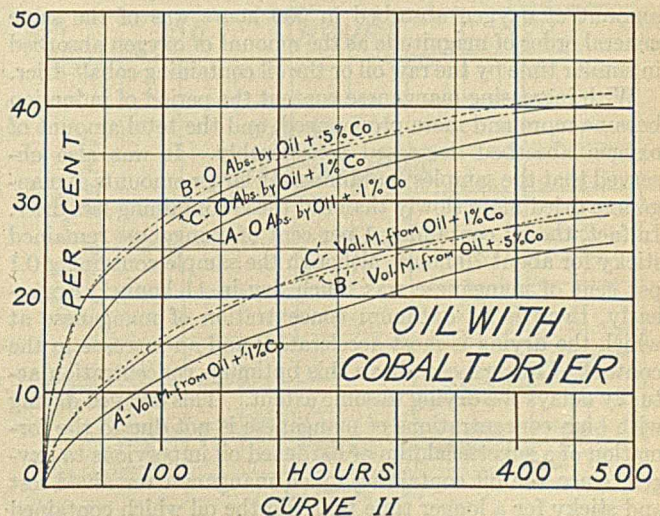
BODIED OIL WITH COBALT DRIER (CURVE II)—In these experiments cobalt paste drier was added to the raw oil and the oil was then bodied as described above. The amounts of drier used were sufficient to contain weights of cobalt (calculated as metal) equivalent to 0.1, 0.5, and 1.0 per cent, respectively, of the weight of the oil.

The addition of the cobalt drier very greatly accelerated the oxidation of the oil; so much so, in fact, that there was no evidence of any period of induction in the drying of any sample that contained cobalt. Moreover, the cobalt drier increased the amount of oxygen absorbed by the bodied oil, as well as the rate of absorption of oxygen. For example, the oil containing 0.1 per cent of cobalt took up approximately 39 per cent of oxygen in 500 hours, while the oil bodied without drier absorbed only 29.5 per cent of oxygen in the same length of time. With the oils containing cobalt the rate of evolution of volatile matter was greater than in the case of the oil bodied without drier but was less than with the raw oil.

The concentration of the cobalt drier in the oil appears to have very little effect on the progress of the oxidation reaction, although the oil containing 0.5 per cent cobalt oxidized a little more rapidly than either of the other samples. That the concentration of drier had so little effect may be explained by the hypothesis that, even with very low concentrations of drier, the actual combination of oxygen and oil took place so rapidly that the apparent rate of absorption of oxygen was determined principally by the rate of diffusion of oxygen into the film. That an increase of cobalt content from 0.5 to 1.0 per cent caused a slight decrease in the rate of absorption may be due to the fact that with the high concentration of drier the oil oxidized so rapidly at the surface that it formed quickly a surface film which was rather impervious to oxygen and retarded the diffusion of oxygen into the oil below.

BODIED OIL WITH LEAD DRIER (CURVE III)—These samples were prepared by a method similar to that used in making up the oils with cobalt drier. Two such samples were prepared, containing 0.5 and 1.0 per cent lead, respectively.

With these lead driers a very peculiar phenomenon was observed. For several hours after the samples were first exposed to the air there was no absorption whatever; then rapid oxidation began. In the case of the oil with 0.5 per cent lead there was no apparent reaction until the sixth hour, whereas



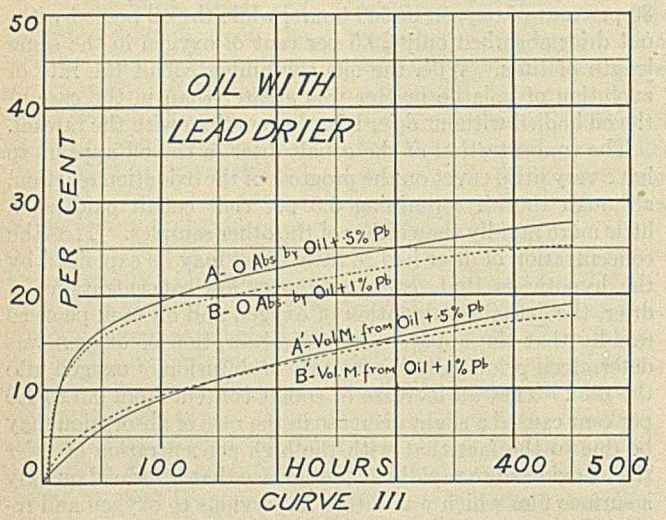
CURVE II

the oil containing 1.0 per cent lead began to oxidize after about 3.5 hours' exposure.

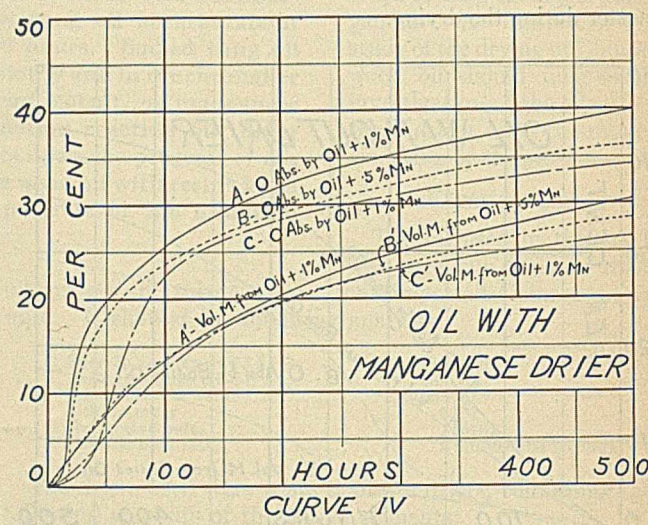
Although the lead drier very greatly accelerated the initial oxidation of the bodied oil (after this short period during which no reaction was apparent), it did not increase the total amount of oxygen ultimately absorbed; in 500 hours the oil bodied with lead drier took up slightly less oxygen than the oil that was bodied without any drier. In this respect lead differed very markedly from cobalt. The effect of the lead

on the rate of evolution of volatile matter was quite similar to its effect upon the absorption of oxygen; the intial evolution of volatile matter was greatly accelerated, but the total amount of volatile products formed was about the same as in the case of the oil bodied without drier.

It is interesting to note that, when a sample of the bodied oil containing 1.0 per cent of lead was spread in a thin film on a glass plate and exposed to the air, it set to a solid film in about 3.5 hours—i. e., before there was any appreciable



CURVE III



CURVE IV

absorption of oxygen. It would seem that the changes responsible for the initial drying of Chinese wood oil may be brought about, under some conditions at least, by a very slight oxidation of the oil.

OIL BODIED WITH MANGANESE DRIER (CURVE IV)—Tung oil bodied with manganese drier gave an oxidation curve that showed a very pronounced period of induction, somewhat similar to that obtained with linseed oil containing a drier. Following this initial period of induction, oxidation took place at first rapidly and then more and more slowly. The total amount of oxygen absorbed in 500 hours was of the same general order of magnitude as the amount of oxygen absorbed in similar time by the raw oil or the oil containing cobalt drier.

With increasing manganese content the period of induction became more and more pronounced, and the total amount of oxygen absorbed decreased considerably. It was also observed that the samples containing the larger amounts of manganese dried more slowly than did those containing less drier. In fact, the oil containing 1 per cent of manganese remained sticky for about 70 hours, although the sample containing 0.1 per cent of manganese was touch dry in 11 hours. Apparently, there is an optimum concentration of manganese at which the drying is most accelerated; and an increase in the content of manganese above this optimum concentration actually delays the drying to some extent. This delayed drying with high concentrations of manganese is not due to the formation of a superficial film of hardened oil impervious to oxygen, since the oil containing much manganese remained soft and sticky for a longer time than did the oil which contained but little manganese.

OIL BODIED WITH ROSIN (CURVE V)—The following experiments were made to obtain some information as to the manner and rate of oxidation of blends of bodied Chinese wood oil and resin such as are used in varnishes. The resins used in the experimental work were rosin and paracoumarone resin, although these are not so extensively employed in commercial varnishes as are Kauri, the copals, or ester gums. The reason for working with rosin and paracoumarone instead of with fossil or semifossil resins was the fact that rosin and paracoumarone can be dissolved directly in tung oil, whereas the fossil resins must first be partly decomposed by heat. The preliminary "running" of the resin which would have been necessary with fossil resins would have complicated the experimental procedure considerably and would have introduced additional variables which might affect the final result.

In preparing the rosin–tung oil mixture, 2 parts by weight of raw tung oil were heated in a copper beaker. Three parts of powdered rosin (Grade WW) were added, and the mixture was heated to 220° C. and kept at that temperature for 45 minutes. The material was then cooled to 190° C., kept at that temperature for 3 hours, and finally cooled. A second lot of material was prepared in the same way except that enough cobalt paste drier to give a weight of cobalt equivalent to 0.5 per cent of the weight of the *oil* was added to the charge before heating.

The oils that were bodied with rosin contained traces of copper—taken up, apparently, from the copper beaker in which the mixtures were heated. The amount of copper was, however, very small (0.014 per cent by weight of the mixture). None of the other samples of oil which were heated alone or with drier or paracoumarone resin gave a qualitative test for copper.

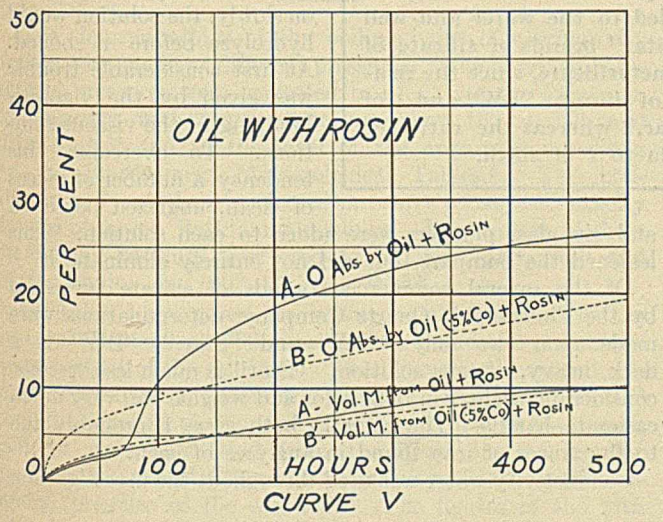
As will be seen from Curve V, the rosin–tung oil mixture, without drier, absorbed oxygen rather rapidly at first. After about 45 hours, however, the reaction apparently ceased; and for the next 20 hours no appreciable absorption of oxygen occurred. Then, after about 65 hours from the start of the run, the reaction began and oxygen was again absorbed, rapidly at first and then more and more slowly. The total amount of oxygen taken up in 500 hours was about 27.5 per cent by weight of the oil in the sample. Substantially identical results were obtained in three separate experiments, so that it is certain that the peculiar and unexpected results are not due to experimental error. In all three of these experiments the sharp break in the oxidation curve came at almost exactly the same point. The drying point of the mixture coincided approximately with this sharp break in the oxidation curve.

There is no very obvious explanation of this peculiar form of the oxidation curve for rosin–tung oil mixtures. It may be that during the cooking of the rosin–tung oil mixture the rosin combines chemically with some of the oil to form a loosely bound compound, and that when the oxidation has proceeded to a certain critical extent in the film this compound again decomposes and liberates the oil in a readily oxidizable form. The break in the oxidation curve may also be due to a change in the physical condition of the film which renders it more per-

meable and thus accelerates the oxidation. There is no visible evidence of such physical change however. Which, if either, of these hypotheses is the real explanation of the observed facts can be determined only by further investigation.

The results obtained in the oxidation of rosin–tung oil mixtures containing cobalt drier were very different from those obtained with the same mixtures without drier. Oxygen was absorbed rapidly at first, then more and more slowly, until at the end of about the fiftieth hour the rate of oxidation became constant. The total amount of oxygen absorbed in 500 hours was approximately 20 per cent of the weight of the original oil. There was no sudden break in the oxidation curve such as was observed in the rosin-oil mixture without drier. The results of this series of experiments are not particularly significant, however, because in this case the outer surface of the film dried very quickly while the interior was still soft and sticky. After the initial period of rapid oxidation the rate of absorption of oxygen was determined by the rate of diffusion of oxygen into the film, rather than by the actual rate of combination of oxygen with the oil. This explains the observation that the rate of absorption of oxygen was practically uniform after the first 50 hours. That this tendency to surface drying was so much more pronounced in the case of the blends of rosin and oil than in the case of oil without rosin was due, of course, to the fact that the blend contained 60 per cent of rosin so that a slight hardening of the oil resulted in a marked hardening of the mixture.

Oil Bodied with Paracoumarone (Curve VI)—In preparing the paracoumarone–tung oil blends, 80 grams of raw tung oil were placed in a copper beaker, heated to 220° C. for 45 minutes, cooled to 190° C., and kept at that temperature until it began to "string" when allowed to drip from a stirring rod. Then 120 grams of paracoumarone resin (varnish grade, melting point 128° C.) were added and the heating was continued for one-half hour until the resin was completely dissolved. In making up the sample containing 0.5 per cent of cobalt the required amount of cobalt linoleate paste was added to the raw oil, then the oil was bodied and the resin was dissolved as described above.



CURVE V

The curve for the oxidation of the mixture of paracoumarone and oil is similar in general form to the curve for the oxidation of the mixture of rosin and oil, although the actual rate of oxidation is much slower with the paracoumarone than with the rosin. The first stage of the oxidation persists for a much longer time, and the second of the oxidation reactions appears only after about 220 hours of exposure. The actual amount of oxygen absorbed at this point, however, is almost exactly the same as the amount of oxygen absorbed by the rosin-oil blend at the time of the break in that oxidation curve—i. e., approximately 2.5 per cent. This coincidence appears to support the hypothesis that in the drying of the blends of resin and tung oil a rather sudden physical or chemical change takes place in the film when the oxidation has proceeded to a certain critical point.

In the experiments made with the blends of paracoumarone resin and tung oil containing cobalt drier the rate of oxidation was rather rapid at first. After about 75 hours' exposure, however, the rate had fallen to a rather low value, which remained constant throughout the rest of the run. In this case, as in that of the blends of rosin and tung oil, the films dried superficially so that the apparent rate of oxidation was determined primarily by the rate of diffusion of the oxygen into the mass of material.

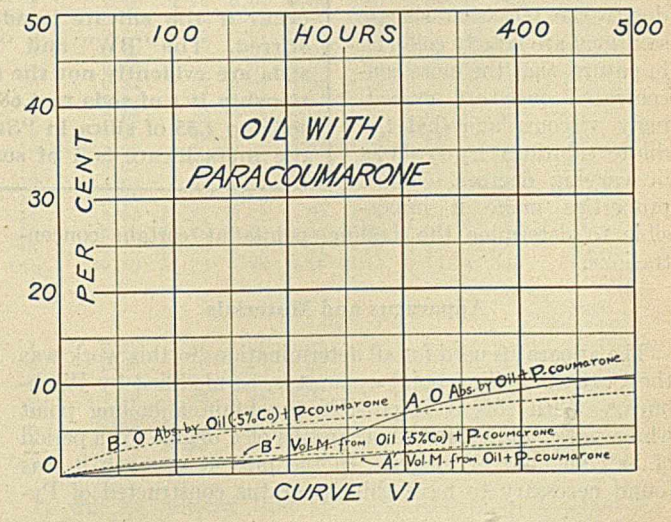
Conclusions

1—The drying of Chinese wood oil is due to the spontaneous oxidation of the oil, with the formation of a solid oxidation product.

2—When a raw tung oil is allowed to dry it absorbs approximately 44 per cent of oxygen in 500 hours and gives off in the same time about 36 per cent of volatile matter. The results of previous investigators, who have stated that the amount of oxygen absorbed by Chinese wood oil in drying is from 8 to 21 per cent, have been in error because these investigators based their conclusions upon the net change in weight of the oil during drying and failed to allow for the evolution of volatile matter.

3—The form of the oxidation curve for raw tung oil indicates that the drying of tung oil, like the drying of linseed oil, is an autocatalytic reaction.

4—When bodied tung oil dries it absorbs about 29.5 per cent of oxygen in 500 hours and gives off, in the same time, about 18 per cent of volatile matter. The net change in weight on drying is therefore about the same as for raw oil. This fact has led previous investigators to the incorrect conclusion that raw oil and bodied oil absorb the same weights of oxygen during drying.



CURVE VI

5—The oxidation of Chinese wood oil, like the oxidation of linseed oil, is accelerated by soaps of lead, manganese, or cobalt. Of these, the cobalt drier appears to be the most effective, since it both accelerates the initial oxidation of the oil and increases the total amount of oxygen absorbed by the bodied oil. Lead drier, after a short period of induction, accelerates the initial oxidation but does not increase the total amount of oxygen ultimately absorbed. Manganese driers show a very pronounced period of induction followed by a

period of rapid oxidation, and cause the bodied oil ultimately to absorb almost as much oxygen as raw tung oil. With comparatively large amounts of manganese drier the oil tends to remain sticky for a long time.

6—When Chinese wood oil is bodied with rosin and exposed to oxygen, the oxidation proceeds in two distinct steps. The first stage of the oxidation starts immediately, and continues until about 2.5 per cent of oxygen has been absorbed. The second and more rapid of the oxidation reactions begins at this point and continues regularly and smoothly until the oxidation is completed.

7—When tung oil is bodied with paracoumarone resin and exposed to oxygen the oxidation proceeds in the same general manner, but more slowly than when rosin is used. The second stage of the reaction appears, however, at the same point in the oxidation—i. e., when about 2.5 per cent of oxygen has been taken up by the oil.

8—The addition of cobalt driers accelerates the initial oxidation, both in the case of mixtures of rosin and tung oil and in the case of mixtures of paracoumarone and tung oil. In the presence of cobalt drier, however, the oxidation takes place regularly and there is no evidence of consecutive stages in the reaction. Mixtures containing cobalt equivalent to 0.5 per cent by weight of the oil cause superficial hardening in both rosin–tung oil mixtures and paracoumarone–tung oil mixtures.

Further work on the oxidation of tung oil in the presence of various resins and on the effects of heat treatment and of driers upon the rate of oxidation is in progress in this laboratory.

Relationship between Composition and Boiling Point of Aqueous Solutions of Sodium Silicate[1,2]

By Jessie Y. Cann and Dorothy L. Cheek[3]

SMITH COLLEGE, NORTHAMPTON, MASS.

The research described in this article shows that for both "BW" and "Star" there is a direct relationship between the soda and silica content and the elevation of the boiling point. At the lower concentrations in solutions of "BW" possibly hydration or some complex formation due to the three-component system takes place. Since the ratios between soda and silica in the two samples, "BW" and "Star," are not the same, two different curves were expected and found. This seems to indicate that the ratio of soda to silica affects the elevation of the boiling point. In handling silicate solutions for dilution, precipitation is less likely to occur if the silicate is added to the water and well stirred. The "BW" and "Star" brands of silicate of soda are evidently not the metasilicate, since the relationship is 1 of soda to 1.68 of silica in "BW" and 1 of soda to 2.55 of silica in "Star," whereas the ratio for the metasilicate is 1 of soda to 1 of silica.

THE object of this investigation was to study the composition and boiling points of the system Na_2O–SiO_2–H_2O—i. e., so-called aqueous solutions of sodium silicate. A search of the literature up to the present time has revealed no published material relating to the boiling points of these solutions. This is probably due to the fact that silicate solutions are largely colloidal in nature, that the more concentrated ones are exceedingly viscous, and that the dilute solutions hydrolyze in varying degrees. These properties make it impossible to determine the boiling points at certain concentrations.

Apparatus and Materials

The apparatus used for all determinations in this work was the Cottrell[4] boiling point apparatus, as modified by Washburn.[5] With this it is possible to obtain a boiling point which varies only a few thousandths of a degree for a period of half an hour or longer. In the present research it was found necessary to have this apparatus constructed of Pyrex glass, since ordinary glass will not stand the heat necessary for the determination of the boiling points of viscous solutions.

After some experimentation it was found that a burner with a sharp-pointed cone and considerable heat was necessary to overcome the viscosity of the solutions. If the heating were carried on slowly, the solution would hydrolyze before it boiled. At first considerable trouble was given by the vigorous bumping of the viscous solutions. To overcome this tendency a number of pieces of clean, unglazed porcelain and six glass plungers were added to each solution. This lessened the bumping, but did not entirely eliminate it.

Of the several commercial brands of silicate furnished by the Philadelphia Quartz Company, determinations were made upon two only—"BW" and "Star." "BW" is a dark, heavy, viscous solution. "Star" is much less viscous, considerably lighter in both color and weight, and very much easier to handle. The color in both cases is probably due to the traces of iron found in analyses of each.

Conductivity water was used throughout the investigation.

Experimental Work

The solutions used for the determinations of the boiling points were made up in two ways—(1) water was added to silicate, and (2) silicate was added to water—with brisk stirring in each case. The latter method was found to be much more satisfactory, because some solutions hydrolyzed when water was added to silicate, but did not hydrolyze when silicate was added to water. In order to handle the viscous solutions more easily a pipet of large bore was

[1] Received October 24, 1924.

[2] The subject of this investigation was suggested by the Division of Chemistry and Chemical Technology (E. W. Washburn) of the National Research Council; and the silicate samples were furnished by the Philadelphia Quartz Company. Since the present paper contains results of the work done on only two of these commercial brands, it may be considered as a preliminary report.

[3] The experimental work of this paper was submitted by Dorothy L. Cheek in partial fulfilment of the requirement for the degree of master of arts at Smith College.

[4] *J. Am. Chem. Soc.*, **41**, 721 (1919).

[5] Washburn and Read, *Ibid.*, **41**, 729 (1919).

constructed and approximately graduated. By means of this it was possible to transfer the silicates from the center of the stock sample without encountering difficulties. From the reputed soda content, solutions of varying approximate percentage composition were made up. It was found that for this apparatus 130 cc. was the most suitable volume.

Kohlrausch[6] in conductivity measurements and Thomson[7] in freezing point measurements found that freshly made solutions gave abnormal results; therefore, no boiling points were determined until after the solutions had stood at least 24 hours.

After the solution was placed in the apparatus, heat was rapidly applied to bring the liquid to the boiling point as quickly as possible. When the thermometer, through the lens, showed that the reading was constant within a few thousandths of a degree, the barometric pressure, the temperature at the barometer, the temperature of the room, and the date were recorded. The barometer used was on the first floor of the building, the research was conducted on the second floor. The distance between the height of the mercury in the barometer and the liquid in the apparatus was 3.7846 meters. All barometric readings were corrected to the level of the apparatus.[8] The instrument used was an observatory barometer of the U. S. Weather Bureau pattern.

It had been thought that trouble might occur with frothing; but no such difficulty arose. It was impossible to redetermine the boiling points of any of the solutions used, because in practically every case precipitation took place immediately after boiling.

The accurate soda content of all solutions was determined by titration with standard acid, using methyl orange as an indicator. The complete analysis of the original sample was carried out according to the accepted methods of Hillebrand.[9] Complete analyses were carried through for the "BW," and also for the "Star" except for the calcium and the magnesium.

Results

Ten determinations of the boiling point of conductivity water were made at different pressures. The observed barometric pressures were corrected to 0° C. for the expansion of mercury with temperature according to Landolt and Börnstein,[10] and to the level of the apparatus according to the Smithsonian Meteorological Tables.[8] The boiling points[11] at these corrected pressures correspond exactly to the observed Beckmann readings. The *average* of these Beckmann readings, corrected to 760 mm. pressure,[11] and corresponding to 100° C., was 0.953.

In Table I are given the boiling point elevations of the silicate solutions at 760 mm. pressure, and the percentage soda content of the solutions. The figures in the second column represent the barometric pressure corrected to 0° C.[10] and the level of the apparatus.[8] The figures in the fourth column were calculated from the Beckmann reading for pure water at 100° C. and 760 mm.—i. e., 0.953 for the corrected pressure of the solution.[11] The figures in the fifth column are the differences between those in the third and fourth columns. The figures in the sixth column were calculated according to Washburn and Read.[12]

[6] *Z. physik. Chem.*, **12**, 773 (1893).

[7] Thesis submitted to Worcester Polytechnic Institute for the degree of master of science, June, 1923.

[8] Smithsonian Meteorological Tables, Table 65, 156 (1918).

[9] *U. S. Geol. Survey, Bull.* **422** (1910).

[10] Tabellen, **1912**, p. 40.

[11] *Ibid.*, p. 365.

[12] *J. Am. Chem. Soc.*, **41**, 738 (1919).

Table I—Boiling Point Elevation of Silicate Solutions

No.	Barometric pressure corrected to 0° C. level of apparatus *B* Mm.	Observed Beckmann reading	Corresponding Beckmann reading for water boiling under pressure *B*	Boiling point elevation of solution at pressure *B*	Boiling point elevation of solution at pressure 760 mm.	Soda content Per cent
			"BW"			
5	766.055	1.261	1.175	0.086	0.086	0.556
4	766.055	1.299	1.175	0.124	0.124	0.685
3	758.766	0.932	0.907	0.025	0.025	0.708
6	763.410	1.238	1.078	0.160	0.160	0.823
2	758.766	0.980	0.907	0.073	0.073	0.897
8	763.410	1.215	1.078	0.137	0.137	0.933
7	763.410	1.219	1.078	0.141	0.141	1.046
1	761.310	1.190	1.001	0.189	0.189	1.100
9	754.794	1.019	0.761	0.258	0.258	1.204
10	755.430	1.129	0.785	0.344	0.345	1.900
11	755.430	1.279	0.785	0.494	0.495	3.010
12	766.829	1.882	1.203	0.679	0.678	4.039
13	766.829	2.040	1.203	0.837	0.835	5.490
14	766.829	2.196	1.203	0.993	0.991	6.650
15	753.157	1.965	0.699	1.266	1.269	8.390
16	753.157	2.171	0.699	1.472	1.475	9.752
			"Star"			
1	752.244	0.763	0.666	0.097	0.097	0.476
2	752.244	0.843	0.666	0.177	0.177	0.849
3	750.308	0.792	0.594	0.198	0.199	1.074
4	750.308	0.829	0.594	0.235	0.236	1.463
6	747.528	1.385	0.491	0.894	0.897	7.359
5	750.308	1.445	0.594	0.851	0.854	8.054
7	747.528	1.448	0.491	0.957	0.961	8.293

Table II gives the complete analyses of the original silicate solutions, and Table III gives the complete analyses and calculated formulas of all the solutions of "BW" and "Star" that were used.

Table II—Analysis of Original Samples

(Per cent)

Soln.	Na_2O	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	H_2O	Fe
				"BW"				
1	19.38	31.74	0.22	0.68	0.13	0.12	...	0.16
2	19.41	31.66	0.14	...	0.11	0.15	...	0.10
Av.	19.40	31.70	0.18	0.68	0.12	0.14	49.79	0.13
				"Star"				
1	10.81	27.06	0.36	0.15	...	...	...	0.17
2	10.80	26.47	0.25	0.41	...	...	...	0.29
Av.	10.81	26.77	0.30	0.28	...	...	61.84	0.23

Table III—Complete Analyses and Formulas of All Solutions Used

No.	Per cent Na_2O	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	H_2O	Ratio of H_2O to Na_2O 1; SiO_2 1.68
				"BW"				
1	1.10	1.79	0.01	0.04	0.01	0.01	97.04	303.79
2	0.90	1.46	0.01	0.03	0.01	0.01	97.59	374.90
3	0.71	1.16	0.01	0.03	0.01	0.01	98.10	477.13
4	0.69	1.12	0.01	0.02	0.01	0.01	98.16	493.82
5	0.56	0.91	0.01	0.02	0.01	0.01	98.51	610.43
6	0.82	1.34	0.01	0.03	0.01	0.01	97.79	409.26
7	1.05	1.71	0.01	0.04	0.01	0.01	97.19	319.94
8	0.93	1.52	0.01	0.03	0.01	0.01	97.50	360.03
9	1.20	1.96	0.01	0.04	0.01	0.01	96.77	276.92
10	1.90	3.10	0.02	0.07	0.01	0.01	94.90	172.09
11	3.01	4.91	0.03	0.11	0.02	0.02	91.91	105.18
12	4.04	6.59	0.04	0.14	0.03	0.03	89.14	76.03
13	5.49	8.95	0.05	0.19	0.03	0.04	85.24	53.48
14	6.65	10.84	0.06	0.23	0.04	0.05	82.13	42.54
15	8.39	13.68	0.08	0.30	0.05	0.06	77.45	31.80
16	9.75	15.90	0.09	0.34	0.06	0.07	73.79	26.06
Orig.	19.40	31.70	0.18	0.68	0.12	0.14	47.79	8.49
				"Star"				Ratio of H_2O to Na_2O 1; SiO_2 2.55
1	0.48	1.18	0.01	0.01	...	...	98.32	711.28
2	0.85	2.10	0.02	0.02	...	...	97.00	393.44
3	1.07	2.65	0.03	0.03	...	...	96.21	308.60
4	1.46	3.62	0.04	0.04	...	...	94.83	223.33
5	8.05	19.95	0.23	0.21	...	...	71.56	30.61
6	7.36	18.23	0.21	0.19	...	...	74.01	34.64
7	8.30	20.54	0.23	0.22	...	...	70.72	29.37
Orig.	10.81	26.77	0.30	0.28	...	...	61.84	19.71

It will be noticed that in calculating the formulas the percentages of the impurities—i. e., Fe_2O_3, Al_2O_3, CaO, and MgO—are ignored. If the Fe_2O_3 and Al_2O_3 were counted as SiO_2, and the CaO and MgO as Na_2O, the ratio of Na_2O to SiO_2 in "BW" would be 1 : 1.70—i. e., the formula would be $(Na_2O)\ (SiO_2)_{1.7}\ (H_2O)_x$. It will also be noticed that for "Star" the percentages of CaO and MgO were not determined. If it is assumed that each of these occur to the extent of 0.1 per cent, and then the Fe_2O_3 and Al_2O_3 are counted as SiO_2, and the CaO and MgO as Na_2O, the ratio of Na_2O to SiO_2 will be 1: 2.55—exactly the same as that listed in

the table. Since Kohlrausch[6] in his work on the conductivity of silicate solutions, and Thomson[7] in his work on the freezing point lowering of silicate solutions, both believe that the silicate exists in solution as the disilicate—i. e., Na_2O-$2SiO_2$—and since Morey[13] has obtained crystalline silicates of both the normal and acid disilicate, and since the results of the authors also seem to point in the same direction, so-called theoretical boiling points were calculated for all solutions used. These values, however, are not listed, because ionization, hydrolysis, and hydration have effects which are totally unknown at the present time.

Table IV—Hydrolysis of Solutions

Method of making	Na_2O Per cent	SiO_2 Per cent	Hydrolyzed soon after making	Hydrolyzed during boiling	Hydrolyzed after boiling
A	0.48	1.18			Slight ppt.
A	0.85	2.10			Slight ppt.
A	1.07	2.65			Slight ppt.
A	1.46	3.62			Slight ppt.
A	8.05	19.95			Slight ppt.
A	7.36	18.23	Hydrolyzed		
B	7.36	18.23			Heavy ppt.
A	8.29	20.54			Slight ppt.
B	8.29	20.54		Slight ppt.	

A—Silicate added to water.
B—Water added to silicate.

Solutions of sixteen different concentrations of "Star," varying from approximately 0.1 or 0.2 to 9 per cent of soda, were prepared by two different methods—(*A*) by adding silicate to water, and (*B*) by adding water to silicate. In each case the solutions were well stirred and allowed to stand. With only seven of these concentrations was it possible to obtain boiling points. Solutions of the other nine concentrations precipitated soon after making.

Figure 1 shows graphically the relationship between the boiling point elevations and the percentage soda content of solutions of "BW" and "Star." It will be noticed that the points on the curve for low concentrations of "BW" apparently do not lie on a straight line. This is somewhat similar to the freezing point–concentration curves of Jones,[14] in which it is shown that with increased concentration, probably due to hydration, the freezing point lowering in dilute solutions at first diminishes and then increases as the concentration increases. In the present boiling point–concentration curves, the boiling point elevation at first increases with decreasing concentration and then increases with increasing concentration. In this case the effect of decreasing concentration in raising the boiling point would seem to indicate that hydration existed in solutions of this dilution, or, if not hydration, some complex formation, since we are dealing with a three-component system. Only by further study can the significance of these boiling points be determined.

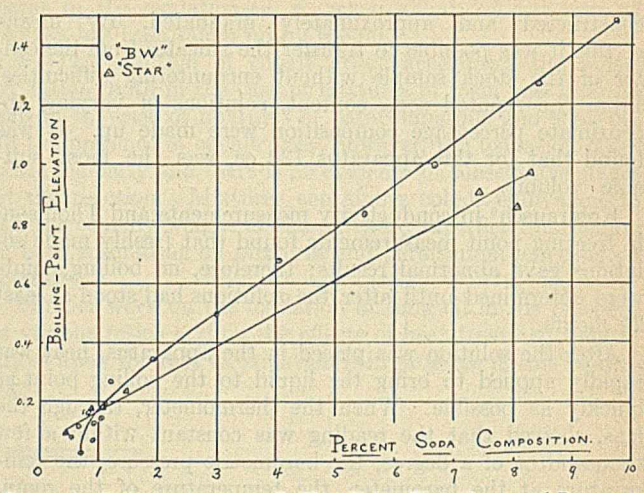
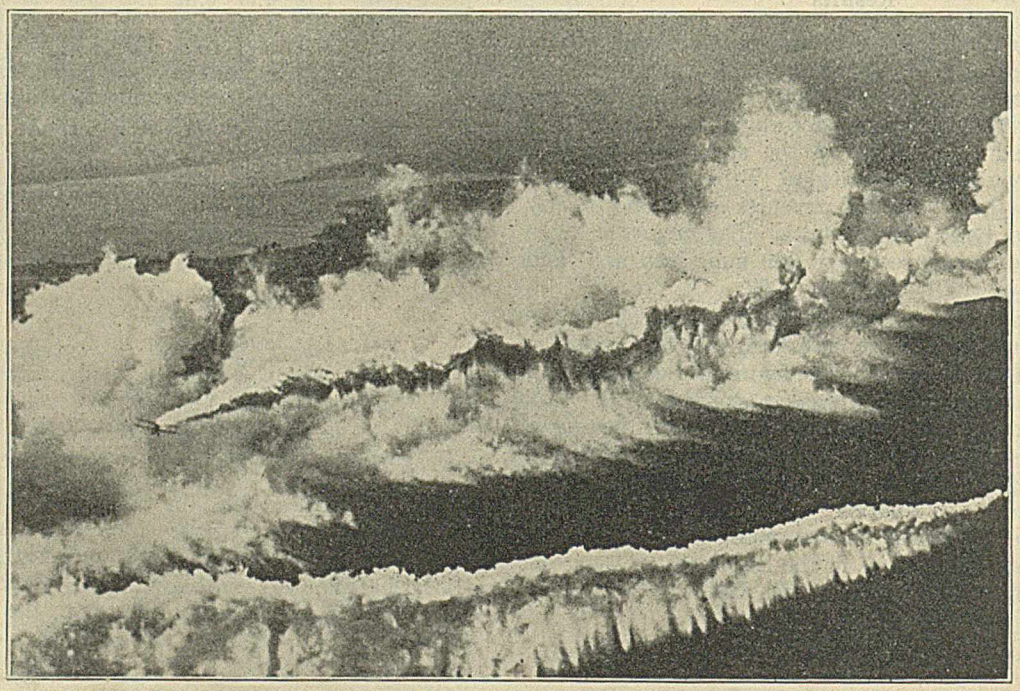


Figure 1—Relation between Boiling Point Elevations and Per cent Soda Content

[13] *J. Am. Chem. Soc.*, **36**, 215 (1914); **39**, 1173 (1917).

[14] *Carnegie Inst. Pub.*, **60**; *Am. Chem. J.*, **22**, 5, 110 (1899); **23**, 89 (1900); **32**, 327 (1904).



This photographic record was made as one airplane laid a smoke screen and another a smoke cloud, both of titanium tetrachloride. It took place at Fortress Munroe while a forty-mile gale was blowing. With evidence of this sort, any one can judge the important part which the combined Air and Chemical Warfare Services are destined to play in national defense, whether on land or sea.

Notes on the Viscosity of Cotton Cellulose[1]

By J. O. Small

HERCULES POWDER CO., WILMINGTON, DEL.

The use of cotton cellulose as a raw material for many industries has become widely extended and, from a practical point of view, viscosity is its most important physical property. A brief outline is given of factors that are believed to influence viscosity from the growth of the cotton plant until the purification treatment has been completed. A method is described which has been used for determining the viscosity of cotton cellulose in cuprammonium solution. Although it is understood that colloidal solutions such as are formed by cellulose in cuprammonium do not have viscosities independent of the rate of shear, the latter factor can be neglected, for it is too small to be significant in industrial application.

IT IS generally understood that there is a considerable variation in the viscosity of different cotton cellulose materials, and even in the same fiber the cellulose is probably in varying degrees of molecular complexity. The viscosity at this point is influenced by the species of the cotton plant, its age or growth, the conditions under which it ripens, and the locality where grown. There exist numerous varieties of the cotton plant, and at the present time it is impossible to make a definite biological classification or to ascertain definitely the ultimate affect on viscosity of the age of the plant or of conditions under which it has matured. There is a growing tendency among those who use cotton cellulose for chemical manufacturing purposes to restrict their raw material to that from a single locality, in order to obtain a more uniform product, since the conditions of growth in so far as they affect viscosity cannot be controlled. Specification as to source can be made only after considerable experimental work, and in the case of linters sharp lines of demarcation cannot be drawn for the several empirical geographical divisions, because cottonseed is sometimes transferred from one locality to another for purposes of removing the linters.

Purification Treatment

During the purification of the cotton cellulose its viscosity is affected by (1) temperature (pressure) of digestion, (2) time of digestion, (3) strength of caustic solution, and (4) method of bleaching. Of these factors, the temperature of digestion exerts the greatest influence. In recent years comparatively high temperatures have become necessary, owing partly to the more extensive use of cheaper and more impure cotton fibers. For the low-viscosity types required in pyroxylin varnishes and similar products longer periods of digestion are often required than were used in purifying cotton cellulose for smokeless powder. Naturally, the cost of material prepared in this manner is relatively high owing to the effect of such drastic treatment upon yields, and a fruitful field is offered here for economies.

The strength of caustic solution employed in the digestion treatment depends upon the grade of raw cotton cellulose being purified and also upon the purpose for which it is to be used. For instance, when dealing with a low grade of linters or with hull fiber, it is necessary to use a higher concentration of caustic solution than with a high-grade linter having a much larger proportion of cellulose. It is generally accepted that lower viscosities result from the use of stronger solutions during the digestion treatment. Any reduction in the amount of noncellulose material introduced into the digester decreases the ultimate consumption of caustic soda per pound of finished product, and when lower grade fibers are being utilized this is most important.

Bleaching when properly conducted causes but a slight reduction in viscosity and under these conditions a product having but a small proportion of material soluble in 7.14 per cent sodium hydroxide or 10 per cent potassium hydroxide results. On the other hand, it is possible to effect enormous reductions in viscosity by bleaching at high temperatures, but this is always accompanied by the formation of oxidation products of the cellulose. Low-viscosity products obtained in this manner have a doubtful value.

The control of viscosity during the purification treatment has assumed considerable importance in recent years, particularly to manufacturers of artificial silk and of nitrocellulose, and it is now customary to purchase purified cotton cellulose on definite viscosity specifications. It would appear that the first step in the control of viscosity should be the determination of viscosity of the raw material prior to the digestion treatment. This can be readily done with fibers of the better grade by making approximately 1 per cent solutions in cuprammonium and determining the viscosity as later described. The importance of blending thoroughly the raw material before digestion treatment cannot be overestimated and provision should be made also for blending the material after digestion if a uniform viscosity is desirable.

Estimation of Viscosity of Purified Material

The importance of viscosity in selecting cotton cellulose for the manufacture of nitrocellulose for the arts has been realized for some time, and until recently it has been the practice of certain manufacturers to nitrate samples of the purified cellulose on a small scale and determine the viscosity value when the nitrocellulose had been dissolved in suitable solvents. This method was more or less unreliable because of the many steps involved. It was desirable, therefore, to develop a method applicable to several types of cotton cellulose materials in order to control properly the viscosity of resultant products.

Ost[2] describes a method for determining the viscosity of various forms of cellulose such as cotton, wood pulp, etc., in cuprammonium solution. This solvent was made by dissolving specially prepared basic copper sulfate in ammonia. A subsequent study of this method of preparation[3] showed that accurate control of the copper and ammonia content was difficult and for this reason duplicate determinations could not be made. Ost refers to progressive changes taking place in the cellulose-cuprammonium solution during solution

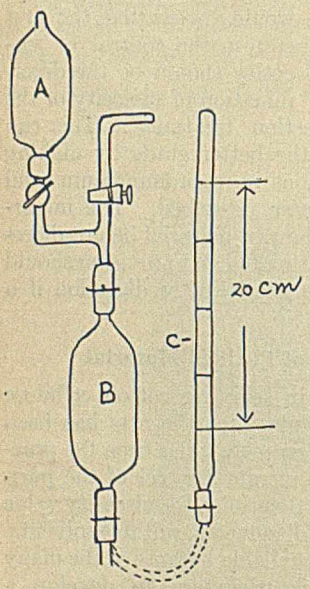
[1] Presented before the Division of Cellulose Chemistry at the 67th Meeting of the American Chemical Society, Washington, D. C., April 21 to 26, 1924.

[2] *Z. angew. Chem.*, **24**, 1892 (1911).

[3] Gibson, Spencer, and McCall, *J. Chem. Soc. (London)*, **117**, 479T (1920).

and up to the time of determining the viscosity. Later work has shown this to be due to exposure to air and light. During the war an extensive study was made of methods for making cellulose viscosity determinations with the aim of developing control methods for the production of propellant explosives. Gibson, Spencer, and McCall[3] describe the method finally adopted. The solvent was prepared by dissolving copper hydroxide, prepared by Dawson's method,[4] in aqueous ammonia. Solutions were prepared using 1 and 2 per cent cellulose and viscosity determinations made both by using a hydrogen capillary viscometer and by the falling sphere method. However, Gibson's method frequently gave widely varying results on the same cotton, the solvent was comparatively difficult to duplicate, and air had to be admitted to the solution just before filling the viscosity tube. Joyner reinvestigated the subject of cellulose viscosities in cuprammonium and published an account of his work showing the effect on viscosity produced by varying the concentration of cellulose, copper, and ammonia, and a design for an apparatus for measuring viscosity without exposure of the solution to air.[5] A modified form of this method has been found to give more reliable results.

In order to obtain a solution with sufficiently high viscosity to be determined by a falling sphere when some of the lower viscosity types of cotton linters were used, a solvent containing approximately 3 per cent copper was required. Attempts were made to obtain this by dissolving copper hydroxide in aqueous ammonia, but the variation in the physical nature of the copper hydroxide and the impossibility of obtaining high copper concentrations by this method made it necessary to prepare the solvent in a manner similar to that used by manufacturers of cuprammonium artificial silk. This involves the oxidation of copper in the presence of ammonia. It was accomplished in the laboratory by bubbling air through a glass column filled with clean copper turnings and C. P. 28 per cent ammonia in which were dissolved 10 grams of sucrose per liter. The sucrose increases the viscosity of the solution somewhat, but it stabilizes the solvent and facilitates the preparation of cuprammonium by keeping the surface of the copper clean. Four hours' bubbling through a 61-cm. (2-foot) column produces a solution containing approximately 3 per cent copper and 17 per cent ammonia. As the copper concentration approaches 4 per cent the solution becomes unstable at room temperature. The solvent should contain 3 ± 0.2 per cent copper, 165 ± 1.2 grams ammonia per liter, and 10 grams sucrose per liter. It was prepared by diluting the solution from the towers with aqueous ammonia of the proper strength containing 1 per cent sucrose. The solution thus prepared, if kept in a dark bottle below 28° C., will remain unchanged for 3 or 4 weeks, except for an increase in nitrites which does not materially affect the viscosity.



A—Storage bulb for cuprammonium solution
B—Bulb for dissolving cellulose
C—Viscosity tube

Careful preparation of the sample by thorough blending and tearing apart by hand is necessary to obtain consistent results. An apparatus identical to that described by Joyner is used, but instead of evacuating by a vacuum pump the bulb into which the sample of cotton cellulose is placed is connected with a reservoir of mercury. The air is forced out of the bulb by the mercury when the reservoir is raised, and a partial vacuum is then produced by lowering the reservoir. It was found that check results could be obtained more readily in this manner. Five grams of the blended sample after having been dried with air at 80° C. are placed in the bulb and the mercury reservoir is adjusted so that the bulb containing the sample is under about 61 ± 12 cm. (24 ± 5 inches) vacuum. A definite quantity (97 cc.) of the standard cuprammonium solution is then drawn in, and the bulb after having been closed tightly is placed in a shaker for 17 hours at a temperature range of 15° to 28° C. The degree of shaking is standardized by fastening the bulbs radially on the face of a disk 46 cm. (18 inches) in diameter rotating one revolution per minute. Although it is possible to use black bulbs and thus protect the solution from light during preparation, it must be exposed when the viscosity determination is made. Since the reducing effect of light may not be the same on all viscosities of cellulose-cuprammonium solution, it was thought best to use transparent bulbs. However, at no time are the bulbs exposed to direct sunlight and viscosity determinations are made after a definite time of standing.

When the time of shaking has elapsed the cellulose-cuprammonium solution is transferred by means of air from the bulb to a glass tube and the viscosity determined by causing a glass sphere 3.3 mm. in diameter to fall through 20 cm. of the solution at 25° C. in a tube 1.5 cm. in diameter and 30 cm. long. Joyner has shown that the use of air in transferring the solution from the bulb does not seriously affect the accuracy of the result.

The method outlined above is particularly applicable to the lowest ranges of viscosity in use at this time. For higher viscosities, such as used in the manufacture of artificial silk, the weight of the original sample must be reduced from 5 grams to 2.5 grams or even 1 gram.

Relation of Viscosity in Cuprammonium to Nitrocellulose Viscosities

A brief study was made to determine whether a definite relation exists between viscosity results as obtained in this manner and the viscosity of the corresponding nitrocellulose prepared under standard conditions in the laboratory. In the latter case viscosity was determined in a pyroxylin solution using the falling sphere method. All the samples were of purified, bleached linters of the type generally employed in making nitro cotton for "dopes." They represent a variety of raw materials and methods of manufacturing, and were selected with regard to viscosity only. All the check determinations on cuprammonia viscosities are given to illustrate the deviation that can be expected.

	A—In Cuprammonium				*B*—Nitrocellulose	
Sample	(1)	(2)	(3)	Av.	solution	Ratio *B*:*A*
1	14.4	11.9	12.2	12.8	9	0.70
2	27.5	29.0	26.3	27.6	29	1.05
3	27.7	27.4	25.5	26.9	49	1.82
4	163	54	79	97.4	83	0.85
5	154	152	161	156	153	0.98
6	192	236	232	222	178	0.80
7	166	146	..	156	188	1.20
8	422	489	473	461	535	1.16

From the table it is evident that consistent results can be obtained on the viscosity of cellulose by the method here outlined and the values so determined can be used to control the viscosity of the nitrated product.

It is interesting to note that Sample 3, which consisted almost entirely of hull fiber, gave a high ratio. The NaOH-soluble on this sample was 10 per cent. Other results on a plant scale have since been obtained which tend to confirm

[4] *J. Chem. Soc. (London)*, **95**, 370 (1909).
[5] *Ibid.*, **121**, 1511 (1922).

this higher ratio when dealing with a linter with high NaOH-soluble. This is reasonable since it is known that the NaOH-soluble portion of linters is low in viscosity. The cuprammonia viscosity is lowered by the presence of the NaOH-soluble portion to a much greater degree than the nitrocellulose viscosity, because a large portion of the NaOH-soluble part of the lint dissolves during nitration and purification of the nitrocellulose.

Apparatus for Determining the Specific Gravity of Aggregates[1]

By F. H. Tucker

Bureau of Entomology, Tallulah, La.

An apparatus has been developed by which the specific gravity of aggregates separated from bituminous mixtures can be determined, without separation into grades, to an accuracy of 2 per cent and better. It is adaptable to the gravity determination of fine materials, as Portland cement and sand, comparing favorably with the LeChatelier flask in results obtained, and requiring one-third as much time per determination. Although it has not been used for the apparent gravity of porous materials, there is nothing in its construction or operation that would prohibit its use in the same way as any apparatus used for that purpose.

The essential features of the apparatus are (1) the special overflow tube, which produces a sharp cut-off of the overflowing liquid and responds to as small an increase in volume as 20 cc. or less; (2) the special lid and funnel combined, which effectually reduces flotation of fine material by introduction beneath the surface of the liquid, and prohibits air inclusions and splashing by providing for the spreading of the material and control of the speed at which the material enters the liquid; (3) the glass jar, which permits the observation of behavior of the material in the liquid and is very easily and quickly cleaned.

For aggregates abstractly considered, absorption, adsorption, and relative solution, are problems for investigation. The unoccupiable pore space in the aggregate material is constant for both the compressed bituminous mix and the aggregate after separation, and affects their respective densities in proportion to the relative percentages by weight.

A CONTEMPLATED study of compressed bituminous road materials involved the specific gravity determination of aggregates separated by extraction in order to determine the theoretical maximum or voidless density of bituminous mixtures. A search of the literature and examination of laboratory practice revealed the need of an apparatus adaptable to the gravity determination of such aggregates.

According to the type of mix, aggregates vary in size of particle from that passing a 200-mesh sieve to that retained on a 4.4-cm. (1.75-inch) mesh. Common practice is to separate the coarse from the fine material and separately determine the gravities by use of apparatus adaptable to the grades. It is highly desirable to eliminate this waste of time and increased chance for error by a single gravity determination of the aggregate as a whole.

History

Buckly[2] pointed out the faulty practice in the methods for specific gravity determinations of building stone, and recommends a procedure for determining porosity. Thorner[3] proposed a method for determining the pore space in building materials, determining the true specific gravity by a Schumaunschen apparatus, and the apparent specific gravity by a device designed by himself, which is essentially a glass jar fitted with a ground-glass top containing an overflow tube and a vertical measuring tube connected to a tube sealed into the lower part of the wall of the jar. Seger and Gramen[4] employed the Thorner principle, but simplified the apparatus and procedure. Hillebrand[5] has a noteworthy discussion pertaining to the importance of correction for absorption by porous materials in the specific gravity determination of rocks. Hubbard and Jackson,[6] after a comparative study of seven methods for the specific gravity determination of aggregates, concluded that an appreciable variation between apparent and true specific gravity is dependent upon the absorption factor of the material and that it is not practical to determine the apparent gravity of fragments smaller than 0.5 inch diameter by any of the methods studied. For larger materials the Goldbeck, Chapman wire basket, and Hubbard-Jackson methods were found to be equally reliable. The Bureau of Standards' modification of the LeChatelier apparatus was pronounced more convenient and rapid than the Jackson apparatus for fine materials with diameters less than 0.5 inch. Rea[7] described a method depending on the difference in specific gravity and the nonmiscibility of water and kerosene, to measure the displaced volume of the aggregate, including any pores that the particles may contain.

Apparatus

The method whereby the displaced volume is measured or weighed outside the parent volume and container was chosen as being in all probability the most practical. The apparatus hitherto used in this method is inadequate for the gravity determination of aggregates. In designing such an apparatus the following physical principles had to be considered:

(1) A liquid such as kerosene is necessary as a medium of comparison and the surface tension of the liquid must be taken into account. The nature of the material determines the liquid to be used and the physical properties of the liquid the form of overflow tube required for an accurate displacement.

(2) The material must be introduced beneath the surface of the liquid in order to diminish flotation of fine material.

(3) Spreading of the material when entering the liquid is essential to air exclusion.

(4) Control of the speed of introduction of the material into the liquid minimizes disturbances, splashing, and air inclusions.

Preliminary gravity determinations were made upon aggregates separated from bituminous pavements, using a liter side-tube flask with tube extended and bent down and a sleeve to introduce the aggregate beneath the surface of the liquid. Reasonably concordant results were obtained for displacements of 200 cc. or more.

[1] Received August 4, 1924.

[2] *Wis. Geol. Nat. Hist. Survey, Bull.* **4**, 63, 70 (1898).

[3] *Chem. Ztg.*, **29**, 744 (1905).

[4] *Ibid.*, **29**, 884 (1905).

[5] *U. S. Geol. Survey, Bull.* **422**, 43.

[6] *Proc. Am. Soc. Testing Materials*, **16**, 380 (1916).

[7] *Proc. Am. Soc. Testing Materials*, **17**, 257 (1917).

In an attempt to overcome the salient weak points of such an apparatus one was designed after the order of the Goldbeck apparatus.[8] The essential parts are the special overflow tube and the combined lid and funnel which are fitted to an ordinary battery jar. When simple straight or bent tubes are used, there is no sharp cut-off on the liquid flow, but a tendency to drip, especially when kerosene is used as the liquid medium of comparison, owing to its comparatively

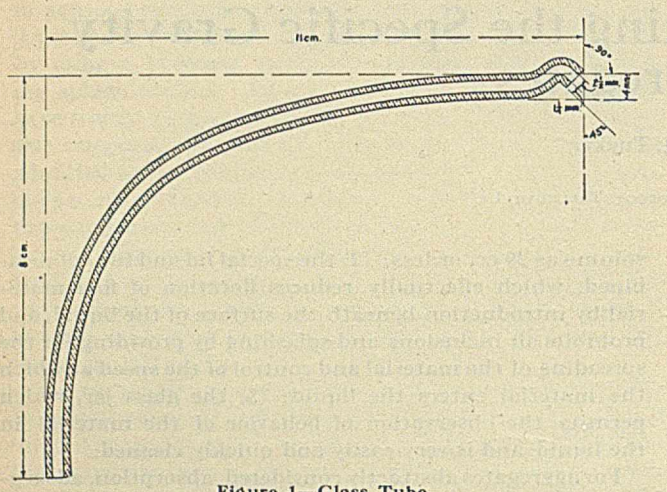


Figure 1—Glass Tube

low surface tension. As such a drip might cause an error in the gravity determination, the principles of the siphon and capillarity were applied to overcome this difficulty. The siphon and internal diameter of the tube were varied and that giving the best results was adopted.

In designing a siphon that will give an abrupt break in the overflow of the liquid it is important that it shall be sensitive to the make as well as the break of the overflow column of liquid. It is desirable to be able to start the overflow of the liquid by a small volume displacement in order that the apparatus may not be limited in its use. A plain siphon with the initial end at right angles to the plane of liquid level is sharp in cut-off, but leaves the liquid out of contact and far below the end of the tube. A comparatively large displacement is required to cause contact of the liquid with the end of the tube before the siphon will function.

The inner end of the tube is therefore bent at an angle of 90 degrees to form a miniature siphon. It is then cut at such distance from the bend that a point inside the tube at the apex of the throat of the miniature siphon and the highest point in the periphery of the bore of the cut end lie in the same horizontal plane. The incline of the free arm of the miniature siphon allows air to enter the upper part of the bore when the liquid is pulled away from the upper arc by gravity, and thus breaks the column of liquid maintained by the siphon effect of the tube as a whole. The tube outside the jar is gradually bent down, terminating vertically about 8 cm. from the plane of the liquid level, which permits emptying the tube by gravity when the column of liquid is interrupted by air. The interruption is intermittent to the point of equilibrium where the surface tension is not sufficient to start the miniature siphon. This leaves the tube primed for action, and a very slight rise of the liquid level of the jar—20 cc. or less—will cause the siphon to function and start an overflow of the liquid.

The adaptability of the apparatus and the uniformity of introduction of the material into the liquid are regulated by a specially designed lid and funnel combined. The combination is made of heavy sheet copper with the stem of the funnel set into the lid at an angle of 45 degrees. If required, a metal with higher chemical resistance may be used. The stem is elliptical, with the least inside diameter 5 cm., making possible gravity determinations of both coarse and fine materials. The large inclined stem provides for the spreading of the material and a low rate of speed of introduction into the liquid, reducing to a minimum included air and loss from splashing. The stem extends 4 cm. beneath the surface of the liquid, thereby wetting fine material which tends to float when introduced upon the surface of liquids. The lid is provided with a flange which encircles the top of the jar outside, and the stem has sufficient clearance of the walls to permit the free turning of the combination about the top of the jar.

The size of the container depends upon the capacity desired. A round battery jar 15 cm. deep and 12.5 cm. in diameter is a convenient size. A 1.5-cm. round hole is cut about 4 cm. from the top of the jar, in which the special siphon tube is inserted, stabilized by a cork collar or button of litharge-glycerol over the cork extension outside of the jar. The jar is of approximately 1.5 liters capacity to the overflow point and, being of glass, affords the operator an opportunity to observe the behavior of the material in the liquid.

Operation

The apparatus should be placed upon a stable base at a suitable height for the receiving graduate, without change of position between the time of liquid level adjustment and that of volume displacement. It is important that the same procedure shall be used for the delivery of the liquid into the graduate, both in the level adjustment and the volume displacement.

The material, previously dried at 110° C., is introduced slowly into the funnel with the minimum disturbance of the apparatus and liquid and in quantity sufficient to allow for freeing the stem, before the overflow is interrupted, of any material that may have accumulated at liquid level. A thin spatula is convenient for dislodging material from the stem at the liquid surface, or it may be washed down by a measured quantity of the liquid used as a medium, correcting for the volume used in washing.

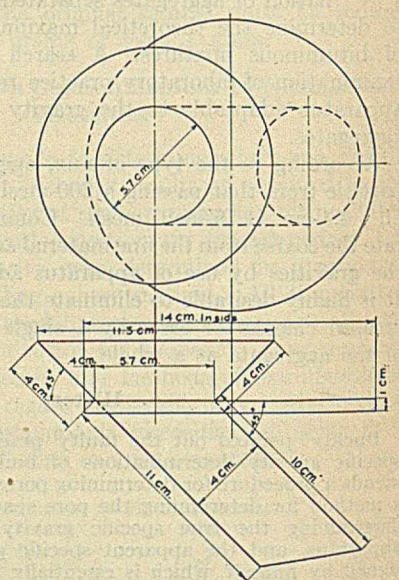


Figure 2—Funnel and Lid Combined

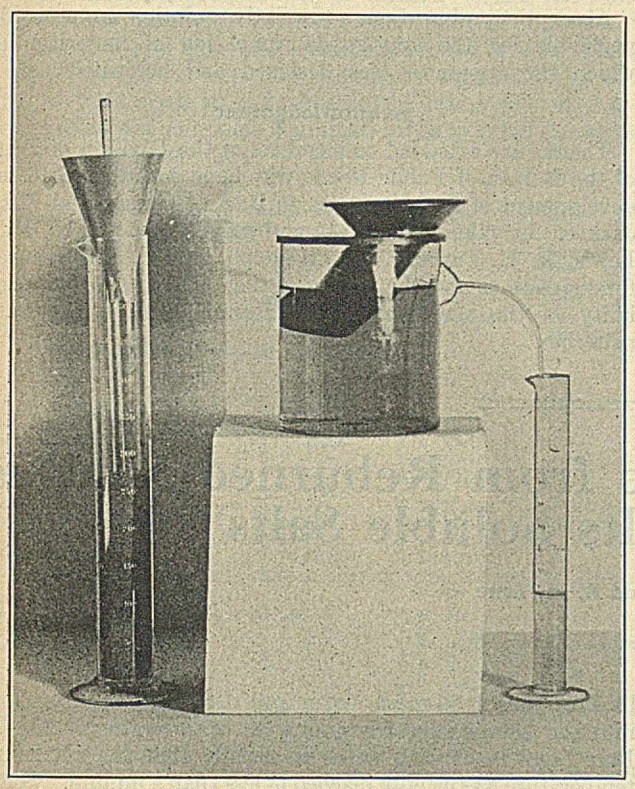
Most materials are heavier than kerosene and readily settle out, so that the special overflow tube works smoothly, thereby insuring the minimum disturbance within the liquid and apparatus. For aggregates containing fine materials which do not settle but diffuse upward through the liquid, a telescoped extension may be used on the funnel stem connected at an angle of 60 degrees to vertical to retard the speed at which coarse materials enter the liquid. In such a case a deep jar is necessary. In the apparent specific gravity determination of porous materials, absorption may be corrected for by previously saturating the material, as in the Goldbeck method, or by determining difference in weight before and after saturation.

[8] *U. S. Dept. Agr., Bull.* **949**, 9.

The internal diameter of the overflow tube and miniature siphon requires modification according to the surface tension of the liquid to be used as the medium of comparison.

Results

Table I contains the results of blank tests for the accuracy and sensitiveness of the apparatus. The measured or weighed



A B C

A—Graduate for measuring the volume of aggregate
B—Apparatus, liquid level adjusted
C—Receiving graduate for displaced liquid

Apparatus for Determining Specific Gravity of Aggregates

liquid volumes were added consecutively to the apparatus, following liquid level adjustment, from a small tared graduate having 0.2-cc. divisions, and the displaced liquid was received in the same graduate, thus eliminating error by imperfect drainage and correcting for inaccuracies of graduation. With small volume displacements, if the overflow is slow in starting, a gentle touch of the exit end of the overflow tube will disturb the apparent equilibrium and immediately start the liquid flow. Test *A* gives results by volume measurement only, whereas Test *B* is a comparison of results obtained by volume and weight and their respective variation from initial volume and weight. The maximum variation for Test *A* is 2 per cent, and for Test *B* by volume is 3 per cent and by weight less than 1 per cent. Weighing of small displaced volumes requires but little, if any, more time than measuring, and gives more concordant results with a higher degree of accuracy.

Table I—Blank Tests at 25° C.

	Test A		Test B			
No.	Volume displaced Cc.	Difference from volume taken Cc.	Volume displaced Cc.	Difference from volume taken Cc.	Weight displaced Grams	Difference from weight taken Gram
1	19.8	0			16.65	0
2	19.6	−0.2			16.55	−0.10
3	19.8	0			16.60	−0.05
4	19.6	−0.2			16.62	−0.03
5	19.9	0.1			16.55	−0.10
6	19.8	0	20.8	0	16.65	0
7	19.8	0	20.8	0	16.65	0
8	19.5	−0.3	20.7	−0.1	16.65	0
9	19.8	0	20.3	−0.5	16.55	−0.10
10	19.8	0	20.4	−0.4	16.59	−0.06
11			20.2	−0.6	16.50	−0.15
12			20.6	−0.2	16.65	0
13			20.2	−0.6	16.50	−0.15
14			20.6	−0.2	16.65	0
15			20.7	−0.1	16.65	0

Table II gives results of comparative tests with this apparatus and the LeChatelier flask, and with varying amounts of material. Nos. 1 and 2 were made in one LeChatelier flask in succession as against Nos. 3, 4, and 5 in the special apparatus. Nos. 6, 7, 8 were made using one LeChatelier flask for each determination against Nos. 9, 10, and 11 made in one special apparatus to compare the time required by the two methods. Nos. 12, 13, and 14 were made in succession in one special apparatus to ascertain the quantity of material that may be used per determination and the number of tests that may be made successively with one apparatus.

Table III—Aggregates Separated from Bituminous Mixtures by Carbon Bisulfide-Gravity Test at 25° C.

	Aggregate				
Compressed Mix Type	Weight Grams	Displaced Kerosene Measured Cc.	Displaced Kerosene Calcd. Cc.	Sp. gr.	Difference from average Cc.
Topping	439.5	170	170	2.59	−0.028
	265	101	100.5	2.63	+0.012
	264	102	101.5	2.60	−0.018
	263	101	100.9	2.61	−0.008
	349	133	133.1	2.62	+0.004
	263.5	100	100.6	2.62	+0.004
	263.8	100	100.7	2.62	+0.004
	264.3	100	100.2	2.64	+0.022
	265.4	101	101	2.63	+0.012
Topeka	454	159	158.4	2.87	+0.01
	453	159	159	2.85	−0.01
Binder	956	328	333	2.87	0
	954	327	332	2.87	0
Bituminous concrete (*a*)	1172	402	399	2.94	−0.01
	939	320	317	2.96	+0.01
(*b*)	943	331	332	2.84	−0.01
	940	327	328	2.86	+0.01
(*c*)	927	330	331	2.78	−0.005
	928	330	331	2.79	+0.005

Table III gives the results of determinations on materials for which the apparatus was primarily designed. The aggregates from these compressed bituminous mixtures consisted of trap rock, Potomac River gravel, and sand and limestone dust as filler. The aggregate was separated from the bitumen with carbon disulfide by means of a Reeves modification of the Dulin centrifuge, the remaining solvent expelled by cautious heating, and its gravity determined as separated from the mix.

This table does not include corrections for loss or lack of

Table II—Comparative Tests at 25° C.

No.	Apparatus	Kind of Aggregate	Grams	Displaced kerosene Cc.	Sp. gr.	Time
1	LeChatelier (*a*)	Sand filler	64	24.1	2.65	
2	LeChatelier (*a*)	Sand filler	60	22.3	2.69	
3	Special (*a*)	Sand filler	64	24.0	2.66	
4	Special (*a*)	Sand filler	60	22.6	2.65	
5	Special (*a*)	Sand filler	60	22.8	2.63	
6	LeChatelier (*b*)	Portland cement	64	21.0	3.05	
7	LeChatelier (*c*)	Portland cement	64	20.8	3.07	55 minutes, including filling of flasks
8	LeChatelier (*d*)	Portland cement	64	20.9	3.06	
9	Special (*b*)	Portland cement	64	21.0	3.05	
10	Special (*b*)	Portland cement	64	20.9	3.06	15 minutes, including filling and level adjustment
11	Special (*b*)	Portland cement	64	21.0	3.05	
12	Special (*c*)	Portland cement	50	16.4	3.05	
13	Special (*c*)	Portland cement	75	24.5	3.06	
14	Special (*c*)	Portland cement	200	65.8	3.04	

uniformity in separation due to transition of material accounted for in the gravity of the extracted bitumen and without consideration in calculating the maximum density of the mix, since the combined gravities are used. The maximum difference is slightly less than 2 per cent and may be due in part to variations in separation. The gravity results were calculated from weight of displaced volume, and the measured displaced volume agrees with that calculated from weight to 1 per cent and better.

The weight of aggregate required per gravity determination varies directly with the size of the included particles. From 260 to 1100 grams were used for each determination, according to the grade of the material, and from two to four determinations were made consecutively in one apparatus depending upon the quantity of aggregate used per gravity determination.

Results for specific gravity upon aggregates as separated are necessary in calculating maximum density and ultimately the voids of the bituminous mix. A measure of the existing interstices of the mix rather than the pores of the aggregate material is desired. Obviously, pores in aggregate material, abstractly considered, affect the gravity results, but if pores from which bitumen has been extracted are in turn filled with kerosene upon immersion, voids as pores for the occupiable portion of the aggregate material are eliminated. The unoccupiable pore space affects the results for maximum and apparent densities of the mix proportionately and mathematically in the same direction, thereby introducing compensating errors in the computation of voids.

Absorption, adsorption, and relative solution are probably negligible for the gravity determination of materials for which the apparatus was designed and herewith used.

Acknowledgment

Thanks are extended to members of the Division of Tests of the Bureau of Public Roads who have contributed to the development of the apparatus, to B. A. Anderson and F. H. Jackson for valuable criticism and suggestions, and to R. L. Lewis, R. H. Parker, I. N. Rudolph, and E. L. Tarwater for suggestions and the testing of the apparatus for its reliability in the specific gravity determination of aggregate materials.

Rate of Hydration of Lime from Reburned Sludges as Influenced by Its Soluble Salts[1]

By A. H. White and R. M. True

University of Michigan, Ann Arbor, Mich.

THE distinction between quick and slow slaking limes has been recognized as caused by the content of silica, alumina, iron oxide, and magnesia, and by the temperature of burning, with other causes such as the density of the original limestone playing a minor role. Specifications do not take into account the possible influence of soluble salts in the lime. This is undoubtedly because native limestones contain a very small amount of soluble salts. The case is different with lime from reburned sludges, where alkali salts may be present in material amounts. There seems to be a general opinion that reburned sludges give slow slaking limes but no data have been found in the literature. The present paper gives some experimental data on the effect of sodium salts and some other salts when present in the sludge before burning.

Table I—Rate of Hydration of Lime

Sample Grams	Water Grams	Fineness Mesh	Time for maximum temperature Minutes
A—Precipitated $CaCO_3$ burned in rotary kiln at 900° C.			
10	50	60	1
20	100	60	1
10	50	1/8-inch lumps	1
B—Precipitated $CaCO_3$ + 2.0 per cent Na_2SO_4 burned in rotary kiln at 900° C.			
10	50	60	16
10	50	60	18
20	100	60	20
40	200	60	18
C—Sludge from sulfate pulp mill burned in rotary kiln at 900° C.			
10	50	60	53
20	100	60	56
20	100	100	54

The method used for measuring the rate of hydration of the limes was a calorimetric one in which the time required for attainment of maximum temperature, instead of the rise in temperature, was determined. The apparatus consisted merely of a Dewar test tube and a thermometer which was also used as a stirrer. The usual method was to grind the lime to pass a 60-mesh sieve, and drop a 10-gram sample into the Dewar tube containing 50 cc. of water at 25° C. Pure limes react with water so rapidly that the maximum temperature was usually reached in less than a minute. Some of the specimens of reburned sludges required over an hour. The method is relatively independent of the fineness of grinding and the absolute amounts of materials used. The accuracy of the method is shown in Table I.

Tests on Sludges from Sulfate Pulp Mills

The first tests were made on sludges from various pulp mills operating by the sulfate process. These were burned in the small rotary kiln in this laboratory at temperatures held as closely as possible at 900° C. and with a time of passage through the kiln of about 30 minutes. The sludges contained variable amounts of silica, alumina, and magnesia, and these must have influenced the rate of hydration. However, the effect of varying percentages of sulfates was indicated, as shown by Table II.

Table II—Rate of Hydration of Sludges from Sulfate Pulp Mills Burned in Laboratory Rotary Limekiln at 900° C.

	Composition of Burned Lime			Minutes for maximum temperature
Designation	SO_3 Per cent	Sulfide S Per cent	Na_2O[a] Per cent	
N	1.34	0.07	1.20	27
S	1.03	0.22	1.23	35
F_1	1.97	0.05	1.63	46
F_2	1.67	0.05	1.39	55
F_3	4.05	0.07	3.27	77

[a] Calculated from preceding columns.

Comparison of Effects of Sulfate, Sulfide, and Sodium Groups

Experiments were next made to differentiate between the effects of the sulfate, the sulfide, and the sodium groups. Synthetic mixtures were made from precipitated calcium carbonate with various additions, and these mixtures were

[1] Received October 24, 1924.

burned, sometimes in an electric tube furnace and sometimes in the laboratory rotary kiln. The effect of the sulfate group alone was determined on samples burned in an atmosphere containing sulfur dioxide, and also by additions of calcium sulfate and ammonium sulfate before burning. Sulfides were introduced by burning in a reducing atmosphere. The effect of sodium salts was tested by the addition of chloride, nitrate, and carbonate, as well as sulfate. When the tube furnace was used the materials were ground intimately together dry, and were also sometimes ground wet to obtain a more intimate mixture and one more comparable with the sludges. Materials to be burned in the rotary kiln were always mixed wet and made into small cubes to avoid excessive loss of dust from the kiln.

Table III—Rate of Hydration of Lime as Affected by Additions of Known Substances before Burning

Ppтd. $CaCO_3$ Plus the Following:	Duration of burning Hours	Material Added, Calcd. as Per cent of Burned Lime Acid	Base	Time required for maximum rise of temperatures Minutes
A—Samples burned in small electric tube furnace at 900° C.				
No addition	1			1
SO_2 gas, 1%	1			1.5
$(NH_4)_2SO_4$ soln.	1	2.0 SO_3		2
$Ca(NO_3)_2$ soln.	1	2.7 N_2O_5	1.4 CaO	2
$Ca(NO_3)_2$, dry	1	2.7 N_2O_5	1.4 CaO	3
$CaSO_4$, dry	1	2.0 SO_3	1.4 CaO	3.5
NaCl soln.	1	0.69 Cl	0.60 Na_2O	7.0
SO_2 gas, 1%	3	4.33 SO_3		7.0
Na_2SO_4, dry	1	2.0 SO_3	1.56 Na_2O	20.5
Na_2SO_4 soln.	1	2.0 SO_3	1.56 Na_2O	34
$NaNO_3$ soln.	1	3.76 N_2O_5	2.16 Na_2O	46
$NaNO_3$, dry	1	3.76 N_2O_5	2.16 Na_2O	53
B—Burned in laboratory rotary kiln at 900° C. Time in kiln, 30 minutes				
No addition	0.5			1
Na_2CO_3	0.5	0.35 CO_2	0.5 Na_2O	6
Na_2CO_3	0.5	0.7 CO_2	1.0 Na_2O	11
Na_2CO_3	0.5	1.0 CO_2	1.5 Na_2O	17
Na_2SO_4[a]	0.5	2.0 SO_3	1.56 Na_2O	17
Na_2CO_3	0.5	1.4 CO_2	2.0 Na_2O	20
Na_2CO_3	0.5	1.7 CO_2	2.5 Na_2O	21
Na_2CO_3	0.5	2.1 CO_2	3.0 Na_2O	15
Na_2CO_3	0.5	2.5 CO_2	3.5 Na_2O	24

a Mixture burned in reducing atmosphere in limekiln so that over half total sulfur was in sulfide form.

The data given in Table III are divided into two groups in accordance with the method of burning. It will be noted that the temperatures in the two kilns were kept as closely at 900° C. as feasible, but that the duration of heating was twice as long in the tube furnace. There is no appreciable difference in the rates of hydration of pure lime in the two series, the maximum temperature being reached in every case by the end of the first minute. The addition of sulfate radicals alone by the use of sulfur dioxide or ammonium sulfate or calcium sulfate has a rather small retarding influence. So also the nitrate group when added as calcium nitrate has little effect. Sodium salts, however, exert a marked influence, which seems to be roughly independent of the nature of the acid radical and to be more a function of the quantity of Na_2O present. The samples burned for an hour in the electric tube furnace are affected much more strongly than those from the rotary kiln, whose hot zone was kept as closely as possible at the same temperature as the tube furnace but with the total time in the kiln only half as long.

The influence of sodium sulfide as distinct from sodium sulfate was studied in one case by burning the mixture in a lime kiln with a strongly reducing atmosphere, so that over half of the total sulfur was in the sufilde state. The test on this lime is given in the fifth line of the second group Table III. It apparently comes in its proper place for its percentage of Na_2O, with no visible effect due to the sulfide group.

The hydration of lime has been studied by Rohland,[2] who tested the effect of soluble salts dissolved in the water in which the lime was hydrated. He confirmed Candlot's earlier work that calcium chloride exerted a strong accelerating action on the hydration and he also listed barium and aluminium chlorides as accelerating agents. He reported sodium chloride, lithium chloride, potassium bicarbonate, potassium nitrate, ammonium hydroxide and calcium hydroxide as indifferent, and potassium hydroxide, sodium hydroxide, potassium bichromate, and boric acid as agents retarding hydration. Rohland's technic differed considerably from that of the writers in that he added so little water that the resulting product was a dry powder. He does not give any quantitative figures as to retardation, but merely indicates the direction of the effect. Neither Rohland nor Candlot included sodium sulfate in the list of salts tested. Kohlschütter and Walther[3] studied the effect of dissolved salts on the rate of sedimentation of lime hydrated in a rather large volume of water, but did not make any observations on the rate of hydration, merely noting that the rise in temperature was slight and soon equalized itself. In the work in this laboratory only qualitative observation was made on the rate of settling, but all the limes containing sulfates settled rapidly. The effect of nitrates was not consistent. At least one sample to which calcium nitrate had been added before burning settled extraordinarily slowly.

Conclusion

The experimental work shows that sodium salts present in lime sludges retard the rate of hydration of the lime burned from these sludges. The acid radicals SO_3 and NO_3 introduced as sulfur dioxide, ammonium sulfate, calcium sulfate, and calcium nitrate exert little effect. Sodium salts introduced as chloride, sulfate, nitrate, and carbonate exert an influence roughly in proportion to the amount of Na_2O present, provided burning conditions are the same. The addition of 2.0 per cent Na_2O to a precipitated calcium carbonate changes the resultant lime so that it hydrates in 20 to 40 minutes instead of in 1 minute. All the limes containing sodium sulfate yield hydrates that settle rapidly.

[2] *Z. anorg. Chem.*, **21**, 28 (1899).

[3] *Z. Elektrochem.*, **25**, 159 (1919).

Amalgamating Metal Used in Molding Asphalt[1]

By L. J. Catlin

The Standard Oil Co. (Kansas), Neodesha, Kans.

IN preparing asphalt for certain tests it can be poured hot into molds and will not adhere to the metal surface when the mold is removed if the surface to which the asphalt is adjacent has been amalgamated thoroughly before using. The following method has been found rapid and very satisfactory for spreading a film of amalgam on the surface of copper or brass:

Thoroughly clean the surface to be amalgamated and then immerse in a solution of mercury bisulfate. The solution lasts longer and amalgamation is more rapid if free mercury is added and the metal brought in contact with the free mercury under the bisulfate solution. This may be kept in stock in this form and be ready for immediate use when desired. If the bisulfate is not at hand, use diluted sulfuric or hydrochloric acid over the mercury, it being merely necessary to have present a negative radical which will allow the mercury to displace the metal to which it is electronegative. This brings clean mercury into contact with clean metal and an amalgam is soon formed which will carry an adherent film of free mercury.

[1] Received March 31, 1925.

Partial Pressure of Water Out of Aqueous Solutions of Sulfuric Acid[1]

By Crawford H. Greenewalt

Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

THE data on the partial pressures of water out of sulfuric acid solutions may be divided into two groups, those for solutions up to 50 per cent strength and those for solutions over 50 per cent strength. Many investigators have determined the vapor pressures of the weaker solutions and their data are remarkably concordant for all temperatures and concentrations. For acids stronger than 50 per cent, however, the data are very sparse and the agreement between various investigators is very poor. This lack of agreement may be seen in the chart in which the logarithms of the vapor pressures for a given concentration have been plotted against the reciprocals of the absolute temperature.

The general form for the vapor pressure equation may be derived from the Clausius-Clapeyron equation

$$\frac{dp}{dt} = \frac{L}{T(V - v)} \qquad (1)$$

where T is absolute temperature in ° C., L the total heat of vaporization, V and v the specific volumes of vapor and liquid, respectively. Assuming that the vapor obeys the perfect gas laws, and that the volume of the liquid is negligible, we have

$$\text{Log } p = A - \frac{L}{2.3.R} \times \frac{1}{T} \qquad (2)$$

It is obvious, then, that the slopes of the curves obtained by plotting log p against $1/T$ will be dependent on the total heat of vaporization of the vapor out of the solution.

Porter gives values for L at various concentrations and temperatures. An examination of these values shows that the latent heat increases with increase in concentration, and for any given concentration decreases with increase in temperature. Applying these generalities to Equation 2, it will be seen that the slopes of the vapor pressure curves should increase with increase in concentration, that instead of being straight lines they will all show a slight concave downward curvature, and that this curvature will become more pronounced as the concentration decreases. These facts afford a basis for a critical examination of the available vapor pressure data.

The investigators who worked with strong sulfuric acids are Burt, Briggs, Regnault, Sorel, and Daudt. Of these Burt is by far the most outstanding. He used a dynamic method which consisted in determining the boiling points of acids of various concentrations at reduced pressures. He seems to have worked with extreme care, which is reflected in the remarkable concordance of his very large mass of data, but his method limited him to vapor pressures not lower than 35 mm., which at high concentrations represent temperatures of 100° to 200° C.

Briggs worked over the same range as Burt, using an air-steaming method in which a known volume of air is passed through solutions of sulfuric acid, and the water vapor in the effluent air absorbed in pumice and sulfuric acid. Unfortunately, Briggs used an incorrect formula for calculating his vapor pressures, which introduced errors in his final results amounting to from 20 to 100 per cent. His original data, when recalculated according to the correct formula, give results which are fairly concordant with those of Burt.

Regnault, although quite consistent with other investigators at low concentrations, deviates greatly at the higher ones. This is in all probability due to his use of the static method, which is not very satisfactory for vapor pressures of less than 1 mm., owing to the extreme difficulty of freeing the measuring tubes from all traces of residual air. The presence of air equivalent to a few hundredths of a millimeter, although introducing but a negligible error at the higher vapor pressures, would cause errors of as much as 100 per cent at very low pressures.

Sorel used an air-steaming method similar to that of Briggs. He says nothing as to the probable accuracy of his various measurements and does not give his original data. His table is simply a tabulation of values obtained by smoothing curves obtained from the data of Regnault and himself. The results for weak acids are consistent with those of other investigators, but those for high strength acids show very serious deviations.

Daudt determined the vapor pressures of strong acids at extremely low temperatures. He used an electrical method which entailed equalizing the thermal conductivity of the vapors of ice and the acid to be measured in two gas conductivity cells by varying the temperature of the ice element while keeping that of the acid constant. At equal thermal conductivities he recorded his two temperatures and assumed the vapor pressure of the acid to be equal to that of the ice at the observed temperature. His results, considering their magnitude (0.003 to 0.754 mm.) are remarkably consistent.

Fortunately, the data of Burt and Daudt at the two temperature extremes agree moderately well as to slope and position of the log p vs. $1/T$ curves, which furnishes sufficient justification for the extrapolation of Burt's values to the lower temperatures.

In preparing the final chart Burt's values were taken as a basis for the higher concentrations, and the mean of the values of all the investigators for the lower concentrations.

Table I—Parameters of the Vapor Pressure Equations

$$\text{Log } p = A - \frac{B}{T}$$

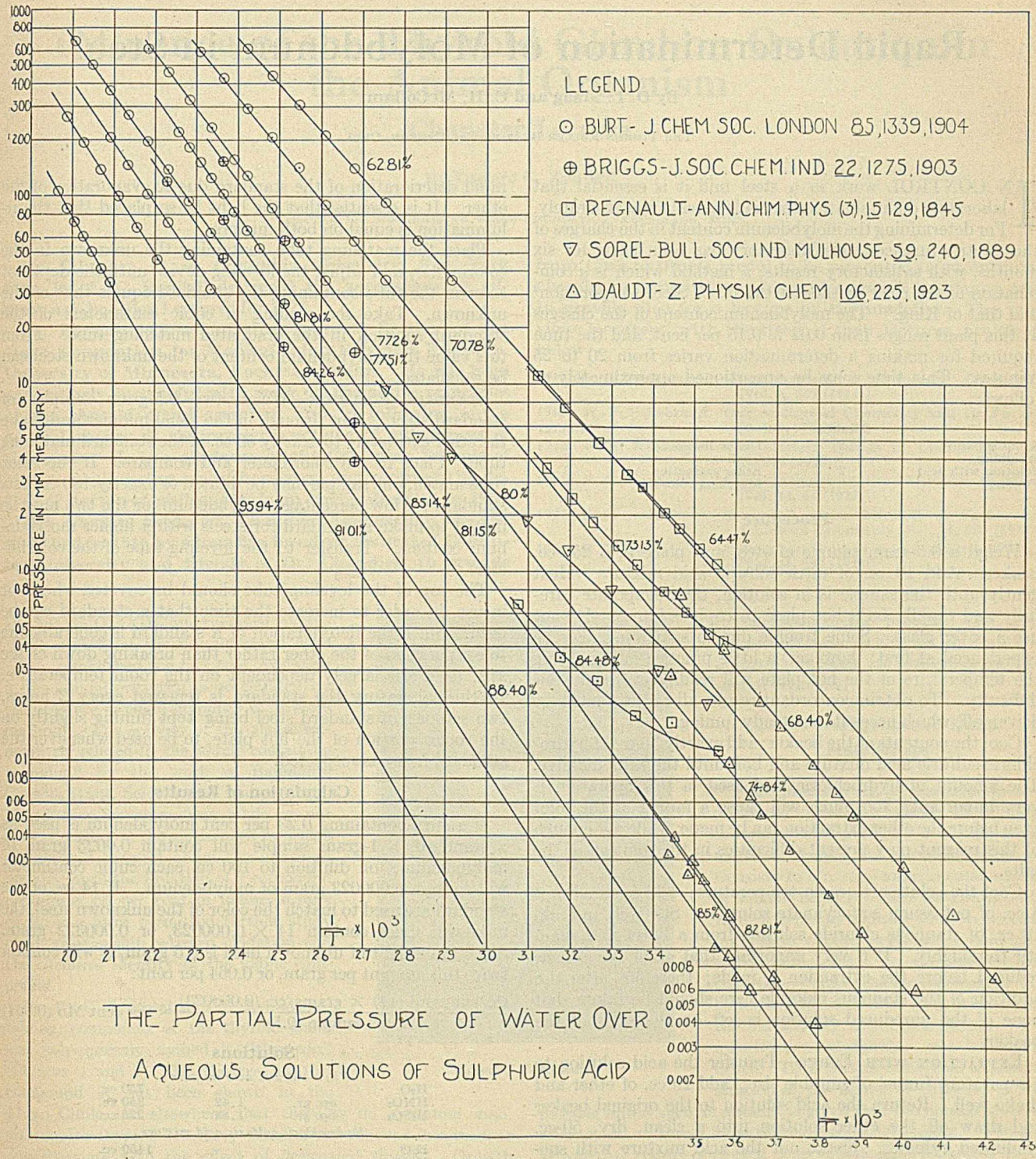
Per cent H_2SO_4	A	B	Per cent H_2SO_4	A	B
0	8.946	2260	60	8.841	2458
10	8.925	2259	65	8.853	2533
20	8.922	2268	70	9.032	2688
30	8.864	2271	75	9.034	2810
35	8.873	2286	80	9.293	3040
40	8.844	2299	85	9.239	3175
45	8.809	2322	90	9.255	3390
50	8.832	2357	95	9.790	3888
55	8.827	2400			

Vapor pressures were plotted against concentrations for even temperatures, and from these curves log p vs. $1/T$ curves taken for even concentrations. The parameters for the equations of these curves are given in Table I.

The heats of vaporization as calculated from the slopes of these curves were compared with those taken from Porter's data and found to agree remarkably well. The boiling points as obtained by extrapolation to 760 mm. were compared with Ferguson's values and found to agree.

Table I gives the parameters of the equation of these curves at 5 per cent intervals in concentration. The values

[1] Received January 13, 1925.



THE PARTIAL PRESSURE OF WATER OVER AQUEOUS SOLUTIONS OF SULPHURIC ACID

obtainable from these equations are accurate to ±2 per cent from 0° C. to the boiling point.

Bibliography

Baur, *Z. Elektrochem.*, **16**, 301 (1910).
Briggs, *J. Soc. Chem. Ind.*, **22**, 1275 (1903).
Brönsted, *Z. physik. Chem.*, **68**, 707 (1910); **64**, 641 (1908).
Burt, *J. Chem. Soc. (London)*, **85**, 1339 (1904).
Daudt, *Z. physik. Chem.*, **106**, 225 (1923).
Dieterici, *Wied. Ann.*, **42**, 513 (1891); **50**, 47 (1893); **62**, 616 (1897); **67**, 865 (1899).
Ferguson, *J. Soc. Chem. Ind.*, **24**, 781 (1905).
Hacker, *Ann. Physik.*, [4] **39**, 1342 (1912).
Helmholtz, *Wied. Ann.*, **27**, 532 (1886).
Lunge, *Ber.*, **11**, 370 (1878).
Regnault, *Ann. chem. phys.*, [3] **15**, 129 (1845).
Roscoe, *J. Chem. Soc. (London)*, **13**, 146 (1860)
Thomas and Ramsay, *Ibid.*, **123**, 3256 (1923).
Raleigh, *Phil. Mag.*, [6] **4**, 521 (1902).
Smits, *Z. physik. Chem.*, **39**, 385 (1902); **51**, 33 (1905); *Arch. Néerland. sci.*, [2] **1**, 97 (1898).
Sorel, *Bull. Soc. Ind. Mulhouse*, **59**, 240 (1889); *J. Soc. Chem. Ind.*, **9**, 175 (1890); *Z. angew. Chem.*, **2**, 272 (1889).
Tammann, *Z. physik. Chem.*, **2**, 42 (1888); *Memo. acad. Petersbourg*, [7] **35** (1887).
Wilson, *J, Ind. Eng. Chem.*, **13**, 326 (1921).
Porter, *Trans. Faraday Soc.*, **13**, 373 (1918).

Swedish Tariff Revision—"Artificial tanning materials, not specially mentioned, wholly or partly organic," have been embodied in an item in the Swedish tariff, and will be free of duty by an Act of March 8, 1925, effective on a date to be determined by the King.

Rapid Determination of Molybdenum in Steel[1]

By O. L. Maag and C. H. McCollam

THE TIMKEN ROLLER BEARING CO., CANTON, OHIO

IN CONTROL work in a steel mill it is essential that laboratory determinations be made quickly and accurately. For determining the molybdenum content in the charges of the electric furnaces, this laboratory has been using for six months, with satisfactory results, a method which is a combination of the color method of the U. S. Steel Corporation[2] and that of King.[3] The molybdenum content of the charges at this plant ranges from 0.02 to 0.15 per cent, and the time required for making a determination varies from 20 to 25 minutes. This time may be apportioned approximately as follows:

	Minutes		Minutes
Sampling	2	Dissolving salts	3
Weighing	1	Cooling	2
Solution with acid	2	Ether extraction	3
Fuming	6	Matching colors	1

Procedure

Weigh a 0.5-gram sample of steel and place in a 250-cc. beaker. Add 10 cc. of nitric-sulfuric acid mixture. Heat gently until the sample is in solution, then evaporate carefully and rapidly on a hot plate to copious fumes. Do not use a cover glass. Some trouble due to spattering may be experienced at first; however, a little practice in regulating the temperature of the hot plate will readily overcome this difficulty. To obtain concordant results all nitrates must be driven off, which necessitates steady fuming.

Cool the contents of the beaker; add exactly 30 cc. of hydrochloric-sulfuric acid mixture and boil until the salts dissolve. The amount of hydrochloric acid used in this operation is very important; too much will cause a fading of the color even before the ether extraction can be made, while not enough of this reagent may present difficulties in the solution of the salts.

Cool the solution to room temperature; add from a buret 5 cc. of potassium sulfocyanate solution. Stir well and add 10 cc. of stannous chloride solution from a buret and again stir thoroughly. It is very important that all of the iron be reduced before the extraction is made; therefore, after the addition of the stannous chloride care should be taken that none of the unreduced solution is left on the sides of the beaker.

EXTRACTION WITH ETHER—Transfer the acid solution to a separatory funnel of suitable size; add 10 cc. of ether and shake well. Return the acid solution to the original beaker and draw off the ether solution into a clean, dry, 50-cc. graduated cylinder. Shake out the acid mixture with successive 10-cc. portions of ether until all color is removed. The volume of ether used for the sample should be approximately the same as is required to give a corresponding color with the standard. Transfer the combined ether solutions to a graduated matching tube.

COLOR COMPARISON—For this operation a Kennicott-Campbell Hurly colorimeter is used in this laboratory. Illumination is supplied by a Wratten Safelight No. 2, made especially for dark-room purposes. This fixture carries a 50-watt bulb, which gives sufficient light and does not materially affect the atmospheric temperature and thus cause a rapid deterioration of the standard due to evaporation of the ether. It is essential that the light be so placed that the illumination is equal on both mirrors.

Place the matching tube containing the unknown in the colorimeter, and adjust the leveling device until the depth of color in the tube containing the standard equals that of the unknown. Take the reading in cubic centimeters of the standard solution in the graduated matching tube. From this value the molybdenum content of the unknown steel can be calculated.

STANDARD SOLUTION—Weigh two 0.5-gram samples of standard steel. Run through in the usual manner and make the ether extract up to exactly 50 cc. in the standard matching tube. Place in the colorimeter and compare. If the color tints match, one sample may be diluted to exactly 100 cc. as a standard for low percentage molybdenum, or the two may be united to make a standard for steels with a higher molybdenum content. Transfer to the leveling tube of the colorimeter.

The top of the leveling tube should be covered when not in use, in order to increase the time that a standard can be used. Since the deterioration of a standard is generally due to evaporation of the ether rather than breaking down of the salt, its life is largely dependent on the room temperature. In this laboratory the standard is renewed every 2 hours, two samples of standard steel being kept fuming slightly on the cooler portion of the hot plate, to be used whenever the standard in use is suspected.

Calculation of Results

If a steel containing 0.23 per cent molybdenum is used as a standard, a 1-gram sample will contain 0.0023 gram of molybdenum; on dilution to 100 cc. each cubic centimeter will contain 0.000023 gram of molybdenum. If 14 cc. of the standard are used to match the color of the unknown steel, the unknown must contain 14 × 0.000023, or 0.000322 gram. Since the weight of unknown used is 0.5 gram, it will contain twice this amount per gram, or 0.064 per cent:

$$\frac{\text{Cc. standard (14)} \times \text{grams/cc. (0.000023)}}{\text{Grams sample (0.5)}} = \text{Per cent Mo (0.064)}$$

Solutions

Nitric-sulfuric acid mixture

H_2O			750 cc.
HNO_3	Sp. gr.	1.42	350 cc.
H_2SO_4	Sp. gr.	1.84	225 cc.

Hydrochloric-sulfuric acid mixture

H_2O			1450 cc.
H_2SO_4	Sp. gr.	1.84	450 cc.
HCl	Sp. gr.	1.19	100 cc.

Potassium sulfocyanate solution

KCNS	50 grams
H_2O	1000 cc.

Stannous chloride solution

$SnCl_2$			250 grams
HCl	Sp. gr.	1.19	200 cc.
H_2O			800 cc.

Dissolve the stannous chloride in the hydrochloric acid, boil until clear, and add the water. Add a few pieces of metallic tin to prevent oxidation.

[1] Received November 10, 1924.

[2] "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Alloy Steels," 1921, 2nd ed., p. 72.

[3] THIS JOURNAL, 15, 350 (1923).

International Industrial Exposition in Bolivia—This exposition will be opened in La Paz on August 6, next, in connection with the celebration of the Bolivian Centennial of Independence. An invitation is extended to the manufacturers of the United States to participate in the exposition.

Influence of the Thyroid Gland on Oxidation in the Animal Organism

Chandler Lecture

By Edward C. Kendall

SECTION ON BIOCHEMISTRY, MAYO FOUNDATION, ROCHESTER, MINN.

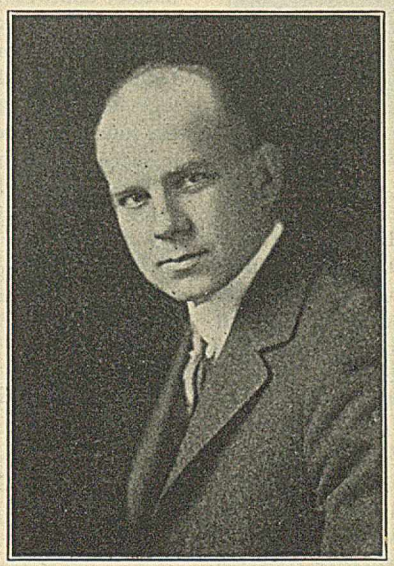
On February 13, at Columbia University, New York City, Dr. E. C. Kendall delivered the accompanying address as Chandler Lecturer for 1925.

Dr. Kendall is head of the Chemical Section of the Mayo Foundation for Medical Education and Research, University of Minnesota, Rochester, Minn. He has been particularly successful with work on the active principles of the thyroid gland secretion and in following out a general theory of the catalytic actions of substances of this class. He is a graduate of the Columbia Schools of Mines, Engineering, and Chemistry, and received the degree of doctor of philosophy from this university in 1910.

The Charles Frederick Chandler Foundation was established in 1910 by about five hundred alumni of Columbia University and friends of Dr. Chandler, to provide from time to time a medal to be presented to an eminent chemist in recognition of his achievements in science, and to provide also for a lecture by the medalist. The previous lecturers, with the titles of their lectures, are given below:

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)]

PHYSIOLOGIC and chemical investigations of the thyroid gland have established the fact that oxidation in the animal organism is accelerated by the presence of small amounts of thyroid material. The activity of the gland was definitely related to the iodine-containing compound by the work of Baumann, Oswald, Hunt, Seidell, and many others. No advance, however, was made in our understanding of the mechanism by which the thyroid brought about this increased activity until the isolation of a compound containing 65 per cent of iodine in pure crystalline form permitted further study of the relationship between oxidation and the chemical identity of the iodine compound.



Edward C. Kendall

In 1914, I isolated the iodine-containing compound of the thyroid gland and subsequently named it "thyroxin" (Figures 1 and 2). By the use of this compound it has been shown in the Mayo Clinic and elsewhere that there is no symptom associated with thyroid deficiency which is not relieved in a manner entirely similar to the effect of desiccated thyroid. Growth is stimulated in the cretin (Figure 3), and all the symptoms of the adult myxœdema patient are relieved by an intravenous injection of chemically pure thyroxin (Figure 4). It is true that there is a difference in the dosage required between desiccated thyroid and pure crystalline thyroxin when experiments are tried on animals, but this discrepancy may be explained by the destruction or loss of thyroxin before it is absorbed and incorporated in the tissues. I believe, therefore, that thyroxin is the essential constituent of the thyroid gland and that nothing has been added to it and nothing has been taken away from it in its isolation. Although it undoubtedly is reincorporated into the functioning protoplasm when it produces physiological effects, this does not materially alter the chemical configuration of the molecule. Nothing is gained by erecting barriers to the full consideration of the problem, but it is our present task to attempt to relate the thyroxin molecule to oxidation in the animal organism.

Effect of Thyroxin on Basal Metabolism

The administration of thyroxin to hypothyroid individuals relieves the clinical symptoms and produces a normal basal metabolic rate. The administration of thyroxin to a normal experimental animal or human being produces the clinical picture of hyperthyroidism, with its attending loss in weight, nervousness, and subjective symptoms. To use the clinical condition of either the hypothyroid or the hyperthyroid individual as a criterion of thyroid activity is not satisfactory. No quantitative relationship can be established. In a normal individual a demonstration of the action of thyroxin is impossible unless such an amount is given that the normal state is altered and an actual hyperthyroidism brought about. The unsatisfactory results of clinical observations have prompted many investigators to find a more satisfactory criterion of thyroid activity. Among those suggested two will be mentioned—the acetonitrile test of Hunt and the effect on the metamorphosis of the tadpole discovered by Guternatsch. Both of these tests will prove the presence of thyroid material, but unfortunately it is impossible to explain the mechanism of the physiological response and relate it to the normal function of the thyroid.

It was therefore with great interest that evidence was accumulated establishing the fact that thyroxin changes the basal metabolic rate and that the change produced is related quantitatively to the amount of thyroxin administered. From 1917 to the present Plummer and Boothby have been studying the quantitative relationship between thyroxin and the basal metabolic rate. In a large series of cases it has been shown that 1 mg.

of thyroxin injected intravenously in a myxœdematous patient will increase the metabolic rate 2.5 per cent, and that, within limits, the increase is in direct proportion to the thyroxin used. When large amounts are injected some of the material is undoubtedly destroyed or excreted before it can be incorporated and function in the organism.

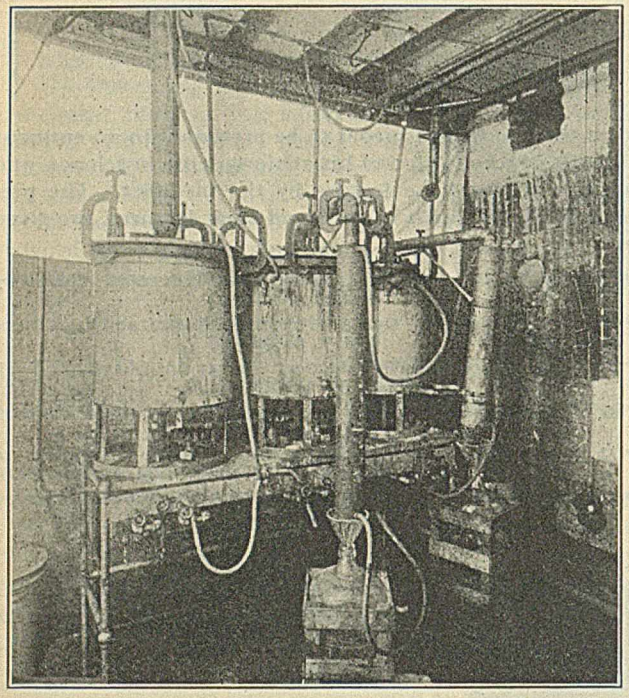


Figure 1—Kettles Used to Hydrolyze the Thyroid Glands for the Original Isolation of Thyroxin

3.5 tons of fresh thyroid material were treated in this apparatus

Neglecting all physiologic influence except the change in basal metabolic rate, I shall point out some established facts and then relate them to our knowledge of the chemical structure of the thyroxin molecule. The change in basal metabolic rate is in all probability primary and is the fundamental reaction directly and indirectly responsible for all the other evidences of physiologic activity; for example, the increased rate of blood flow, the increased moisture on the surface of the skin, and the decrease in the conduction time in the nerves of the heart are indirectly due to the increased rate of metabolism. The increased rates of utilization of oxygen and output of carbon dioxide are directly due to the functioning of thyroxin.

Prolonged Action of Thyroxin

By a quantitative study of the effect of thyroxin on the basal metabolic rate Plummer and Boothby have shown that thyroxin functions for a long time after a single injection and the increased activity results in the combustion of an amount of material, expressed in terms of carbon dioxide, which is enormously greater than the amount of thyroxin administered. The injection of 1 mg. of thyroxin will produce an increase in the carbon dioxide output of approximately 400,000 mg. of carbon dioxide. No further discussion of this action can be given, but the evidence already published and now in press establishes the fact that thyroxin appears to exert its influence by acting as a catalyst.

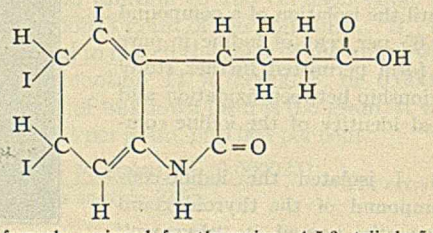
Following the injection of thyroxin there are three distinct parts to the curve of response. There is a well-defined delay and 6 to 8 hours are required before the basal metabolic rate is affected. The significance of this delay is not entirely apparent and will not be discussed at this time. The effect, however, has been demonstrated in all the cases studied. Following the delay period there is a rapid increase in the basal metabolic rate. In a few hours it increases, according to the amount injected, but the maximal response to the injection is not reached until the eighth to the tenth day following the injection. An average of a large number of cases gave the tenth day for the maximal response to a single injection. After reaching the maximum the metabolic rate slowly drops to the level preceding the injection and Boothby and Baldes have shown that this return to normal, or the rate of decay of thyroxin, is proportional to the amount present. (Figures 5 and 6)

The physiologic effect of thyroxin is in striking contrast of the response of the animal organism to adrenaline. Following an injection of adrenalin there is an almost instantaneous increase in the basal metabolic rate, which rapidly reaches a maximum and then soon drops back to normal. The entire effect on the basal metabolic rate of 0.5 mg. of adrenaline in a normal adult is over in less than 4 hours. A single injection of from 5 to 10 mg. of thyroxin affects the basal metabolic rate for 5 or 6 weeks. When desiccated thyroid is given by mouth there is a delay of the same duration as when thyroxin is given, before the basal metabolic rate is increased.

Chemical Nature of Thyroxin

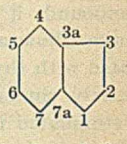
As soon as it was shown that thyroxin in pure crystalline form possessed physiologic activity which is in every respect similar to desiccated thyroid, it became evident that the opportunity was presented to relate physiologic activity to chemical structure. With this object in view the investigation assumed five definite lines of endeavor: (1) to establish the empirical and structural formula of thyroxin; (2) to synthesize thyroxin; (3) to prepare closely related compounds in order to establish the effect of alterations in the thyroxin molecule; (4) to establish the physiologic activity of thyroxin and its derivatives; and (5) to relate the function of thyroxin in the animal organism to other oxidizing agents and other related physiologic processes.

The empirical formula of thyroxin is $C_{11}H_{10}O_3NI_3$. The evidence for the empirical and structural formula has been published elsewhere and it will suffice here to note that the work since 1919 has confirmed the structure of thyroxin assigned at that time in every particular, except the position of one of the double bonds.



Structural formula assigned for thyroxin; 4,5,6 triiodo-5,6-dihydro-2-oxindolepropionic acid

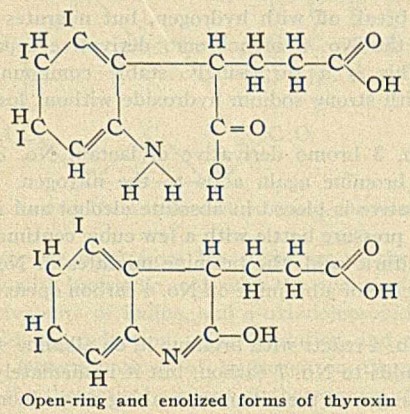
The indole ring will be referred to as follows:



The reasons for the position of the double bond are given below. Further light has been thrown on the structure of thyroxin by Hicks, of Cambridge, England. In a personal communication he has informed me that by the use of the ultra-violet absorption spectrum he has been able to identify the indole nucleus in thyroxin. These results will be published in the near future.

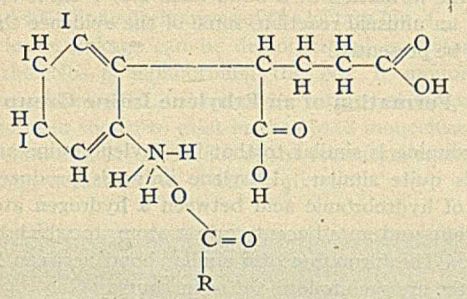
One of the most striking chemical properties of thyroxin is the ease with which the pyrrolidone ring opens. When the sodium salt of thyroxin is treated with carbon dioxide the pyrrolidone ring opens. It is interesting to note further that the ring closes in the presence of dilute alkali or strong mineral acid. Dilute or weak organic acids will not close the ring. Apparently, sodium hydroxide does not open the ring but produces a migra-

tion of the hydrogen from the nitrogen, with an enolization of the carbonyl adjacent to the nitrogen.



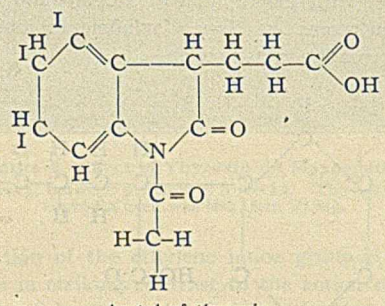
Open-ring and enolized forms of thyroxin

Another surprising chemical property of thyroxin is the basicity of the amine in the open-ring form. With this amine group the sulfate, chloride, and phosphate can be formed, and in addition the oxalate, the acetate, and even the carbonate are sufficiently stable to be washed with water and dried.



Form of salt between thyroxin and an organic acid

The formation of salts with the amine would be impossible in the presence of the acid group which normally forms the pyrrolidone ring unless this carboxyl group is weak. Derivatives of thyroxin which we have prepared bring out the fact that this carboxyl is exceedingly weak. The only other chemical reactions that were established with pure crystalline thyroxin are the formation of derivatives in which the hydrogen of the amine group is replaced by such groups as the acetyl or ureide.



Acetyl of thyroxin

Both the acetyl and ureide were prepared and we are surprised to find that these two substances are physiologically inert. The reason for this is given below.

From a study of the chemical properties of thyroxin and its derivatives there is no suggestion of any catalytic action which can be brought about by the molecule. The secret of its activity, however, is bound up in the molecule itself and the physiologic behavior of the substance was a challenge prompting the thorough investigation of this and related substances. The maximal degree of thyroid deficiency seen in the human being causes a drop in the basal metabolic rate to a position 40 per cent below normal, and since the administration of pure crystalline thyroxin alone restores the basal metabolic rate to normal, at least 40 per cent of the total energy produced when the patient is at rest is due to thyroxin. It therefore seemed highly desirable to establish in minute detail the mechanism by which such a large part of the total energy is produced, as a definite relationship must exist between thyroxin and those agents responsible for the remaining 60 per cent.

Synthesis of Compounds Related to Thyroxin

After establishing the structural formula and chemical properties of thyroxin no further investigation was carried out with thyroxin itself, and five years ago work was begun on the synthesis of compounds related to thyroxin with the hope of finding an explanation of the functioning of thyroxin in the tissues. The details of this synthesis will be published elsewhere, but the general scheme of attack was to build up lactones corresponding

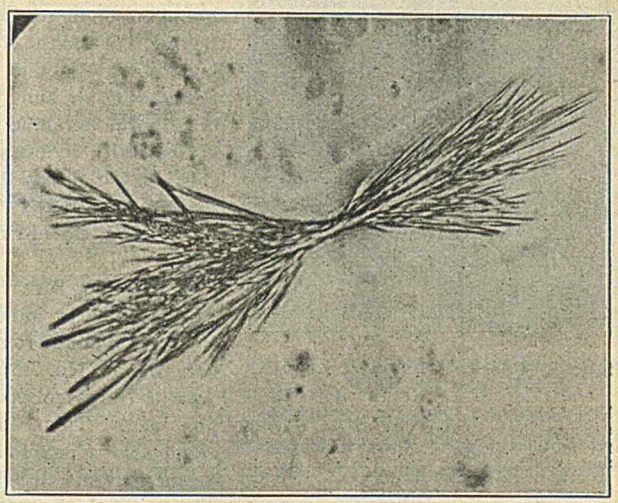
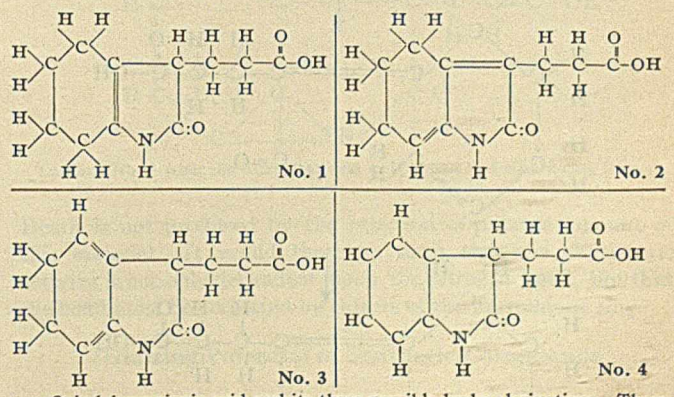


Figure 2—One of the Crystal Forms in Which Thyroxin Separates from an Alcohol Solution

to α-oxindolepropionic acid and then to replace the oxygen in the lactones with nitrogen. Including α-oxindolepropionic acid, the precursor of thyroxin, and the hydro derivatives of this compound, there are five possible lactams, only four of which are stable enough to exist. The completely reduced α-oxindolepropionic acid is unstable and in an aqueous solution the amine is replaced with the hydroxyl group. The other four possible lactams have all been prepared, and in order to relate the physiologic activity of thyroxin to a series of substances of known structure, I shall outline some of the chemical properties and the physiologic activity of a number of these substances that have been prepared synthetically.



α-Oxindolepropionic acid and its three possible hydro derivatives. These will be referred to as lactam Nos. 1, 2, 3, and 4, which are numbered in the order in which they were synthesized

The chemical properties of the four possible lactams are well illustrated by their reaction towards bromine. Lactam No. 1

reacts with bromine, adding an atom on No. 7 carbon. This monobromo compound is stable and can be boiled in water without alteration. A very significant change, however, takes place in the terminal carboxyl and in the stability of the pyrrolidone ring. When the pyrrolidone ring is closed the terminal carboxyl will not affect phenolsulfonephthalein in aqueous or alcoholic solution. When the ring is open the carboxyl is titratable. Furthermore, the influence of bromine on No. 7 carbon is to make the ring open easily in the presence of mineral acids. The treatment of the open-ring form with dilute alkali tends to close the ring. When the No. 7 monobromo lactam is treated with sodium hydroxide the bromine is replaced with hydroxyl. This No. 7 hydroxyl derivative also exists in open- and closed-ring forms.

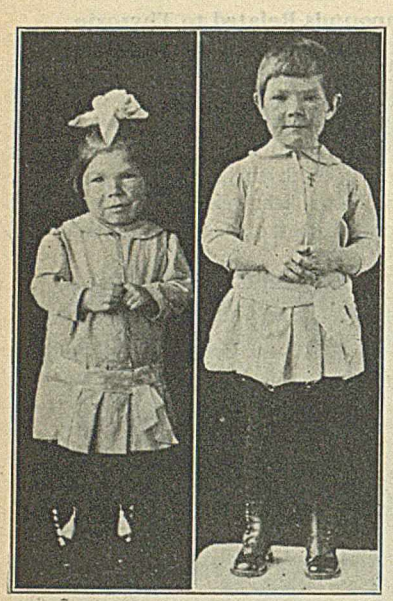
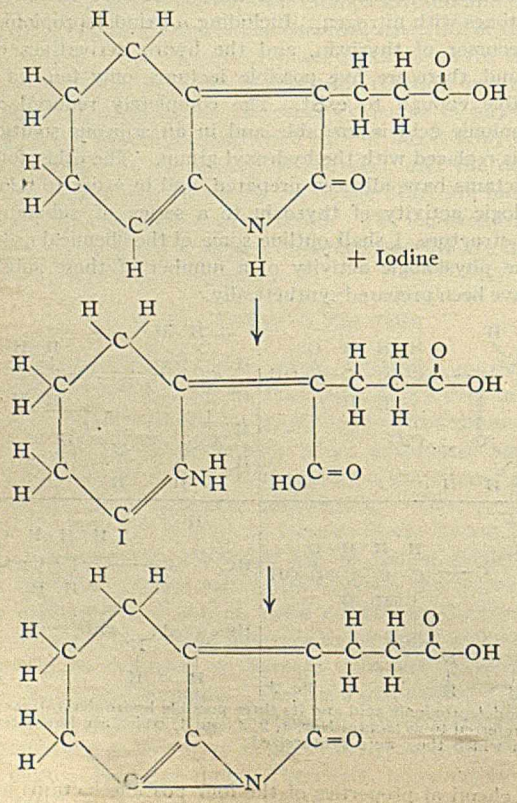


Figure 3—Effect of Thyroxin on Growth of a Cretin

The illustration shows the same child, in the same dress, before and after receiving thyroxin for one year. Increase in height 6 inches

Lactam No. 2 reacts with bromine or iodine and forms a monobromo derivative on No. 7 carbon with the pyrrolidone ring open. This compound is not so stable as the monobromo derivative of lactam No. 1. When boiled with dilute acid the bromine breaks off as hydrobromic acid and forms a bond from No. 7 carbon to the nitrogen. At the same time the pyrrolidone ring closes.



Reactions between lactam No. 2 and iodine showing the formation of an ethylene imine linkage

Lactam No. 3 brominates on the nitrogen but if this is made acid, even with acetic, the bromine does not remain on the nitrogen or break off with hydrogen, but migrates to position No. 3 and the No. 3 monobromo derivative separates from solution. This is a surprisingly stable compound and can be boiled with strong sodium hydroxide without losing its bromine.

If the No. 3 bromo derivative of lactam No. 3 is further brominated bromine again adds to the nitrogen. If this dibromo derivative is placed in absolute alcohol and is heated to 100° C. in a pressure bottle with a few cubic centimeters of concentrated sulfuric acid, the bromine migrates to No. 4 carbon, but the presence of a bromine on No. 4 carbon opens the pyrrolidone ring.

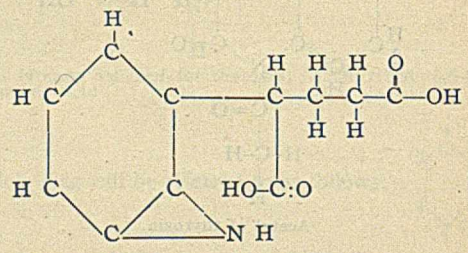
Lactam No. 4 reacts with bromine in an alkaline solution and apparently adds to No. 7 carbon, but it immediately breaks off with the hydrogen of the nitrogen, making a bond similar to the one formed when lactam No. 2 is treated with bromine. In acid solution the bromine migrates to No. 6 carbon. Further bromination results in the formation of the 4,6-dibromo derivative, but the bond from the nitrogen to No. 7 carbon is easily formed in lactam No. 4.

Since the formation of a bond from No. 7 carbon to the nitrogen is an unusual reaction, some of the evidence that it does exist will be presented.

Formation of an Ethylene Imine Group

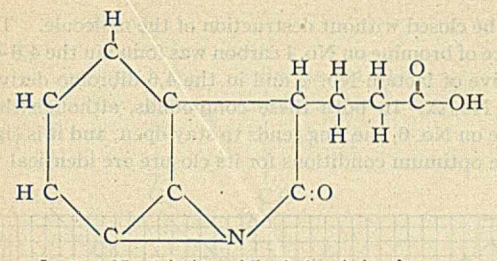
The grouping is similar to that in ethylene imine and its formation is quite similar. Ethylene imine is produced by the removal of hydrobromic acid between a hydrogen atom of an amine group and an adjacent carbon atom, to which bromine is attached. The formation of a similar bond between No. 7 carbon and the nitrogen follows the same course.

The change in lactam No. 4 when this bond is formed is striking. If α-oxindolepropionic acid is dissolved in four equivalents of sodium hydroxide and two equivalents of iodine are added to this solution, it is found that almost no free iodine is present when the solution is made acid. However, no iodine is organically combined. The solution may be made acid, the hydriodic acid removed, the water solution evaporated to small volume, and crystals will separate which are much more soluble in water than the original material. Analysis of these crystals shows them to agree with the formula of a compound which contains two hydrogen atoms less than α-oxindolepropionic acid and in which the pyrrolidone ring is open.



Lactam No. 4 in its oxidized open-ring form

The carboxyl group titrates one equivalent, using phenolsulfonephthalein as indicator. When these crystals are heated to 175° C. they melt, water is given off, and the material that now can be crystallized from water is much less soluble. Its analysis agrees with that of a compound containing two hydrogen atoms less than α-oxindolepropionic acid but with the pyrrolidone ring closed. The carboxyl in this compound does not affect phenolsulfonephthalein in aqueous or alcoholic solution. Its melting point is 90° C. On boiling with alkali the open-ring form of α-oxindolepropionic acid with the bond from No. 7 carbon to the nitrogen is again recovered.



Lactam No. 4 in its oxidized closed-ring form

Furthermore, the bond from No. 7 carbon to the nitrogen reduces easily with hydriodic acid, with the quantitative liberation of two equivalents of iodine, and α-oxindolepropionic acid is recovered after the reduction. The oxidation and reduction are reversible. Determinations of hydrogen in these compounds agree with the theoretical content of the compounds having the identity suggested, and since the reaction is reversible and the change in solubility, melting point, and the ionization of the carboxyl accompanies the change in the oxidized and reduced form, I believe that the formulas given for these two substances are correct. The ethylene imine linkage, moreover, occurs in the No. 6 monobromo and monoiodo derivatives and in the 4,6-dibromo and 4,6-diiodo derivatives of the lactam No. 4. The same ethylene imine linkage can be demonstrated in lactam No. 2, and in the No. 6 monobromo, the No. 6 monoiodo, the 5,6-diiodo and the 4,5,6,-tribromo derivatives of lactam No. 2. It has also been shown to exist in the No. 3 monochloro derivative of lactam No. 1. Evidence of the formation of the ethylene imine linkage in lactam No. 3 will be given.

Figure 4—Effect of Thyroxin on Myxoedema
The time interval between pictures is 3 weeks. The total amount of thyroxin used was less than 20 mg.

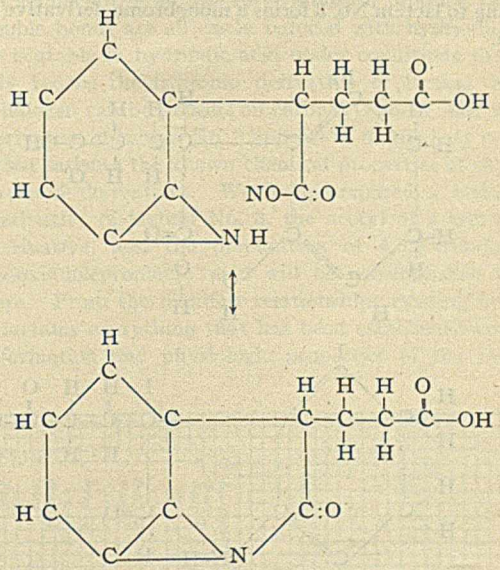
The formation of the ethylene imine group in this series of compounds is in striking contrast to the action of bromine on isatin. Although bromine adds to isatin, it does not make this bond even when treated with alkali. I shall designate this bond as the "nitrogen bond."

Formation of Imine Group with Molecular Oxygen

If the formation of the nitrogen bond in this series of compounds could not be brought about except by means of iodine or bromine in glacial acetic acid, it would remain of only academic interest and before it could be of any importance to biology there must be found some other reaction which would bring it within the sphere of oxidation that we know exists in the animal organism. Such a reaction was discovered October 17, 1924, when we found that a slightly alkaline solution of α-oxindolepropionic acid will react with molecular oxygen and will lose two atoms of hydrogen, forming the nitrogen bond. It was of still greater significance when it was shown that the presence of two atoms of bromine on carbon 4 and 6 accelerated the rate of oxidation with molecular oxygen and that the presence of iodine in the molecule caused an even more rapid oxidation of the hydrogen and formation of the nitrogen bond. The reaction with molecular oxygen takes place at ordinary room temperature and in dilute alkali but it is necessary to have the pyrrolidone ring open.

Physiologic Activity of Synthetic Compounds

These substances, either with or without the nitrogen bond, would still be merely of passing interest if they did not possess physiologic activity which could be related to oxidation in the animal organism. We were, therefore, pleased to find that, although the injection of lactam No. 2 produced no demonstrable physiologic activity, the injection of the same substance with the nitrogen bond in the molecule produced such a marked effect that the injection of too large an amount caused the death of the animal (Figure 7). The physiologic response consisted of an increase in the rate and amplitude of respiration, marked increase in the pulse rate, drop in the blood pressure, and increase in the basal metabolic rate. This reaction was repeated many times, and the fact was established that no physiologic activity was demonstrable except when the compound was injected in the form of its nitrogen bond. After the production of the nitrogen bond in lactam No. 4 it was also injected into a normal dog under ether anesthesia. When lactam No. 4 is injected there is no physiologic response. When the lactam No. 4 with its nitrogen bond, but with the pyrrolidone ring open, is injected, there is no response, but when lactam No. 4 with the nitrogen bond and the pyrrolidone ring closed, is injected, there is a response similar to that produced by lactam No. 2 with the nitrogen bond but apparently of not quite so intense a nature (Figure 8).



Lactam No. 4 with the nitrogen bond in its open and closed-ring forms

Death is not produced by the injection of a large amount of this material. It would therefore seem that the physiologic activity is not only dependent upon the nitrogen bond, but that the bond must be activated by closure of the pyrrolidone ring.

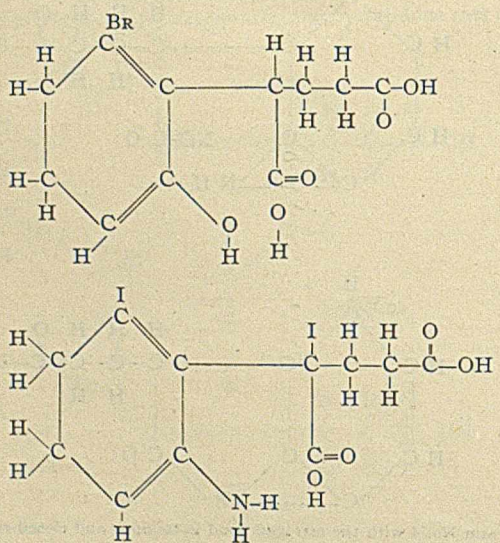
Oxidizing Potential of Synthetic Compounds

The physiologic response to these compounds was so striking that it suggested a difference in the chemical properties of these substances which could be measured in more precise terms and expressed as a quantitative relationship. Through the work of LaMer, Conant, Clarke, and others, the oxidizing potentials of

many organic compounds have been measured, and when the oxidizing potential of lactam No. 4 in the form of its open and closed pyrrolidone ring, and in the presence and absence of its nitrogen bond, was measured, a change in the oxidizing potential which could be directly related to the physiologic effect was found. Briefly stated, the oxidizing potential of the closed pyrrolidone ring with the nitrogen bond is about 0.3 volt higher than the oxidizing potential of the open-ring nitrogen bond when each is present in solution with an equal amount of α-oxindolepropionic acid, in corresponding form but without the nitrogen bond. Further work must be done on these substances in order to establish all the relationships and the factors affecting the oxidizing potential, but it can be stated at this time that the closure of the pyrrolidone ring in the presence of the nitrogen bond increases the oxidizing potential of the molecule. The significance of this finding will be discussed in connection with thyroxin.

Influence of the Iodine in Thyroxin

One of the most interesting problems concerning the thyroid gland has been connected with the presence and function of the iodine in the gland, and some of the most important problems concerning thyroxin are associated with a study of the properties imparted to the molecule by the presence of the iodine. There appear to be three effects of the iodine on the thyroxin molecule: (1) It increases the rate of metamorphosis of the tadpole. This action is little understood and will not be discussed here, but that iodine is intimately associated with the rate of metamorphosis is well established. (2) It facilitates the formation of the nitrogen bond. Iodine attached to the benzene ring accelerates the rate of formation of the nitrogen bond with molecular oxygen. (3) It influences the ease of opening and closing the pyrrolidone ring. It can be shown that the lactone corresponding to lactam No. 3 forms a monobromo derivative on No. 4 carbon.



Lactone corresponding to lactam No. 3 and the 3,4-diiodo lactam No. 3, showing the influence of halogen on carbon No. 4, holding the ring open

Although this lactone without bromine resists opening when treated with sodium hydroxide the presence of bromine on No. 4 carbon results in opening the lactone ring, and it has been found impossible to close the ring and leave the bromine on No. 4 carbon. If the ring is closed the bromine migrates from No. 4 to No. 3 carbon. The same influence is brought out in the 3,4-dibromo derivative of lactam No. 3. The bromine on carbon No. 3 tends to close the pyrrolidone ring and keep it closed, but so great is the effect of bromine on No. 4 carbon to open the ring, that it remains open in the 3,4-dibromo derivative and it cannot be closed without destruction of the molecule. The same influence of bromine on No. 4 carbon was found in the 4,6-dibromo derivative of lactam No. 4 and in the 4,6-dibromo derivative of lactam No. 2. In both these compounds, although there is a bromine on No. 6, the ring tends to stay open, and it is significant that the optimum conditions for its closure are identical with the

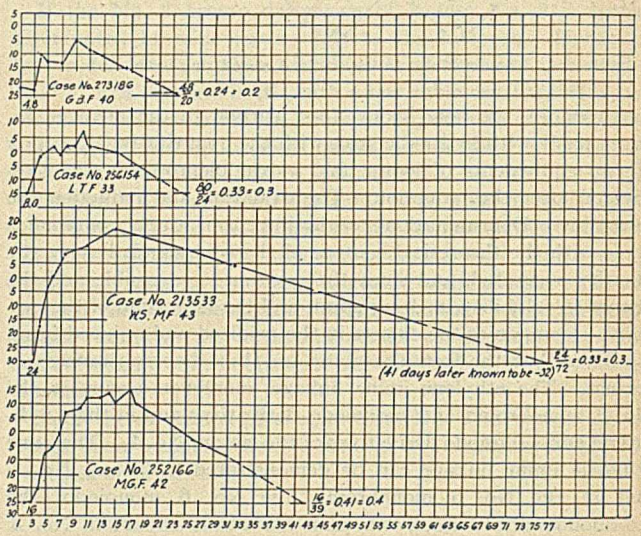
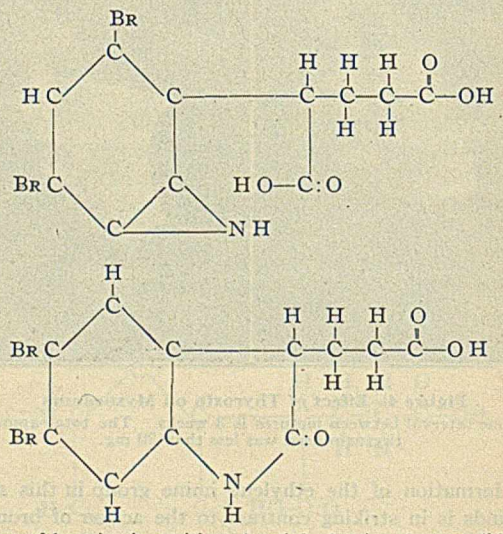


Figure 5—Response in Basal Metabolic Rate after Injection of Thyroxin (Boothby and Sandiford)

conditions for the closure of the thyroxin molecule when it exists in open-ring form. In striking contrast to bromine on No. 4 carbon, bromine on No. 5 and No. 6 tends to close the ring, so that in the 5,6-dibromo compounds the pyrrolidone ring tends to stay closed and can be opened only with difficulty.

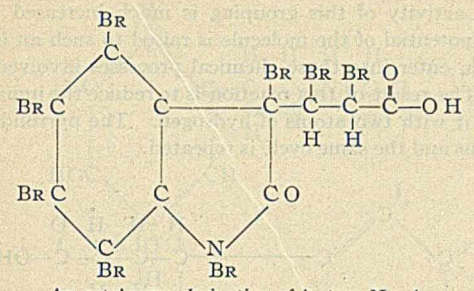


Influence of bromine in positions 4 and 6, showing the pyrrolidone ring open, due to the bromine on carbon No. 4, and the pyrrolidone ring closed in the 5,6-dibromo of lactam No. 4

In thyroxin these opposing effects of the halogen atoms in the benzene ring, on the pyrrolidone ring, are very nearly equalized, so that it is easily opened and easily closed.

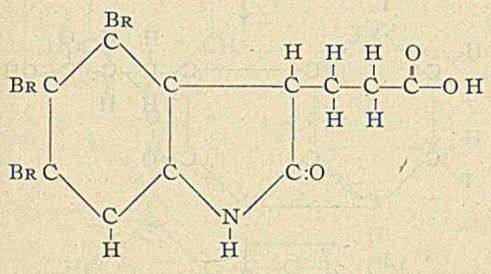
Halogenation of Thyroxin Nucleus

The properties of α-oxindolepropionic acid when treated with excess bromine are striking. In the presence of 80 per cent acetic acid and a small amount of sulfuric acid bromine acts on every available carbon and the nitrogen, forming an octabromo compound, which can be isolated in pure crystalline form and is remarkably stable.



An octabromo derivative of lactam No. 4

It forms a tetrabromo derivative containing the nitrogen bond, the bromine adding in the 3,4,5,6 positions. This, with hydriodic acid, loses bromine on No. 3 carbon and the nitrogen bond is reduced, giving 4,5,6-tribrom-α-oxindolepropionic acid.

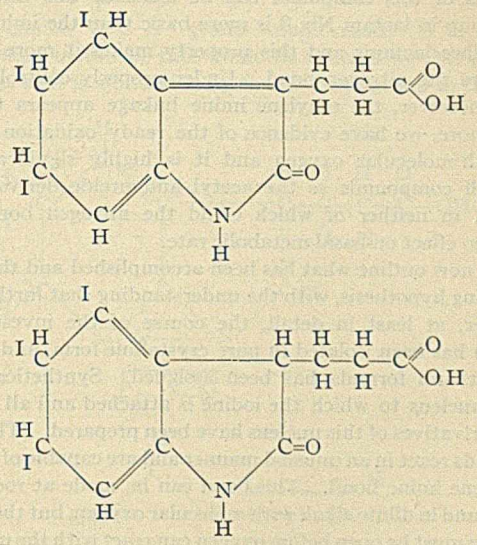


4,5,6-Tribromo derivative of lactam No. 4. This compound has not the essential characteristics of thyroxin

This substance does not resemble thyroxin. The nitrogen is not basic, the pyrrolidone ring does not open easily, and the substance is not easily soluble in sodium hydroxide. I therefore believe that the structure of thyroxin cannot be 4,5,6-triiodo-α-oxindolepropionic acid. Two extra hydrogen atoms must be present in the molecule, and the only positions for them are on carbons No. 5 and No. 6. The iodine cannot be on carbons No. 3 or No. 7, because whenever halogen is present on either of these carbons it is readily reduced with hydriodic acid.

Chemical Configuration of Thyroxin

The study of the derivatives of α-oxindolepropionic acid has brought out some striking resemblances and relationships with thyroxin. Granting the presence of the indole nucleus, which has been independently confirmed and which is amply shown by the properties of a large series of compounds we have prepared, and granting the correctness of the empirical formula, which has been many times confirmed, there are two possible formulas for thyroxin. In one the double bond is in the pyrrolidone ring from carbon 3 to 3*a*; in the other the double bond is in the benzene ring between carbons 3*a* and 4.



The two possible isomeric forms for the structural formula of thyroxin. The known properties of thyroxin are not possessed by the top figure. From the chemical properties of thyroxin and its synthetic derivatives the formula which best represents thyroxin is 4,5,6-triiodo-5,6-dihydro-2-oxindolepropionic acid

Before the synthetic work was begun there was no way of determining which formula was correct. It was found, however, that lactam No. 2 will not add three atoms of iodine, but it will add three atoms of bromine in positions 4, 5, 6, and it will readily form a nitrogen bond which is easily reduced. However, the bromine atoms in positions 4, 5, and 6 are not stable to alkali, and, most significant of all, the three atoms of bromine and one of the double bonds are all easily reduced with hydriodic acid. Thyroxin is stable in hydriodic acid under conditions that will completely reduce the tribromo derivative of lactam No. 2. Since no halogen can be present on carbons 3 and 7, the 4, 5, 6, triiodo derivative of lactam No. 3 appears to be the only possible formula that satisfies the known chemical properties of thyroxin and its related derivatives. We have prepared a tetrachlorethoxy derivative of lactam No. 3, the acetyl of a tribromhydroxyl derivative, and the preparation of 4,5,6-triiodo, 5,6-dihydro-α-oxindolepropionic acid will be accomplished in the near future. From the manifest relationships existing between the four lactams everything that has been established concerning the formation and physiologic properties of the nitrogen

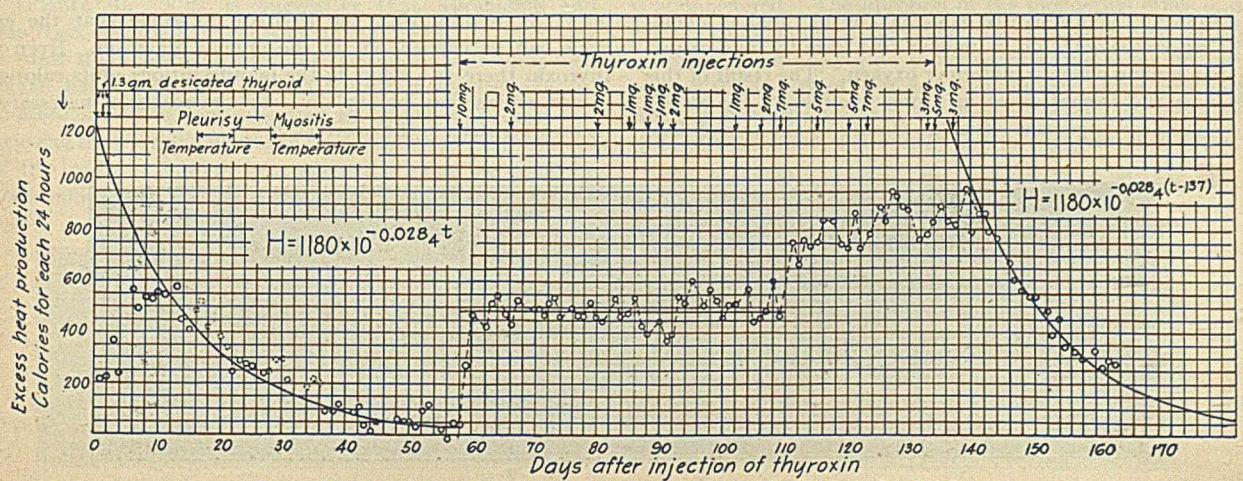
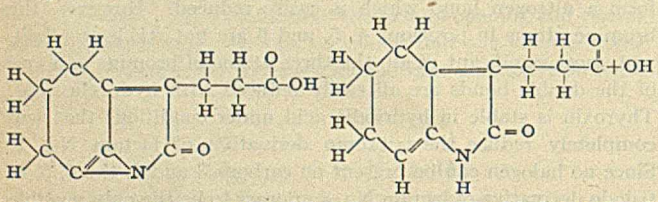


Figure 6—Chart Showing the Basal Metabolic Rate of a Patient for 160 Days

During the first 3 days desiccated thyroid was given and then the patient was allowed to return to normal for 57 days; during the following 50 days the patient was maintained at approximately a constant level by frequent injections of thyroxin; in the next 30 days the basal metabolic rate was increased to a higher level and the curve of decay is shown for the following 20 days (Boothby and Baldes)

bond of the other lactams can be applied to lactam No. 3. The nitrogen bond has been prepared in lactam No. 3, but the work is of such recent date that no conclusions concerning the chemical properties of this compound can be made at this time. The imine group in lactam No. 3 is more basic than the imine group in the other lactams and this property makes it more difficult to prepare the nitrogen bond. Under properly controlled conditions, however, the ethylene imine linkage appears to exist. Furthermore, we have evidence of the ready oxidation of thyroxin with molecular oxygen and it is highly significant that with such compounds as the acetyl and ureide derivatives of thyroxin, in neither of which could the nitrogen bond exist, there is no effect on basal metabolic rate.

I shall now outline what has been accomplished and then state our guiding hypothesis, with the understanding that further work may alter, at least in detail, the course of the investigation. Thyroxin has been isolated in pure crystalline form, and a tentative structural formula has been assigned. Synthetically, the organic nucleus to which the iodine is attached and all possible hydro derivatives of this nucleus have been prepared. These new compounds react in an unusual manner and are capable of forming an ethylene imine bond. This bond can be made at room temperature and in dilute alkali with molecular oxygen, but the pyrrolidone ring must be open before oxygen can react with the molecule. The compounds with the imine grouping have marked calorigenic action when the pyrrolidone ring is closed, but not when the ring is open. Finally, the oxidizing potential of the closed pyrrolidone ring compound is about 0.3 volt higher than the oxidizing potential of the open-ring compound when each is present in solution with an equal amount of the corresponding form but without the imine group. The oxidation and reduction of these compounds is a reversible reaction.

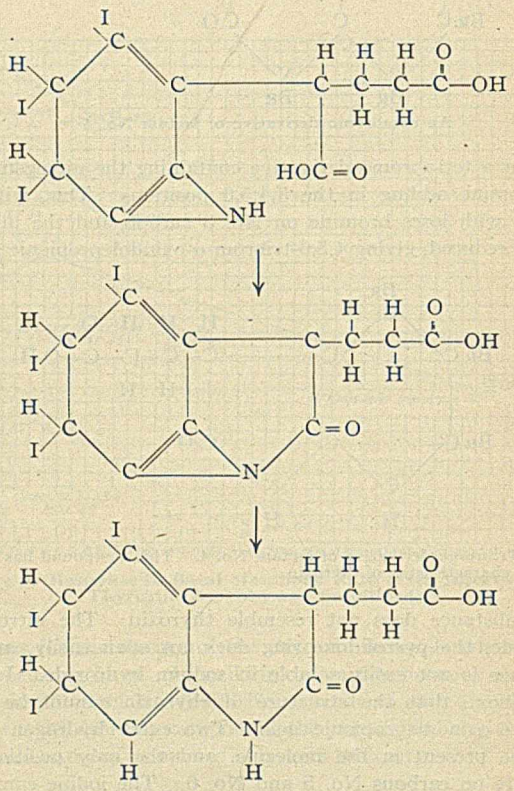


The formation and reduction of the ethylene imine bond in lactam No. 2 is an easily reversible reaction

From a comparison of the properties of the compounds prepared synthetically and thyroxin, there are many indications that these reactions also apply to thyroxin, and it seems probable that thyroxin can exist in the corresponding oxidized and reduced forms.

Hypothesis of Catalytic Action of Thyroxin

As a working hypothesis thyroxin may be pictured as a compound that can be acted on in its open-ring form by mild oxidizing agents, among which is molecular oxygen. The result of this oxidation is the formation of an imine grouping. By an intramolecular rearrangement—that is, closure of the pyrrolidone ring—the activity of this grouping is much increased and the oxidizing potential of the molecule is raised to such an intensity that it can enter into those chemical processes involved in oxidation. The result of this reaction is to reduce the imine group, replacing it with two atoms of hydrogen. The pyrrolidone ring again opens and the same cycle is repeated.



The cycle of the chemical reactions in the thyroxin molecule when it functions as a catalyst, showing the formation of the nitrogen bond in the open-ring form, the closure of the pyrrolidone ring and reduction of the nitrogen bond

Two of the essential steps in this cycle are the opening and closing of the pyrrolidone ring, and in both these reactions the iodine in the benzene ring exerts a dominating influence. The iodine produces the finely balanced state of the molecule which acts as the governor of the rate at which it can react.

Accompanying each oxidation there must be the coincident opening and closure of the pyrrolidone ring.

Although the compounds prepared synthetically possess calorigenic action in their oxidized form, they do not have power to act as a catalyst and their effect is over as soon as they have reacted once. It is only with the thyroxin molecule that the entire cycle can be carried out in the animal organism. Even with thyroxin there is a delay in the manifestations of its calorigenic power, which may be explained by the reactions necessary for its incorporation in the protoplasm.

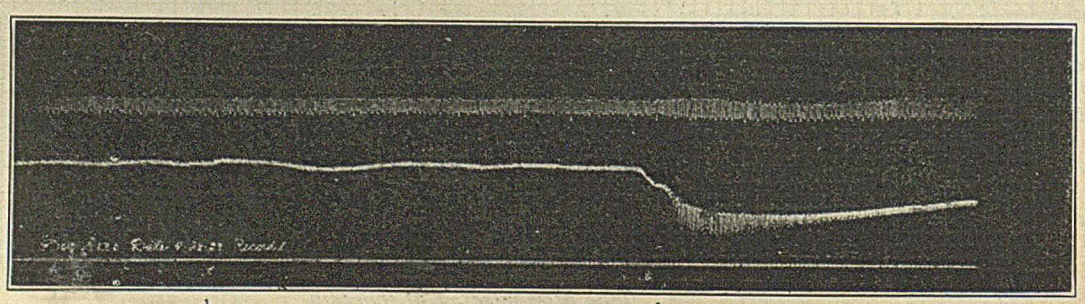
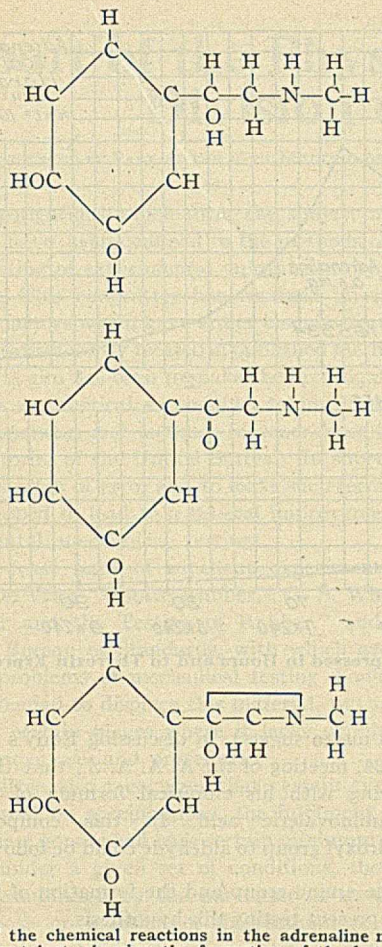


Figure 7—Kymographic Tracing Showing Blood Pressure of a Dog

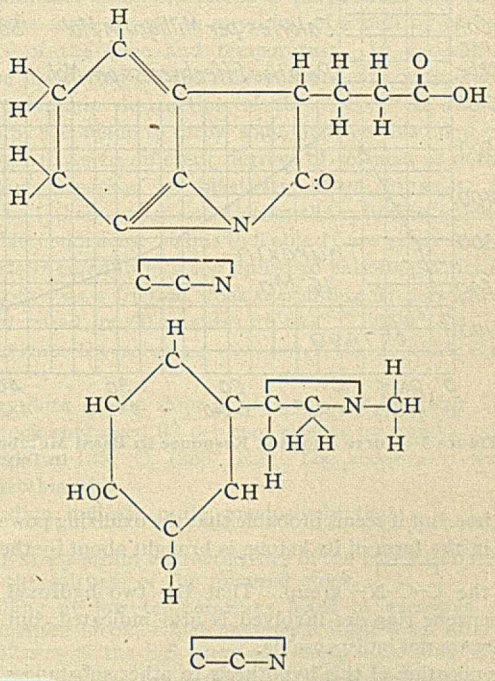
At 1, lactam No. 2 was injected. At 2, the same amount of lactam No. 2 in the form of its nitrogen bond and closed ring was injected



The cycle of the chemical reactions in the adrenaline molecule when it functions as a catalyst, showing the formation of the ketone followed by enolization with the hydrogen of the methyl amine group

Other Catalysts Affecting Rate of Metabolism

If it is true that thyroxin acts as a catalyst and that its catalytic activity is accomplished through its alternate oxidation and reduction, and, furthermore, that the intensity of action of its oxidized form is increased by closing the pyrrolidone ring, it seems probable that other substances which are known to influence basal metabolic rate and which also act as catalysts must function in a similar manner. Physiologists have long suggested that adrenaline acts as a catalyst, and Boothby has shown that the curve of response to adrenaline, when expressed in hours, and the curve of response to thyroxin, when expressed in days, can be superimposed (Figure 9). This is suggestive that adrenaline and thyroxin react essentially in the same manner—that is, that they do the same thing although the time relationships are different. Adrenaline has been shown to react with molecular oxygen, but no mechanism has been suggested which would be comparable to closing the pyrrolidone ring in thyroxin, by which the intensity of the oxidizing power of the adrenaline molecule could be increased sufficiently to act as a stimulant to oxidation. The essential active group in thyroxin appears to be $\overline{\text{C–C–N–}}$. If in adrenaline the hydrogen attached to the nitrogen could enolize with the ketone formed by the oxidation of the two hydrogen atoms, a similar $\overline{\text{C–C–N–}}$ group would result. It is possible that the basal metabolic rate would be affected by this group in adrenaline, as it is stimulated by the identical group in thryoxin.



The $\overline{\text{C—C—N—}}$ grouping in lactam No. 3, with the same grouping which may occur in adrenaline in its oxidized form

In order to test this hypothesis adrenalone was administered to a normal dog, and it was found that, without any change in blood pressure and when the adrenalone was injected in a dilute solution slowly, 0.4 mg. increased the basal metabolic rate of a 14-kg. dog about 30 per cent. This is approximately the same amount that adrenaline increased the basal metabolic rate when similarly injected.

d-Adrenaline,[1] which has much less effect on blood pressure than *l*-adrenaline, was also found to produce marked influence on the basal metabolic rate. If, then, the hydroxyl group in adrenaline is prevented from oxidizing to the ketone group, enolization with the hydrogen from the nitrogen would be impossible and there should be no increase in basal metabolism when this substance is administered. The injection of the monoethyl ether of adrenaline produced no change in the basal metabolic rate. Also the injection of an anhydride of adrenaline, the ether linkage occurring through the O—H group of the side chain, was without effect on basal metabolic rate. Further work with other derivatives of adrenaline is necessary and is being carried out at the

[1] The writer wishes to express appreciation to H. A. Metz Company for the adrenaline derivatives used in this work.

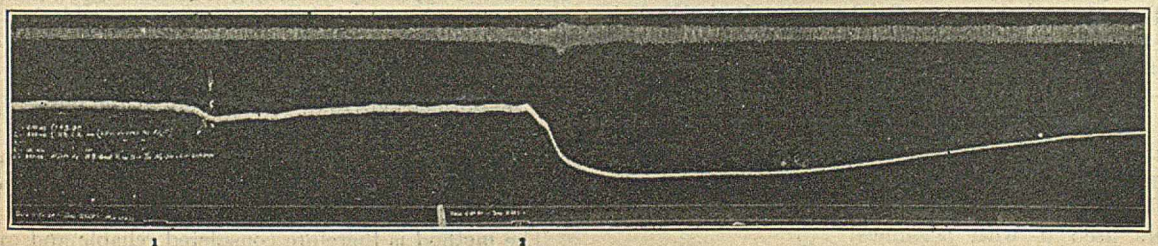


Figure 8—Kymographic Tracing Showing Blood Pressure of a Normal Dog under Ether Anesthesia
At 1, 200 mg. of lactam No. 4 with the nitrogen bond, but open pyrrolidone ring, were injected with no appreciable effect. At 2, the same amount of lactam No. 4 with its nitrogen bond, but with the pyrrolidone ring closed, was injected

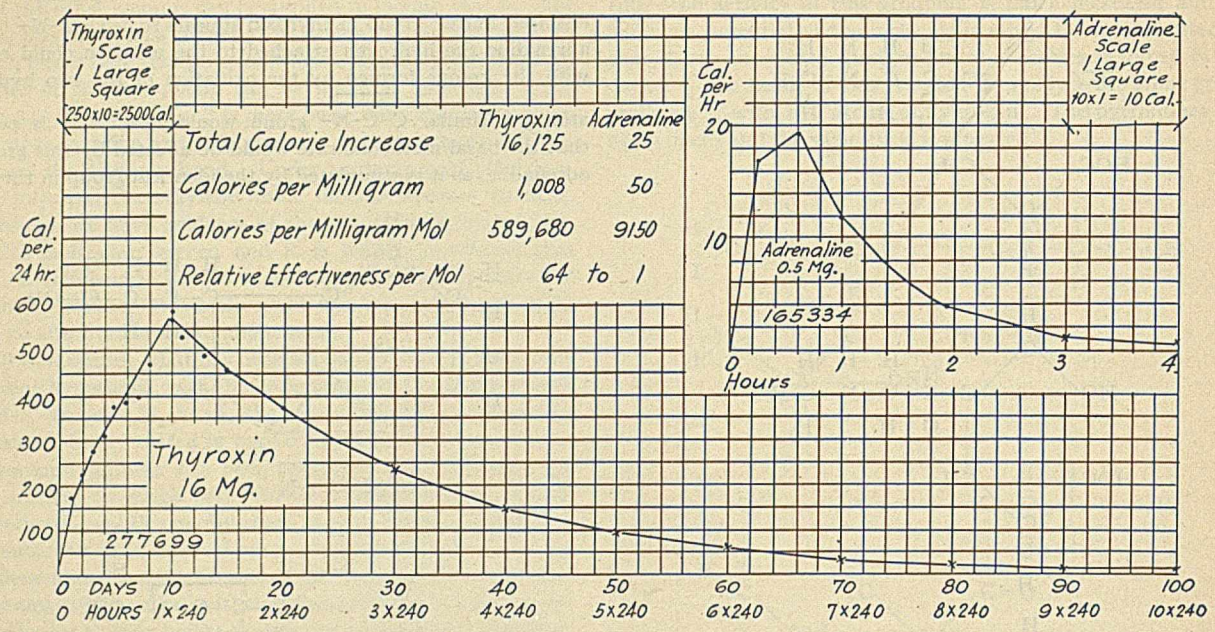


Figure 9—Curve Showing Response in Basal Metabolic Rate to Adrenaline Expressed in Hours and to Thyroxin Expressed in Days (Boothby and Sandiford)

present time, but it seems probable that the oxidizing power of adrenaline in the form of its ketone is brought about by the formation of the $\overset{|}{C}-C-N-$ group. That the two hydroxyl groups on the benzene ring are involved is also indicated, but apparently they are not indispensable.

The application of this hypothesis to other substances is very inviting and the reactions of bios described by Eddy and his co-workers led me to suggest, in discussing Eddy's paper at the December, 1924, meeting of the A. A. A. S., that the structural formula agreeing with his empirical formula of $C_5H_{11}O_3N$ is δ-hydroxyl-γ-aminovaleric acid. In this compound oxidation of the hydroxyl group to aldehyde could be followed by enolization with the amine group and the formation of the $\overset{|}{C}-C-N-$ link. I am at present testing this hypothesis.

Detection of Diethylphthalate in Perfume[1]

By Frederick Breithut and P. Max Apfelbaum

The College of the City of New York, New York, N. Y.

RALEIGH and Marie[2] report that the official test for the detection of diethylphthalate in ethyl alcohol "has been found by the writers to be unreliable, as a distinct fluorescence will develop with grain alcohol known to be free from diethylphthalate."

As diethylphthalate is one of the denaturants the use of which is permitted in the manufacture of perfumes (Formula 39-B, specially denatured alcohol), the reliability of the test for diethylphthalate is sometimes a matter of importance. This truth was brought forcibly to the writers' attention in a recent court case. One of the points at issue was whether or not diethylphthalate was present.

Blank tests showed that the official test for diethylphthalate is unreliable. A marked fluorescence develops even when diethylphthalate is absent. These results therefore agree with the findings of Raleigh and Marie on this point. By replacing resorcinol with phenol, however, a substitute test was developed which was found to be reliable, not only with grain alcohol alone, but also with perfumes.

The following gives the technic of the modified test as the writers used it with perfumes:

Ten cubic centimeters of the perfume were treated with a saturated solution of sodium chloride and the resulting mixture was centrifuged to remove the oil layer. The water layer was then placed in a distilling bulb, 5 cc. of sodium hydroxide (10 per cent solution) added, and the mixture distilled. (The distillate was used for other tests.) The residue from this distillation was then evaporated on the steam bath, and finished just to dryness on a hot plate. The dry residue was mixed thoroughly, when cooled, with an equal amount of phenol. A portion of this mixture was treated with five or six drops of concentrated sulfuric acid and kept at 160° C. for 3 minutes. One cubic centimeter of water was added to the fused mass, which was then made alkaline with dilute sodium hydroxide solution. A pink color, discharged on making the solution acid and re-appearing on making it alkaline again, indicates the presence of phenolphthalein in the mixture, and therefore the presence of diethylphthalate in the original substance.

Blank tests employing all of the reagents used in making this determination, individually and in all possible combinations, gave negative results in all cases. When diethylphthalate itself, or mixtures containing this substance were tested in exactly the same manner, positive results were obtained in all cases.

The method is therefore considered reliable and can probably be used in testing for diethylphthalate in mixtures other than perfume.

[1] Received March 2, 1925.

[2] *J. Am. Chem. Soc.*, **47**, 589 (1925).

Report of the Physical Testing Committee of the Division of Rubber Chemistry[1]

PRESENTED IN PART AT THE 67TH MEETING OF THE AMERICAN CHEMICAL SOCIETY, WASHINGTON, D. C., APRIL 21 TO 26, 1924

THE investigations which form the subject matter of this report have been confined to the methods of preparation and testing of experimental vulcanizates by the so-called tension tests. This committee has confined its efforts to the elucidation of factors which have either been in dispute or which have not been satisfactorily treated in published methods on physical testing. Its aim has been to make the investigations and recommendations as practical as possible, taking into due account the present apparatus and methods in general use in the rubber testing laboratories of the United States. In short, it has tried to point out sources of error and to make such recommendations as might be hoped to lead to a general improvement in routine and experimental mechanical testing.

There is a vast fund of excellent experimental procedure available in De Vries' "Estate Rubber," G. S. Whitby's "Plantation Rubber and the Testing of Rubber," and *Circular* 38 of the U. S. Bureau of Standards, with which everyone interested in the problems of mechanical testing should be familiar. It was not intended to displace this material, but rather to supplement it in certain places where it lacks definiteness to the needs of American uses and procedures.

This committee also recognizes that certain types of rubber products are sold on specifications, the fulfilment of which demands that these goods shall pass certain minimum requirements when tested under a given set of conditions, these conditions having been established by the purchaser or its agents. It is not the purpose or function of this committee to specify in what manner these conditions of mechanical testing should be changed or modified. It rests with this committee only to recommend a procedure which will best suit the needs of the members of this SOCIETY in their routine and research methods for the physical testing of experimental compounds.

Following the decision of the Council of the A. C. S. with regard to the use of the metric system in all SOCIETY activities and publications, the data are reported in metric units, together with the English equivalents in most cases.

Table I

Roll diameter	Cm.	15	15	20	15	20
	Inches	6	6	8	6	8
Roll length	Cm.	30	30	30	30	40
	Inches	12	12	12	12	16
R. p. m.	Slow roll	18	..	10	23	20
	Fast roll	26	..	13	23	29
Surface speed in feet per minute	Slow roll	28	42	27	36	41
	Fast roll	41	50	35	36	54
Surface speed ratio		1.44	1.18	1.30	1.00	1.30

Milling

A wide latitude exists as to size and speed of mill rolls, friction ratios, etc. As a matter of interest Table I gives specifications of experimental mills in use in several large rubber laboratories.

[1] Received March 5, 1925.

The main fact to be considered is that rubber can be broken down to the same degree on any kind of a mill by suitable adjustments of the time and temperature. In general, rubber should be plasticized on the mill under such conditions as will cause a minimum destruction of the "nerve" of the rubber. An attempt was made to throw some light on this point by milling rubber stocks to different degrees of softness as determined by Williams' method for plasticity [THIS JOURNAL, 16, 362 (1924)], and then curing and testing the resulting stocks under comparable conditions. Thus in Table II are given the physical tests on slabs cured from stock milled to various plasticities (K).

The stock was a friction stock containing 93 per cent rubber by weight cured for 60 minutes at 143° C. (290° F.). The K values indicate the softness; the lower the K value the softer the stock.

Further data of the same type are given in Table III.

This stock contained 93 per cent rubber by weight, curing in 30 minutes at 125° C. (258° F.). The accelerator was mercaptobenzothiazole.

These data indicate quite conclusively that:

1—The stress-strain characteristics of the cured slab run parallel with the softness of the uncured stock.

2—Milling at low temperatures leads to excessive softness of the uncured stock, which manifests itself even after curing in the softness of the S-S curve and more noticeably in tensile.

3—The higher the temperature of the stock on the mill the less the time factor; that is, increase in length of milling time is less injurious at high milling temperatures.

4—The effect is purely physical, the rate of combination of sulfur being unaffected.

The same sort of experiments were next extended to stock compounded with zinc oxide. In a stock containing 50 smoked sheets, 50 pale crepe, 60 ZnO, 6.2 sulfur, and 0.5 Hexa by weight cured for 60 minutes at 143° C. (290 ° F.), the results given in Table IV were obtained.

Table IV

Stock	K according to Williams	Kg./Sq. Cm. at: 300%	400%	500%	600%	Tensile Kg./sq.cm.	Elong. Per cent
*M*15	1.1	40	65	106	177	262	690
16	3.0	34	57	93	152	260	735
17	4.2	30	51	86	142	242	735

These results are directly contrary to those obtained on very lightly compounded stock (Tables II and III). The experiments were therefore repeated by a different laboratory. The cure was 60 minutes at 141° C. (287° F). in same four-cavity mold (Table V).

These results indicate a softness of the cured stock and low tensile properties which parallel the softness of the uncured

Table II

Stock	Milling Conditions Temp. ° C.	Time Min.	K	Kg./Sq. Cm. at: 500%	600%	700%	800%	Tensile Kg./sq. cm.	Elong. Per cent
*M*1	40	25	1.1	16	28	56	100	138	865
2	100	25	4.3	18	34	64	109	130	840
3	100	5	4.9	25	42	76	134	142	815

Table III

Stock	Milling Conditions Temp. ° C.	Time Min.	K	Kg./Sq. Cm. at: 500%	600%	700%	800%	Tensile Kg./sq. cm.	Elong. Per cent	Combined S Per cent
*A*1	100	13	4.7	18	35	65	116	144	845	1.07
2	100	25	3.7	18	32	59	106	144	860	1.13
3	100	55	3.0	15	27	52	96	146	880	1.16
4	40	30	2.0	12	20	38	70	105	870	1.13
5	40	60	1.6	10	15	23	40	72	915	1.07
6	40	120	1.3	6	8	13	25	44	890	1.05

stock. The S-S results for Stock *X2* are anomalous, although the tensile figures are regular.

Table V

Stock	Milling Conditions Temp. ° C	Time Min.	*K*	Kg./Sq.Cm. at: 400%	500%	600%	Tensile Kg./sq.cm.	Elong. Per cent
X1	100	23	5.2	45	83	140	240	730
2	80	30	3.5	51	91	153	240	710
3	40	55	2.2	45	83	140	200	685
4	40 (tight mill)	55	1.7	42	77	128	160	650

Still another series of tests was made using the following formula: 100 rubber, 60 ZnO, 4 sulfur, and 1.5 of triphenylguanidine. The cure was 120 minutes at 141° C. (287° F.) in same four-cavity mold (Table VI).

Table VI

Stock	Milling Conditions Temp. °C.	Time Min.	*K*	Kg./Sq.Cm.at: 400%	500%	600%	Tensile Kg./sq.cm.	Elong. Per cent
X5	100	17	4.6	60	101	169	249	690
6	80	22	2.8	57	96	158	212	670
7	80	100	1.4	53	88	142	156	620
8	40 (tight mill)	100	0.9	57	96	...	113	530

The tensile figures drop off with increasing softness of the uncured stock, as do the intermediate points on the S-S curve, with the exception of *X8*, which is slightly stiffer than *X7*.

The general conclusions are, that increased softness of the uncured stock quite probably leads to lowered physical properties of the cured stock.

Further data show that the volatility of the accelerator may cause wide variations. The stock used contained 50 smoke sheet and 50 pale crepe, 6 ZnO, 3 sulfur, and 0.9 Hexa. The cure was 60 minutes at 141° C. (287° F.) and all stocks were cured and tested under identical conditions (Table VII).

The percentage of combined sulfur is taken as the index of the extent of the vulcanization reaction, and it will be noted that this figure varies from 1.25 to 1.55 per cent, the lower figure being obtained at the higher temperatures of milling. It would appear, therefore, that the accelerator escapes at the high temperatures, and naturally more escapes the longer the milling time. The data in this table are at direct variance with the data in Table III, where the accelerator used is not volatile and gives practically constant values for combined sulfur. In that case the plasticity of the uncured stock exerts a marked effect on the properties of the cured stock. In the present case the same conditions which give high *K* values also lead to volatilization of the accelerator, and the loss of accelerator more than offsets any advantage to be gained by trying to degrade the rubber to a lesser degree by less drastic milling.

The precise conditions of time and temperature of milling which should be used in routine testing are thus rendered rather difficult of elucidation, but since the milling operations in the factory are generally carried out at rather elevated temperatures (generally in excess of 80° C.), the following recommendations seem to be justified:

1—Mill at as high a temperature for as short a time as consistent with thorough mixing and good dispersion of pigment.

2—Endeavor to standardize both time and temperature of milling, with regard to the composition of the stock. In general, stocks high in rubber content should be milled at temperatures from 80° to 100° C., and the time need rarely exceed 20 minutes. Highly compounded stocks generally require somewhat lower temperatures but rarely lower than 60° C.

3—Regulate the volume of the batch to the size of the mill and adjust the opening between the rolls to a definite standard.

Order of Mixing—No new experimental work has been done on this item. The general experience of the committee sanctions the following order—viz., rubber, reclaimed rubber, pitches and waxes, accelerator, liquid softeners, fillers, sulfur. In most cases the sulfur may be added with the fillers. Where reclaimed rubber is used it is best to break the crude rubber and reclaimed rubber separately and then blend them together.

Details of Mixing Operation—After the ingredients have been incorporated the stock should be thoroughly mixed by cutting and rolling, etc., and if lumps of compound are visible the stock may be refined by passing through tightly set rolls one to three times. Ordinarily, 3 to 5 minutes' mixing is ample. The mill rolls should then be set to gage and the stock allowed to run for 1 minute to "set the grain." The mills should be set at such gage that the stock when cold is from 10 to 25 per cent thicker than the cured slab.

Preparation for Curing—The uncured sheets should be aged overnight before curing. As a matter of fact, sheets aged for 30 minutes before curing gave tensile results only 5 per cent lower than stocks aged overnight. Two-hour age periods gave results identical with longer periods. However, the longer period is recommended as a precautionary measure. For general test purposes the uncured stock should be cut to fit the mold cavity, and the sheets are best placed in the mold in such position that the test pieces are died out in the direction of the "grain"—i. e., in the plane of the mill or calender.

Curing

The committee makes no recommendations for any particular manufacturer's product as regards presses or press equipment for temperature indication or control. Neither does it recommend curing in a press in preference to some other method of curing—for instance, in an oil bath, or in a steam vulcanizer. However, since most rubber laboratories use the hydraulic platen press, it has confined its work to this type of apparatus.

Requirements for Proper Operation of Platen Presses—1—It is imperative that no condensed water be allowed to collect on the surface of the platens in contact with the molds. If this condition does exist it is quite impossible to maintain the proper temperature. The surface of the platens will always be at a lower temperature than the steam, because the layer of condensed water greatly retards the conduction of heat from the steam to the face of the platen. Therefore, the thermometer in the steam may indicate the required temperature, but the actual temperature of the stock in the curing mold may be considerably lower. This condition may be remedied as follows:

(*a*) By the use of presses of the bored platen type.

(*b*) If the platens are of the chamber type, satisfactory conditions may be maintained by insuring good drainage by placing the steam outlet pipe so that it is slightly below the bottom of the steam chamber.

2—It is equally important that a good flow of *live pure steam* be kept in constant circulation through the platens. This

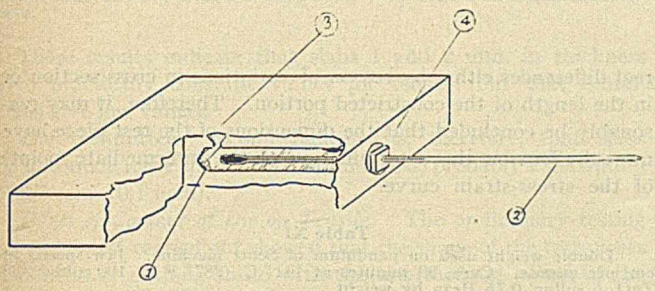
Table VII

Stock	Milling Conditions Time Min.	Temp. ° C.	*K* at 70° C.	Kg./Sq. Cm. at: 500%	700%	Tensile Kg./sq. cm.	Elong. Per cent	Combined S Per cent
1	25	40	1.82	27	93	146	780	1.44
2	25	55	2.08	26	89	166	805	1.43
3	25	70	2.50	25	86	159	810	1.40
4	25	90	2.77	23	79	148	810	1.28
5	10	90	3.32	25	87	168	815	1.36
6	20	90	3.17	24	78	153	815	1.25
7	5	90	3.72	26	92	175	820	1.45
8	25	25	1.63	25	89	148	790	1.54
9	40	25	1.55	26	89	146	790	1.55
10	10	55	2.67	27	97	172	800	1.48

can ordinarily be obtained by allowing a portion of the steam to by-pass the steam trap.

3—Temperatures should be determined by a mercury thermometer, preferably one to each platen, mounted in the platen in such fashion that circulating steam is in contact with the bulb or well of the thermometer. It is also advisable to check the surface of the platens for *uniformity* of temperature by means of thermocouples, or by the means suggested in the next paragraph.

4—Owing to the large temperature coefficient of the vulcanization reaction it becomes imperative for accurate curing to be able to determine the actual temperature of the mold with precision. For a very complete exposition of the effect of the temperature on curing see de Vries, "Estate Rubber," p. 543. Briefly, if the temperature coefficient is 2.6 per 10° C., a difference of 1° C. will make a difference of about 10 per cent in the curing effect, corresponding to about 6 minutes on a 60-minute cure.



1—Mercury well
2—Standard thermometer
3—Overflow cavity
4—Stuffing box

Figure 1—Press Standardizing Block

The apparatus shown in Figure 1 has been found exceedingly helpful in standardizing and controlling the curing press. It is simply a block of soft steel of the thickness of the curing mold, and having the length and breadth dimensions of the test sheet. A small vented well is drilled into the block in such fashion that a small accurate thermometer of the Anschutz type (reading to 0.1° C.) may be inserted through a stuffing box. The well is then filled with mercury and the block can then be placed between the platens of the press and the temperature reading obtained at intervals until constant. By using a standard thermometer one can readily adjust the steam requirements of the press to give the required temperature and can also check the operation of the presses from time to time.

5—There are two systems of piping in use: one, the so-called series system, wherein the steam outlet pipe on the top platen connects to the steam inlet pipe on the next lower platen, etc.; the other, the so-called parallel system, admits steam to all platens through a common header, and the outlet pipes are connected to another header. Either arrangement is satisfactory.

The presses should be sheltered from direct drafts of air, as the radiation and convection factors can become quite appreciable. It seems almost unnecessary to add that the platens of the press should be flat and parallel so that good contact with the mold at all points is assured.

Molds—1—Engraved steel molds with a rigid steel cover plate are recommended as giving more perfect cured slabs than frame type molds—i. e., the thickness of the cured slab is more uniform. The thickness of each half of the mold should be not less than 1 cm. (0.4 inch) to secure sufficient rigidity. Uniformity of gage of cured slab is an important consideration in securing accurate test data.

2—The molds should be of such size with reference to the area of the platens of the press that the edges of the rubber slabs are at least 8 cm. (about 3 inches) from the edge of the platens. Radiation from the sides of the platen tends to lower the temperature of the press and the mold at the extreme edges.

3—The molds should be well heated before any cures are made. Ordinarily, 20 minutes in the press with platens closed is sufficient to heat the molds thoroughly. With the molds well heated, cures may be made without allowing for the temperature lag of the mold except for very short cures. If delays occur between successive heats, the molds should be covered and the press plates closed in order to keep the molds up to temperature. Cured sheets should be removed from the molds immediately after the cure is finished, and in the case of ultra-accelerated stocks, curing in a few minutes, should be placed in cold water immediately on removal. Naturally, the thickness of the mold cavity—i. e., of the cured slab—will determine to a large extent the actual value of the so-called "mold lag." The committee has determined the temperature rise, experimentally by thermocouples, of the center of slabs 1, 2, and 4 mm. thick (0.04, 0.08, and 0.16 inches) and from the temperature-time curves thus obtained has calculated the "equivalent cure." This equivalent cure is the time in minutes that would be necessary if the stock could be maintained at the press temperature during the entire curing period.

Table VIII

Thickness of slab	In press		
Mm.	5 min.	10 min.	15 min.
0	5	10	15
1	4.5	9.5	14.5
2	3.3	8.2	13.2
4	1.5	5.3	10.4

Thus, even for thin sheets, 2 mm. (0.08 inch), there is a lag of approximately 2 minutes for cures under 15 minutes.

Testing

Preparation of Test Specimens—The cured slabs should not be tested until 24 hours after removal from press. The test pieces may be died from the sheet by a die and mallet or the die may be mounted in an arbor press. Either method is acceptable provided it gives test strips with *straight, parallel* edges. Any other condition is to be avoided. In general, the thicker the slab the more difficult it is to cut acceptable strips by either method. The width of the die also has an influence. Thus it is practically impossible to cut perfect test strips from slabs 4 to 5 mm. (0.16 to 0.2 inch) thick with a 3-mm. (0.13-inch) die using the die and mallet method, whereas a 6-mm. (0.25-inch) die gives much better strips. A sharp blow gives a better result with the thick slab than does a slower one.

Naturally, the dies should be kept well sharpened, and furthermore, dull dies tend to cut wider strips than sharp dies. As will be shown later, since slight changes in the contour of the test piece may make appreciable differences in the tensile, it becomes necessary to guard against changes in the die due to sharpening, warping, etc. This is best done by checking against a template from time to time.

The width of the test pieces should be checked occasionally. This actual width will generally be found to coincide within 1 per cent of the dimension of the die. The width of the test piece may be determined by means of a micrometer caliper using only the very least pressure necessary.

Gaging the Test Piece for Thickness—The general practice is to determine the gage—i. e., thickness of the test piece in the constricted area—and to use the minimum gage for figuring the cross-sectional area. The pressure exerted on the test piece will naturally have an effect on the determination of gage. The following experiments indicate the nature and magnitude of this effect.

Factors Influencing Determination of Thickness. A Randall and Stickney thickness gage was revised by removing the tension spring and arranging for the application of pressure by means of dead weights. Rubber test pieces 6.5 mm. (0.25 inch) wide were then gaged, the diameter of the presser foot and the pressure being varied. Rubber stocks of varying degrees of hard-

Table IX

	Stock	Shore Durometer hardness	Dead Wt.	Apparent Tensile, Kg./Sq. Cm. 0.63 cm. = 0.25 in. dia. foot		1.25 cm. = 0.5 in. dia. foot			
			grams	56(185)[a]	112(370)	225(740)	56(46)	112(93)	225(185)
			ounces	2(40)	4(80)	8(160)	2(10)	4(20)	8(40)
1	Pure gum	35		100.5	101.7	103.9	97.9	99.0	100.0
2	Red inner tube	40		99.8	101.5	102.6	97.7	98.6	100.0
3	Belt friction	40		100.0	101.3	103.1	98.2	98.7	100.0
4	Friction containing 20% reclaimed tires	45		100.4	101.3	102.6	98.8	99.4	100.0
5	Black auto tread	50		100.3	100.7	101.5	99.3	99.5	100.0
6	Bumper stock	80		100.1	100.7	100.7	99.4	99.7	100.0

[a] Figures in parentheses indicate pressure per square inch (per sq. cm.).

Table X

Conditions: Double weight used on pendulum of Scott machine. Jaw speed, 50 cm. (20 inches) per minute

Die	Width Mm.	Thickness Mm.	Cross section Sq. mm.	Length of constricted portion Cm.	Kg./Sq. Cm. at: A 300%	A 400%	A 500%	A 600%	B 300%	B 400%	B 500%	B 600%	B 700%
A	10	2	20	2.5	65	107	161	221	14	20	31	59	107
B	10	2	20	2.5	64	107	161	221	14	20	31	58	109
C	10	2	20	2.5	63	107	162	224	13	20	30	58	110
D	6.5	2	13	2.5	63	107	162	224	14	20	31	59	112
E	10	2	20	5.0	65	107	163	227	13	20	32	61	114
F	10	2	20	5.0	64	107	161	228	14	20	32	62	114
G	10	2	20	5.0	65	107	165	228	14	20	33	62	113

A— Tread stock, approximately 20 vol. gas black per 100 vol. rubber.
B— Inner tube, 93% rubber by weight.

ness (Shore Durometer) were used in these tests, the thickness of the test strip being measured at the same location on the test strip, under the various conditions.

Taking the 1.25-cm. (0.5-inch) diameter presser foot, and a load of 225 grams (8 ounces) as the standard condition, the results are expressed in terms of the apparent tensile strength in kilograms per square centimeter, assuming the standard conditions to give a tensile of 100 kg. per sq. cm. By multiplying by 10 the same comparison on the basis of 1000 pounds per square inch can be made. Thus, if the pressure is increased the gage reading (thickness), and therefore the cross-sectional area, will be decreased. Using the thus determined cross-sectional area in calculating the tensile strength, higher values for tensile per unit area are obtained. Table IX gives these values.

Stock 1 varies from 97.9 to 103.9 or 6 per cent, as the pressure increases from 46 to 740 grams per sq. cm. (10 to 160 oz. per sq. in.). This is the softest stock tested.

Stock 6 (the hardest stock) varies only from 99.4 to 100.7 or 1.3 per cent, as the pressure is increased.

The desired pressure is that which gives the best average results for all kinds of stock and this seems to be best secured by a pressure of 185 grams per sq. cm. (40 oz. per sq. in.). The committee therefore recommends a presser foot 1.25 cm. (0.5 inch) in diameter and a spring tension of 225 grams (8 ounces). This agrees with most specifications.

Influence of Die Dimensions on Stress-Strain Data—The testing machines in most common use are of the vertical type, the strain being applied to the test piece by a traveling clamp, stress being taken up by a pendulum lever. The rate of movement of the traveling clamp is commonly 50 cm. (20 inches) per minute. This later condition naturally necessitates that the stress-strain data be not obtained under definite conditions of either constant rate of application of load or of elongation, as the characteristics of the stock under test determine the rate at which the load will be taken up, and a variation in the length of the test piece will affect the latter. The committee has a considerable amount of data bearing on these points, which data will be considered with respect to their bearing on the intermediate points of the stress-strain diagram and the final points—i. e., tensile and elongation.

Effect of Length of Constricted Portion on Intermediate Points of Stress-Strain Curve. Each individual result in Table X is the average of the results of ten strips. The results show conclusively that for high-grade compounds of the above types there is no difference on test pieces whose constricted portions are 5.0 and 2.5 cm. (2 and 1 inches) in length.

Effect of Cross Section (Table XI). Each individual result is the average of at least eight strips. These results show no real differences either by reason of variations in cross section or in the length of the constricted portion. Therefore, it may reasonably be concluded that the dimensions of the test piece have no real effect on the determination of the intermediate points of the stress-strain curve.

Table XI

Double weight used on pendulum of Scott machine. Jaw speed, 50 cm. per minute. Cure, 90 minutes at 141° C. (287° F.). 100 rubber, 30 ZnO, 5 sulfur, 0.75 Hexa by weight.

Die	Width Mm.	Thickness Mm.	Cross section Sq. mm.	Length Cm.	Kg./Sq. Cm. at: 300%	400%	500%	600%	700%
1	12.7	2.0	25.4	5.0	23	38	72	141	..
5	6.5	2.0	13.0	5.0	22	36	71	141	245
3	12.7	2.0	25.4	2.5	23	39	74	142	232
6	6.5	2.0	13.0	2.5	21	35	71	140	240
7	6.5	2.0	13.0	2.5	22	36	70	137	236
9	3.2	2.0	6.4	2.5	22	35	67	143	252
4	10.0	2.0	20.0	2.5	21	35	68	136	..
2	10.0	2.0	20.0	5.0	21	36	69	136	..
2A	10.0	2.0	20.0	5.0	22	36	70	138	..

Effect on Tensile—*Influence of Die Dimensions on Tensile.* The effects of cross-sectional area and length of the constricted portion of the test piece on the values for tensile are rather difficult to elucidate. The committee has some data, however, which bears on these points. In Table XII are given the results on several compounds tested with two dies identical in contour except that the lengths of the constricted area were 5.0 and 2.5 cm., respectively. At least ten strips were tested for each result in the table, those values being rejected which varied by more than twice the average deviation from the mean.

Table XII

Die	Die length Cm.	Compound I T	I E	II T	II E	III T	III E	IV T	IV E	V T	V E
5	5	253	725	224	760	270	660	239	635	262	535
6	2.5	281	745	268	820	281	670	251	650	290	570
		Formula, by weight									
Rubber		100		100		100		100		100	
ZnO		30		5		80		100		12	
Gas black										35	
Sulfur		5		6		6		6		6	
Hexa		0.75		1		1		1		1	
Cure at 141° C. (287° F.), minutes		90		75		90		75		75	

T = tensile in kg. per sq. cm. E = per cent elongation.

These data indicate conclusively that the long die gives lower tensile figures. Using the same rate of travel of the jaw of the testing machine, this means, of course, that the load is applied to the longer strip at a slower rate. This finding is in harmony with the data of *Circular* **38**, 4th ed., page 60 of the Bureau of Standards, wherein it is shown that, using the same test piece, an increased rate of stretching leads to higher tensile values. The intermediate points on the S-S curve were identical for the two dies.

In an attempt to determine the effect of variations in cross section on the tensile results, the data in Table XIII were accumulated. The direct experiment was to determine the effect of varying the thickness of the cured slab, but indirectly it was hoped to be able to compare results on test pieces of the *same cross-sectional area* but of varying *width* and *thickness*. This comparison does not hold because the contour of the different dies used varied so widely as totally to mask the effect sought.

Table XIII

Die	Width Mm.	Thickness Mm.	Area Sq. mm.	Length Cm.	Tensile Kg./sq. cm.	Elong. per cent
6	6.5	1	6.5	5.0	222	650
9	3.2	1	3.2	2.5	253	685
8	6.5	1	6.5	1.75	224	655
6	6.5	2	13.0	5.0	227	658
9	3.2	2	6.5	2.5	240	670
8	6.5	2	13.0	1.75	227	658
6	6.5	4	26.0	5.0	210	635
9	3.2	4	12.8	2.5	196	615[a]
8	6.5	4	26.0	1.75	216	645

[a] Results somewhat low because with 3.2-mm. (0.13-inch) die and thick slab (4 mm.) the test piece was not perfect—i. e., the die-cut edges were concave.

These results indicate that slabs 1 and 2 mm. in thickness give practically constant values for tensile, but that 4-mm. slabs give low values.

The committees' recommendation is, therefore, that slabs be not much more than 2 mm. in thickness, probably a maximum of 2.5 mm. (0.1 inch).

Effect of Contour of Die on Tensile. The preliminary testing program first carried out showed that the shape of the test pieces had little or nothing to do with the intermediate points of the stress-strain curve but profoundly affected the tensile and elongation results. About ten variously shaped dies were tested and the results are given in Table XIV and also in Figure 2.

The figures for tensile are the average of not less than fifteen test strips—individual tests being rejected if their deviation from the mean was more than twice the average deviation. The error was on the average ±3 kg. per sq. cm. (±50 lbs. per sq. in.).

Die 9 gives the highest figures, but has a width of 3 mm. (0.13 inch), and for general test purposes (particularly for S-S data) is considered unreliable, owing to its small cross section.

Standards Die *B* (*Circular* 38, 4th ed., page 50), except that the length of the constricted portion has been reduced to 1.25 inches (to accommodate 1-inch bench marks).

The contours of the dies are shown in Figure 2. The position of the breaking point is quite characteristic for each die and is shown as the irregular line across the test specimen. The peculiar break at the shoulder of the test piece is due to a localization of stress at that point, sometimes referred to as a cross-stress. This localization can be demonstrated very neatly by printing a design consisting of intersecting lines making squares about 3 mm. on a side, on to the rubber test specimen while under the highest tension possible short of breaking the test piece. When the tension on the test piece is released the squares (as printed) are deformed, the cross lines being arced similarly to the breaking line. At some point at the shoulder of the test piece the lines across the specimen will be a minimum distance apart, and it will be at this point that the test piece will break, for here the rubber is stressed the most (Figure 3).

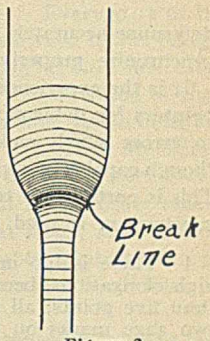


Figure 3

Of course, the ideal design for a die would be of such contour that the cross-stresses would be absent and the stresses would be highest and of uniform intensity in the constricted portion of the test piece. However, the contour of the die which will produce this desired condition cannot be determined, because every different sample of rubber will react differently depending on its ultimate elongation. A very extensible sample will deform to an entirely different final contour at the instant of break than will a stock of low extensibility. In general, a variation in the original contour of the die has less effect on the breaking values of stocks of low elongation. Naturally, pure gum stocks are the most dependent on the original contour of the die.

Methods of Securing Stress-Strain Data—In using a non-recording testing machine of the vertical type (such as the Scott rubber tester) it becomes necessary to devise some system for ob-

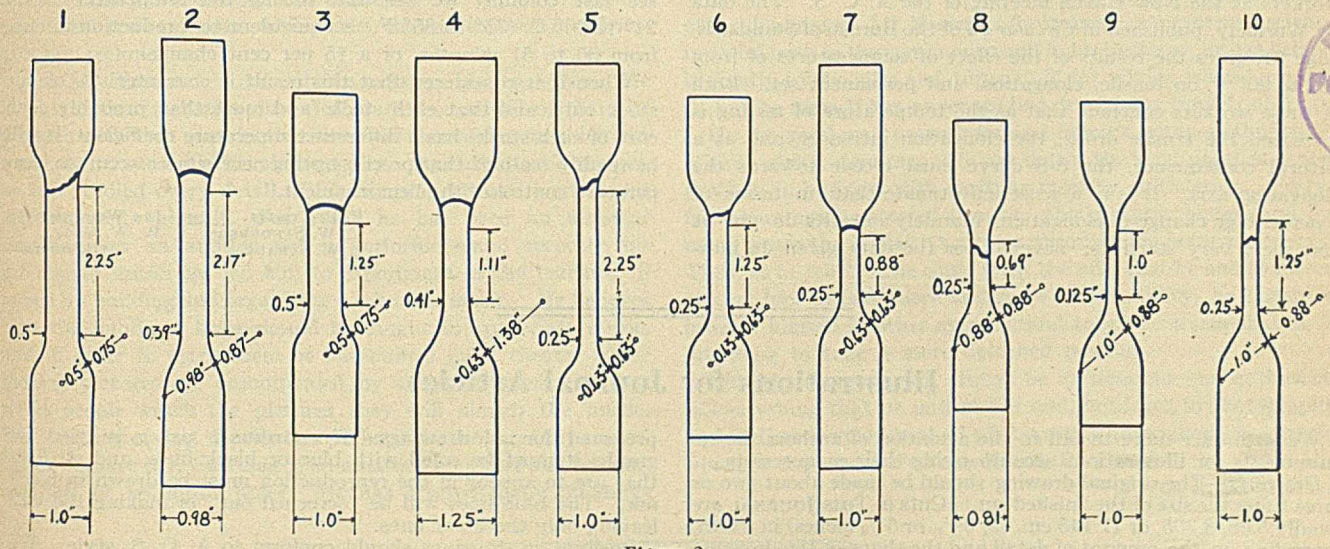


Figure 2

Dies 6, 8, and 10 are very close together, but Die 8 was rejected owing to its shortness (length 0.7 inch), which necessitates the use of gage marks only 0.5 to 0.6 inch apart. This leads to considerable error in determining the length of the specimen in tension and consequently makes for inaccuracy of S-S data under ordinary working conditions.

This narrows the choice down to Dies 6 and 10, either of which are acceptable. Die 10 has the same dimensions as Bureau of

taining simultaneous readings of the loads and elongations. This is ordinarily done by the so-called "two-observer" method or by means of some semi-automatic device such as described by Burkley, *India Rubber World* for October, 1922. The common procedure is for the operator to determine the length of the test specimen in tension and as certain definite lengths are reached to obtain the corresponding load readings from the dial of the machine. The important part of the whole procedure is to

Table XIV

(Die measurements in inches)

Die	1	2	3	4	5	6	7	8	9	10
Length of constriction	2.25	2.17	1.25	1.15	2.25	1.25	0.88	0.7	1.0	1.25
Width of die	0.5	0.40	0.50	0.40	0.25	0.25	0.25	0.25	0.125	0.25
Inside radius of shoulder	0.5	1.00	0.50	0.63	0.63	0.63	0.63	0.88	1.00	1.00
Outside radius of shoulder	0.75	0.87	0.75	1.37	0.63	0.63	0.63	0.88	0.75	0.88
Compound I—100 rubber, 30 ZnO, 5 sulfur, 0.75 Hexa; cure 90 min. at 141° C. (287° F.)										
Lbs./sq. in.	3000	3150	2800	3200	3600	3400	3300	4050	4150	4000
Kg./sq. cm.	211	222	197	227	253	281	232	285	292	281
Elongation, per cent	680	690	670	700	725	745	710	740	750	745
Compound II—100 rubber, 100 ZnO, 6 sulfur, 1.0 Hexa; cure 75 min. at 141° C. (287° F.)										
Lbs./sq. in.	3200	3170	2900	3250	4000	3570	3300	3500	3860	3550
Kgs./sq. cm.	225	223	204	229	239	251	232	246	272	250
Elongation, per cent	620	600	590	625	635	650	625	645	660	650

determine accurately the length of the specimen in tension and to synchronize properly the reading or recording of the load.

It is the experience of the committee that the use of trammel pointers for determining the length of the test piece is subject to errors which make the method intrinsically inaccurate although capable of giving good check results by the same operator. This is particularly true when a die 5 cm. (2 inches) long in the constriction is used, for the following reasons:

1—There is too much error due to parallax, particularly at high elongations, because the operator's eye must follow no less than five points, all moving with respect to one another—viz., two gage marks on the test specimen, two pointers, and one indicator on the tape.

2—For this reason the operator has a strong tendency to delay recording the load until the elongation has passed the determined point, thus leading to high values for the load.

In view of these facts experience has shown that the length of the specimen is best determined by means of a ruler of appropriate length, one end of which may be lightly held in position against one gage mark on the test strip. The load is then recorded as the other gage mark passes. The length can be determined with a sufficient degree of accuracy and the results are more nearly absolute because the operator is required to follow only one moving point.

Effect of Temperature during Testing on Stress-Strain Data. Very little has been published in this connection, the only data extant having been presented by Dr. Bruni in behalf of his coworkers at the New Haven meeting of the A. C. S. The data by Wormely, published in *Circular* **38** of the Bureau of Standards, page 61, gives the results of the effect of temperatures of from 50° to 90° F. on tensile, elongation, and permanent set. Both of these workers conclude that as the temperature of testing is increased the tensile drops, the elongation increases, and as a natural consequence, the S-S curve must recede towards the elongation axis. It is in a sense unfortunate that, in terms of a percentage change in elongation, Wormely's results do not at first seem very startling; nevertheless the data given do indicate a decided shift in the stress-strain curve. Some figures obtained in connection with some work for the Crude Rubber Committee by R. P. Dinsmore may be mentioned here.

The stock contained 100 smoked sheet, 6 ZnO, 3.0 sulfur, and 0.9 Hexa. Cures were obtained at 45, 60, and 75 minutes at 141° C. (287° F.) and gave the following properties when tested at 25° C. (75° F. room temperature):

Cure Min.	Kg./Sq. Cm. at: 500%	600%	700%	Tensile Kg./sq. cm.	Elong. Per cent
45	19	32	60	130	845
60	23	42	80	163	830
75	29	54	105	175	790

The 60-minute cures were then tested at 21° to 30° C. (70° to 85° F.) with the following results:

Temp. of test ° F.	° C.	Kg./Sq. Cm. at: 500%	600%	700%	Tensile Kg./sq. cm.	Elong. Per cent	Calcd. equiv. cure. Min.
70	21	25	45	85	167	825	63
75	24	23	42	80	163	830	60
80	27	22	39	74	170	845	55
85	30	22	36	67	150	840	51

No particular importance is attached to the tensile figures, inasmuch as enough strips were not broken to determine this figure with exactness. The S-S data, particularly at 700 per cent, are much more significant.

The results at the higher temperatures are similar in all respects to the results obtained from the shorter cures. By interpolation (on the modulus at 700 per cent *vs.* time of cure curve, see last column) we see that raising the temperature from 24° to 30° C. (75° to 85° F.) is equivalent to a reduction in cure from 60 to 51 minutes, or a 15 per cent change.

When it is considered that this result is characteristic of one stock only, and that each stock (and more than probably each cure of each stock) has a different temperature coefficient, it will be readily realized that precise testing necessitates accurate temperature control of the "environment."

E. B. Curtis
C. W. Sanderson
J. W. Schade
Ira Williams
W. W. Vogt, *Chairman*

Illustrations for Journal Articles

We wish once more to call to the attention of authors the requirements for illustrations accompanying their manuscripts.

Drawings—The original drawing should be made about two or three times the size of the finished cut. Cuts in This Journal are usually 5.08, 8.305, or 17.145 cm. (2, 3¼, or 6¾ inches) in width, depending on the amount of detail and the shape of the drawing. Most satisfactory results are obtained when authors have this in mind, especially in lettering their drawings. On the other hand, some figures have to be redrawn simply because the lettering is so small that it cannot be read upon reduction. Numbers and letters should be plain, without attempt at ornament, and at least 1.6 mm. (1/16 inch) high in the reproduction. Care should be taken not to waste space, as this usually means greater reduction and a less satisfactory illustration. Often it is possible to combine several curves in one figure and thus not only save space, but enable the reader to make comparisons at a glance.

A pure white paper or tracing cloth and black India ink are preferred for all drawings. If coördinate paper is used for graphs it must be ruled with blue or black lines, and all lines that are to appear in the reproduction must be drawn in black ink. The blue lines will be "screened out" in making the cut, leaving only the black lines.

Spelling on drawings should conform to A. C. S. style. We dislike to see one style of spelling on the cut and another in the text, but it is an added expense to have new drawings made for this reason alone.

Half-Tones—Photographs should be clear cut, with fine details and rather pronounced contrasts; glossy prints give the best results. They need not be mounted, but should be sent flat, protected by cardboard, as all cracks and creases show in the reproduction.

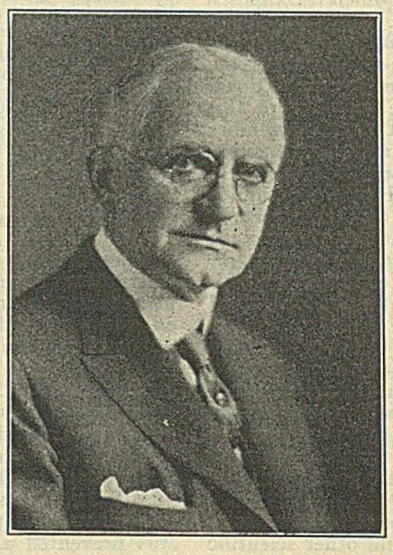
Each illustration should be plainly marked with number and title, such designation to be made under the illustration and not a part of it.

AMERICAN CONTEMPORARIES

George Eastman

IN AN interview published a short time ago Mr. Eastman described himself as "an amateur photographer." The interview deals especially with the "photographer," with the growth and development of the business which Mr. Eastman has made; but the characterization of George Eastman which is the most significant of the man is the word "amateur."

Occasionally some writer, forgetting the history of his subject, writes disparagingly about "amateur scientists." Grant Allen has an essay entitled "Mere Amateurs," in which he castigates a critic who dared to use the phrase "in the fatherland of Bacon, Newton, and Darwin." Presumably the critic thought that the word "amateur" was synonymous with "beginner" instead of meaning, as it does, one who does things for the love of doing them. Men do things for many reasons: to earn their bread, to obtain riches and luxury, to attain power, for the approval of their fellows; but the things that are done best are done for the love of the doing.



George Eastman

Chemists, remembering the development of their science, are scarcely likely to forget their debt to the amateurs who created it; and photography owes its existence and progress to amateurs. Fox Talbot, Scott Archer, R. L. Maddox, George Eastman—all became interested in the taking of pictures and in pursuit of their hobby worked out the improved processes and methods which are the milestones of photographic technic.

But Mr. Eastman is not only an amateur photographer. He is an amateur in half a dozen other fields, and all of them he pursues with that same enthusiasm and thoroughness which has made such a success of his photography. An enthusiastic camper, he has studied every detail of his camping kit and worked out improvements himself. For years he has been an amateur musician—as an auditor not a performer—and recently his interest in music has led him to experiment in the teaching of music by building and organizing a school of music. He believes that the public at large should be taught to appreciate music, and in order to teach them he has built a great theater where motion pictures are accompanied by excellent music, so that while people watch the pictures they will absorb the music. The building of that theater was perhaps the more readily undertaken because Mr. Eastman is an amateur architect and builder, and one of no mean order. He has erected many buildings in connection with his business, and the construction of most of these has been very closely supervised by him. The Kodak building in London is notable among the business buildings of that city, and although it was built by a famous architect it owes a great deal to the suggestions made by Mr. Eastman. And what fun he had building that theater! Every part of it was studied; each growth was watched; and when it was being finished he all but lived there. Today, among his chief interests are the running of the theater, assisting in the direction of the Music School, and making suggestions to the builders of the School of Medicine which he has helped to give to Rochester. For George Eastman is like other amateurs; he is young at heart, and there is nothing like an absorbed interest to keep one young. That interest with him is perennial.

In spite of the interest he takes in his work and his play, Mr. Eastman is no faddist. Some enthusiasts, especially some wealthy and successful enthusiasts, are full of fads and insist on carrying them out in everything they do. Mr. Eastman does not; he consults experts in his business, in his music, and his building; he secures the best advice available, and when he does something unusual it is due, not to impulse, but to conviction founded on careful study and knowledge. Also, while his interests are wide, they are by no means universal. He becomes so deeply interested in certain matters that it is necessary to limit his attention in other directions. Mr. Eastman, for instance, believes pure science is useful both to the community and to his business; he has helped it greatly by his gifts and turns to it for advice when he needs it, but he himself has never studied deeply any branch of it.

He is a good man to work for and to work with—enthusiastic, critical, strict, exacting. He can detect the vital point in a new problem in business with startling rapidity and clarity. Forty-five years ago he started to make photographic plates, and for many years the Kodak Company absorbed his immense energy. Then, as he felt that he could trust the men that he had gathered around him to take more and more responsibility, he began to interest himself in other matters, and today he states that he is intending to take a more detached position.

But Mr. Eastman will always be an amateur—an enthusiast in everything that he undertakes and, not least, in photography and in that development of photography throughout the world which is the business of the Kodak Company.

C. E. K. MEES

Water Temperatures—*U. S. Geological Survey Water-Supply Paper* **520-F**, on temperature of water available for industrial use in the United States, contains a map showing the temperature of water from nonthermal wells at depths of 30 to 60 feet throughout the United States. Another map shows the approximate mean monthly temperature of surface waters during July and August. A table gives mean monthly temperatures of surface water and of air, and maximum daily temperatures of water for July and August at twenty-one places, with records over periods varying from one to twelve years.

The temperature of ground water is generally from 2° to 3° F. above the mean annual air temperature if the water is between 30 and 60 feet below the surface of the ground. The mean monthly temperature of a surface water at any place is generally within a few degrees of the mean monthly air temperature when the air temperature is above the freezing point. The maximum water temperature in any of the warmer months is usually from 2 to 6 degrees higher than the mean monthly water temperature.

NOTES AND CORRESPONDENCE

A. C. S. Committee Reports

COMMISSION ON STANDARDIZATION OF BIOLOGICAL STAINS

The Commission on the Standardization of Biological Stains came into being as a result of the difficulties of biologists in procuring stains which would function satisfactorily, after the supply of imported material was shut off during the late hostilities. The National Research Council started an investigation of the situation and organized a committee, which functioned for some time, until its work developed to the stage where it was deemed wise to launch it as a separate commission. Since that time, the work has been carried on by the commission, which is composed of representative biologists and other scientists. The direction of the commission is vested in its executive committee of five members each of whom, according to the constitution of the commission, must be a duly qualified representative of one of the national scientific societies. Since there are only five members of this executive committee, it has been agreed that when a member ceases to represent his national society, he can no longer function on the committee, and his place must be filled by the representative of a society not already represented. Hence, continuity of representation is essential for membership on this important committee. The commission early realized that coöperation with the chemists was necessary for the accomplishment of its work, and elevated the writer to membership on its executive committee in order to secure the closest possible coöperation and chemical guidance in its efforts.

The commission has a twofold objective: (1) by coöperation of the various types of biologists and chemists, to gather all available data regarding those properties of dyes which relate to their use as microscopic stains; (2) by coöperation with the manufacturers of dyes, to assure that the stains available to American scientists are of the highest quality as shown by their chemical properties and, most important of all, by their performance in actual staining technic.

The first object is being partly brought about by a series of publications and notes appearing in biological and other scientific publications. A book is at present in preparation which will contain the history of staining technic and a description of all the dyes used in microscopic work.

The second object is slowly being effected by a plan of certification of those batches of stain which have been found by actual test to be satisfactory. In this phase of the work, the manufacturers and dealers are in hearty accord with the commission and are aiding the work in every way possible. At the moment of writing, batches of the following stains have been certified: methylene blue, orange G, Sudan III, basic fuchsin, crystal violet, methyl green, acid fuchsin, aniline blue water-soluble, pyronine, eosin yellowish, safranine O, hematoxylin, methyl orange, Sudan IV, Bismarck brown, light green SF yellowish, brilliant cresyl blue, thionine, toluidine blue, cresyl violet, and Wright's stain.

The revenue of the commission is derived from contributions from the Chemical Foundation and dealers in stains, from the certification of the dyes for staining purposes, and from the sale of labels to be used on the certified batches.

The work of the commission has been of great benefit in other important aspects. It has revealed the fact that modern American dyes are often superior to the pre-war stains with which the biologists were supplied. They are generally purer and more concentrated. It has also revealed to the biologists that more basic research is needed on the technic of staining, with particular attention to the identity of the stain and the effect of impurities on the result. In some instances the impurities, rather than the chemical individual whose name appeared on the label, were found to be more important in certain phases of the work. The effect of hydrogen-ion concentration is also being investigated. In short, the biologists—and chemists, too—were amazed by the paucity of real scientific data in this important field. Staining technic developed, like so many other branches of science, in a haphazard, rule-of-thumb manner, and was really more an art than a science. Now, however, the subject is being reduced to a scientific basis as rapidly as is possible. Scientific specifications are being applied to the stains themselves in order to assure uniformity of material and of performance, and there is a movement starting toward establishment of simplified and improved manner of procedure. This movement will require time, education of technicians, and close coöperation between all the biological sciences and chemistry before it can produce permanent results.

One of the most noteworthy facts brought out by the commission's work is the remarkable spirit of coöperation shown by the manufacturers and dealers. Their efforts to supply satisfactory stains and their willingness to experiment and follow up suggestions of the commission are very gratifying, particularly when it is considered that the volume of this business is small in point of poundage, and that consequently the profits are meager at best, and often on the wrong side of the balance sheet.

The outlook of the commission is bright. More stains will be certified as fast as the preliminary work, testing, and drawing up of specifications will allow. Facts and information regarding these dyes are developing fast and there is every indication that as this work progresses this phase of science will become a distinctive credit to this country. Continued support of the commission is needed and recommended.

JOSEPH A. AMBLER,
A. C. S. Representative

.....

COMMITTEE ON INDUSTRIAL ALCOHOL

Since the last annual meeting of the SOCIETY, the Judiciary Committee of the House of Representatives, which had granted a hearing on the Cramton Bill H. R. 6645, reported this bill out in an amended and somewhat less objectionable form than the original bill. During the closing days of Congress it was brought up in the House by suspending the rules, was amended so as to give the Prohibition Commissioner more control over industrial alcohol, and was passed and sent to the Senate. The Senate Judiciary Committee to whom the bill was referred passed it back to the Senate, not only without having granted hearings, but without the formality of having given it regular consideration. Just before the adjournment of Congress last June, sponsors of the bill vainly sought to bring it to a vote in the Senate, but this was prevented and Congress adjourned, leaving the bill in a threatening position as a pending order of business to be taken up in December.

Prior to the meeting of Congress last December, members of the SOCIETY, alcohol-using industries, and the Committee on Industrial Alcohol made such a strong demand on Senators and the Senate Judiciary Committee that the bill was referred back to this committee for hearings. Short hearings on the bill were granted in December and continued on January 7, 1925. At these hearings, which were held before a subcommittee, the objectionable features of the bill were pointed out by numerous representatives of the industries, several of whom were members of the SOCIETY, and by the Industrial Alcohol Committee. In spite of this, the bill in slightly amended form was reported to the Judiciary Committee and by this committee to the Senate. It is a matter of some satisfaction that the arguments given before the committee were not without fruit, as they formed the basis for a minority committee report against the bill and later furnished material that helped to defeat it when it was brought up on the floor of the Senate.

During the closing hours of Congress, when it became apparent that the bill would meet with serious opposition, an effort was made to amend it so as to cut out every feature except the placing of the present Prohibition Unit under Civil Service. Opposition to the bill even in this form was voiced in the Senate and it was allowed to die without having been put to a vote.

Thus far, those interested in the manufacture, distribution, sale, and use of industrial alcohol, both pure and denatured, have been content to try to live up to existing laws, and have paid little attention to needed and prospective legislation until bills have actually been introduced which would take away some of their rights and which have thus put them on the defensive. One after the other, these objectionable bills have been blocked by the industries, fighting with their backs to the wall to prevent unnecessarily burdensome restrictions from being placed upon the manufacture, distribution, sale, and use of alcohol. None of these measures would have added any authority actually helpful or necessary to prohibition enforcement.

It is probable that bills of this kind will continue to be introduced and will again put the industries on the defensive unless

some definite constructive proposals come from the industries themselves. One such proposal that may be worked out satisfactorily, if the legitimate interests are given the consideration they deserve, is to establish the Prohibition Unit as a part of the Department of Justice and to give it all strictly prohibitive features of the law but none of those which regulate legitimate acts coming under the law, leaving these to a Division of Chemistry and Industrial Alcohol to be under the Commissioner of Internal Revenue.

Several of the states have also taken up alcohol legislation during the past year and some bills of this kind are still pending. A bill has just been killed in Pennsylvania which would have been most drastic and even in some respects unconstitutional had it passed. This bill would have extended arbitrary authority over anything containing, or capable of developing, as much as half a per cent of *any alcohol*. This would have put very objectionable restrictions on the manufacture, sale, or use of all kinds of things, including even completely denatured alcohol and such things as tincture of iodine and glycerol. Great credit is due to a number of the members of the SOCIETY residing in Pennsylvania for their active opposition to this bill.

In the opinion of the Committee on Industrial Alcohol the need for such a committee still exists, and it is highly desirable that it should have the backing of the entire membership of the SOCIETY in its efforts to show the need for the encouragement of the manufacture, sale, and use of alcohol for lawful purposes, and also in its attempts to have the administration of these lawful features placed under the direction of an experienced chemist trained in these matters, rather than under a prohibition commissioner who, though he may be given all necessary proper authority over actual prohibition matters, should be given no control over legitimate acts.

MARTIN H. ITTNER, *Chairman*
RAYMOND F. BACON
J. H. BEAL
E. H. KILLHEFFER
EDWARD MALLINCKRODT, JR.
R. H. MCKEE
FREDERIC ROSENGARTEN

. . . . . .

CORROSION COMMITTEE

Since the last annual meeting the committee has continued to work with the Corrosion Committee of the National Research Council. The chairman has met with that committee and discussed methods of procedure. He has agreed to furnish them with a short outline of the progress of this committee and, with the consent of the SOCIETY, will send them a copy of this report.

As a logical first step in studying the theory of corrosion, a symposium was held before the Division of Industrial and Engineering Chemistry at the Baltimore meeting. [THIS JOURNAL, 17, 335 (1925)]. This symposium describes the status of corrosion theory and should be a starting point for further work. Nearly all the leading authorities on corrosion in the United States presented papers or took part in the discussion, and representative papers from other countries were secured.

The following extract from the chairman's introductory note to the symposium summarizes the situation in theoretical study:

> The last few years have been prolific producers of useful data. Worthwhile new alloys have been developed, and our knowledge of older metals and the factors of corrosion exterior to the metal has increased, thereby opening new channels for research which promise to be of extreme value.
>
> The striking corrosion-resisting properties of some new alloys are still unexplained. Uncovering of the laws governing this resistance to corrosion, with the resulting development of better alloys, does not seem remote. Additions to electrochemical theory have removed part of the past difficulties in applying electrical considerations to predict the course of corrosion and explain present experience.
>
> The basic cause of pitting is clearer than ever before. Pitting seems to be due more to differences in oxygen supply than in the metal. Investigators differ as to the exact mechanism of the action. This matter can be cleared up by further study, and from the results a method of preventing pitting might be expected. Quantitative work on the effect of dissolved oxygen is getting at the basis of variations in corrosion rate in the same solution. This work applies to almost all other corrosion study, and with these quantitative data the other work can proceed where it has been at a standstill.
>
> The production and properties of films have been studied. Knowledge of how films may affect the course of corrosion has been obtained in special cases, but the acquisition of quantitative data has only begun. Microscopic study of the progress of corrosion has produced interesting results, and the possibilities for new results in studying film formation and electrochemical effects are great. The phenomenon of passivity is still unexplained, but the progress along other lines is so rapid that we can reasonably expect it, if continued, to lead to a solution of the passivity conundrum.

It would seem that the gaps in the knowledge as indicated might be readily filled by some correlated research, and there is mention in the papers of the value of study by a centralized laboratory organization. Such an organization should operate with the advice of the present national corrosion committees. It would study the general problems which would not be undertaken by other laboratories but whose solution would be of direct value to many industries.

The committee has discussed the possibility of taking certain constructive steps along this line, but full agreement as to action has not been reached. It does not believe that the building of new laboratories for the purpose is advisable. It stands ready to coöperate if such an organization is formed, as the laboratory work would be closely allied to this committee's work as projected.

ROBERT J. MCKAY, *Chairman*
W. S. CALCOTT
J. H. REEDY
A. E. STEVENSON
W. G. WHITMAN
R. E. WILSON

Calendar of Meetings

American Oil Chemists' Society—16th Annual Meeting, New Orleans, La., May 11 and 12, 1925.

American Association of Cereal Chemists—Annual Meeting, St. Louis, Mo., June 1 to 5, 1925.

Third National Colloid Symposium—University of Minnesota, Minneapolis, Minn., June 17 to 19, 1925.

American Society for Testing Materials—28th Annual Meeting, Atlantic City, N. J., June 22 to 26, 1925.

American Institute of Chemical Engineers—Providence, R. I., June 22 to 27, 1925. Joint meeting with British Institution of Chemical Engineers, Leeds, England, July 13 to 23, 1925.

National Chemical Equipment Association—Providence, R. I., June 22 to 27, 1925.

American Chemical Society—70th Meeting, Los Angeles, Calif., August 3 to 8, 1925.

American Electrochemical Society—Fall Meeting, Chattanooga, Tenn., September 24 to 26, 1925.

National Exposition of Chemical Industries—New York, N. Y., September 28 to October 3, 1925.

Reclamation of Automobile Crank-Case Oil—Correction

In our article under this title [THIS JOURNAL, 17, 416 (1925)] the last paragraph on page 422 should read:

The energy input is 280 watts for the rectifier, and 107 for the settling tank heater—387 in all, or between 0.27 and 0.31 kilowatt hour per liter (1.03 and 1.16 kilowatt hours per gallon) of oil entered.

CHARLES VAN BRUNT AND P. SCHUYLER MILLER

Production and Sales of Dyes Decline

Preliminary figures compiled by the United States Tariff Commission indicate a domestic production for 1924 of about 67,000,000 pounds of coal-tar dyes, valued at about $36,000,000. This quantity represents a 28 per cent decline from that of 1923, which was the largest in the history of the industry. The sales of dyes in 1924 were about 63,200,000 pounds, valued at $33,800,000. This is a 27 per cent decrease in quantity and a 28 per cent decrease in value from sales during 1923.

The principal reason for this decline was the decreased activity of the textile industry. Among other contributing factors were: (1) stocks carried over from 1923, amounting to over 7,000,000 pounds; (2) increased imports following the 15 per cent reduction in the tariff, effective September 22, 1924; and (3) a reduction in exports amounting to 2,211,109 pounds.

In 1924 commercial production in the United States of many valuable dyes was first reported. These include colors which have been previously imported, in certain cases in large quantities. In addition to the new vat dyes, the prototypes of diaminogen blue, trisulfon brown B, geranine, cyananthrol R X O, and B G A O O were produced. Other additions include representatives of each class of dyes applied to cotton, silk, wool, and leather, including several alizarin dyes.

BOOK REVIEWS

Fuel: Solid, Liquid, and Gaseous. By J. S. S. Brame. 3rd edition. Longmans, Green & Co., New York. Price, $6.00 net.

If one wished to describe this book by one very brief phrase, it would be—"100 per cent British." All the fuels described —methods of manufacture and processing, methods of burning, analytical methods, and the economic aspects of fuel technology—are based on conditions as they exist in Great Britain. This point should be kept in mind, because fuel technology is quite different in England than it is in the United States.

This edition of Professor Brame's book includes many changes from the first two editions. This has been necessary because "there has been very considerable extension of our knowledge of fuels for internal combustion engines, of the use of powdered coal as fuel, on the subject of the ignition point of fuel of all classes, on the velocity of combustion of gaseous mixtures, and on the problems of low temperature carbonization."

The book divides itself into four parts: (1) solid fuels, (2) liquid fuel, (3) gaseous fuel, and (4) fuel analysis, calorimetry, and control of fuel supply. In the case of manufactured fuels, no great amount of data on details of manufacture is given. This is perfectly proper and necessary in a book of this size covering such a vast field. The properties of all fuels are well described. The book could be greatly increased in value if descriptions and drawings of apparatus for the burning of coal and other solid fuel were added. The various nozzles and burners for utilizing fuel oil are described in some detail, but there is simply a passing reference to automatic stokers. The portion of the book dealing with gaseous fuels contains a particularly thorough exposition of British producer gas practice.

It is evident that painstaking care has been taken to make the book free of errors. The general field of English fuels seems to have been covered with commendable thoroughness. The book is rich in references to original work, practically all of which, however, are English.

It can thus be seen that this book could have little value in this country as a general reference book on fuels, despite its apparent excellence as an English fuel text. However, it should be a valuable addition to the American industrial or educational library which specializes in fuel technology.

A. R. Powell

The Manufacture of Pulp and Paper. A Textbook of Modern Pulp and Paper Mill Practice. Prepared under the direction of the Joint Executive Committee on Vocational Education representing the Pulp and Paper Industry of the United States and Canada. Vol. V. 550 pages, including index of 11 pages. McGraw-Hill Book Co., New York, 1925. Price, $5.00.

This textbook, the fifth and last of a series, is divided into six sections, some of which are subdivided, as follows: I—Paper-making Machines; II—Hand-made Papers and Tub Sizing; III—Paper Finishing; IV—Coated Papers; V—Paper Testing and Analysis; VI—General Mill Equipment, with Subsections on Pumps, Electrical Equipment, Heating and Ventilation, and Lubrication and Water. At the end of each section or subsection is a list of examination questions. These are well selected from the descriptive topics, and the problems are clearly stated, properly illustrated, and supplied with answers.

The subject matter is of the same general type as that of the other volumes. Section II, Part 1, on hand-made papers, is interesting and instructive reading, but not applicable to American conditions. In Section IV it would be better procedure to use only one temperature scale, or always employ the two, one in parentheses. The bibliography at the end of the section on paper testing suggests extended and profitable reading. In Section VI, Part 1, the information with graphs on total working head in connection with stock pumping is of special interest at present. In Part 3 of this section the articles regarding ventilation and humidity in paper mills are also of much present interest as viewed from labor, production, quality, and maintenance factors.

The number of topics incorporated represented a difficult task for the editor and his staff and a review can only be of a very general nature. Many new procedures and pieces of equipment are described which have to date been described only in periodicals. To the reviewer it appears desirable to include in future editions a dictionary of paper-making terms, a classified list of papers and their uses, and an average selling price comparison from which relative manufacturing costs could be deduced. Section I, on paper machines, logically belongs in Volume IV with the other four parts on the same subject. Some of the details of machinery construction might well be eliminated, as they are specialized items even for mechanical and electrical engineers and millwrights. Elimination of such details would leave space for more information regarding the making of different kinds of paper. More half-tone illustrations of actual working machines, cuts showing machine and auxiliary equipment layout, and routing of orders would also be desirable.

As a whole this book represents a definite and valuable contribution in the field of paper technology and was made possible only through contributions of many thousands of dollars by the pulp and paper manufacturing concerns of the United States and Canada. It is a good textbook and will be used extensively by paper mill employees.

C. A. Brautlecht

Agitating, Stirring, and Kneading Machinery. By Hartland Seymour. 139 pages. **Mechanical Mixing Machinery.** By Leonard Carpenter. 138 pages. Chemical Engineering Library, Second Series. Ernest Benn, Ltd., London, 1925. Price, each, 6 s. net.

In these two recent additions to the Chemical Engineering Library, mixing processes are divided into three classes: (1) mixing liquids, (2) mixing solids, and (3) mixing solids with liquids. The first and third are treated in Seymour's book, the second in Carpenter's.

Seymour terms the mixing of liquids "agitating" or "stirring;" of solids, "mixing;" and solids with liquids, "kneading." In his preface he admits that some of the machines described may be used for more than one of these processes. In fact, as there is some overlapping between the two books, they might well have been combined into one entitled "Mechanical Agitating, Mixing, and Kneading Machinery."

Omitting all theory, Seymour's book is a description of two or three dozen of the host of varieties of mixing machinery that have been introduced from time to time to meet the multitudinous problems encountered in the operation of this unit process. The chemical engineer in search of the most suitable machine to solve his particular problem will here find practically all of the more important styles of mixers passing in review, and ably, if briefly, described; yet he may be disappointed at the end to find his question unanswered. Is it not that only by knowing the theory and principles of mixing one can possess the touchstone by which mixers can be judged? All will agree with Seymour that our present knowledge of the theory is quite inadequate and sadly in need of overhauling and extension. On the other hand, considering the great diversity of materials to be mixed, with their widely varying properties, does it seem possible to find any constant factors on which to lay hold and build up a universal theory?

Turning to Carpenter's book, it is quite refreshing to find an attempt to establish such a theory. Treating his subject in a scholarly manner, with definitions at once simple and lucid, the author admits the obstacles to approaching mixing problems in any but the empirical manner, and proceeds to lay down three fundamental principles favoring a close approximation to perfect mixing.

Carpenter classifies all mixtures as either "homogeneous" or "heterogeneous," meaning by the former that all the constituents are in the same phase, as all solids, or all liquids mutually soluble, and by the latter that the constituents are in different phases, as solid and liquid, or liquids mutually insoluble. He then proceeds to apply his principles to these types of mixtures.

In Chapter II are outlined the principal operations of mixing, and in Chapter III are described various types of machinery for mixing solids, both dry, semidry, and wet. Characterizing all mixers as either of the batch or continuous type, he gives some valuable advice on the importance of accurately feeding the continuous type.

Under Intensive Mixing are described the most recent developments in colloid mills and homogenizers. Subsequent chapters sketch the mixing practice followed in such large industries as cement, ceramics, fertilizers, soap, but there will be found only passing mention of the rubber industry, with no discussion of its peculiar problems and the latest developments in machinery.

Together, these two books are a valuable contribution to the literature of chemical engineering. They are replete with illustrations, especially Seymour's volume, and happily show cross sections rather than mere photographs of the exterior of machines, so often a disappointing feature of manufacturers' catalogs.

H. B. VOLLRATH

The Dust Hazard in Industry. By WILLIAM E. GIBBS. 168 pages. Chemical Engineering Library, Second Series. Ernest Benn, Ltd., London, 1925. Price, 6 s. net.

In the preface the author explains that it has been his aim to make readily accessible the data and information on the dust hazard now scattered through the technical and scientific press. Examination shows that he has succeeded in collecting and compiling in the form of a convenient and ready reference book the important results of the research and investigational work done on the subject. The material is not new, but it has been carefully selected from the works of investigators in the United States, England, France, and Germany. This little book will be of special interest and value, not only to those interested in studying the effect of dust on the health of employees in dusty industries, but also to that body of investigators striving to determine the fundamental principles of dust explosions and the methods of eliminating this hazard. The book also contains information of value to the owners and operators of dust-producing industries, who are interested in selecting and installing in their plants the equipment and devices found to be most effective in reducing the dangers of dust explosions.

There are in the first few chapters a number of tables containing data on the quantity and size of dust particles, the effect of various dusts on health, and the death rate in various dusty industries.

Under explosive combustion of dust there are many tables giving the ignition temperatures of gases and dusts, the relative inflammability of various dusts, the limits of concentration, the pressures developed, and the rate of flame propagation.

The author also discusses some of the controversial subjects on which the various investigators have formed different opinions or advanced different theories, such as the value of inert material in the dust, or inert gas in the carrying medium, as means of preventing dust explosions. The effect of moisture in the air as a dust-explosion retardant is discussed, and there is also a clear-cut and convincing reference to the possibility of a dust explosion occurring spontaneously.

The final chapters are devoted to a discussion of the causes and methods of preventing dust explosions in factories, mines, and coal grinding or storage plants.

The references throughout the text to the publications from which information has been taken are convenient guides to any one who wishes to make a further study of the subject.

HYLTON R. BROWN

Chemistry in the Service of Man. By ALEXANDER FINDLAY. 3rd edition. 300 pages. Longmans, Green & Co., London, New York, 1925. Price, $2.00.

That this interesting book has now reached its third edition is proof sufficient that it has won a place in the literature addressed to the general public. Its story of the service of chemistry to man is full and very attractive.

There may be portions of the book which the ordinary layman will not understand because he has never come in contact with the elements of chemistry. However, in these days when everybody is educated, it is probable that the readers of the book will be exceedingly numerous, and to them it may be said that its pages bring reliable data and demonstrate how closely chemistry approaches the life work of us all.

It is a scholarly production and, although not written in the exuberant and enthusiastic spirit of a daily paper or many of the modern magazines, it presents its material in a dignified form, sure to leave a wholesome impression. He who reads the book will go forth to his daily tasks in a thoughtful mood, and strive earnestly to understand the thousands of projects, based on chemical principles, which surround him. The book deserves a place in every library.

EDGAR F. SMITH

Bituminous Substances. By P. E. SPIELMANN. xv + 206 pages, 6 × 9 inches. Ernest Benn, Ltd., London, 1925. Price, 15 s. D. Van Nostrand Co., New York, 1925. Price, $4.50.

The author attempts to review the present position of scientific knowledge concerning bituminous substances, covering the subject in four chapters, entitled Composition and Origin; Physical and Chemical Properties; Effect of Heat, Aging, and Solvents; and Physical and Chemical Tests. After reading these four chapters one is driven to the conclusion that but little progress has been made in the development of any real science of bituminous substances other than some appreciation of the colloidal nature of these materials, and the effect of oxidation, thionization, and polymerization on the formation and modification of bitumens.

The author adds further confusion by introducing new empirical terms—"petrolites," "kerotenes," "kerols," "keroles," and "kerites"—as names of constituents of bitumens. He accepts the cellulosic theory of the formation of coal and asphaltenes without making any reference to the work of other investigators which indicates that lignin is probably the major contributing substance in humins and coal formation.

The chapter on Physical and Chemical Properties contains some interesting information on light reactions and an important contribution on colloidal phenomenon, but it lacks a well-classified exposition of the physical and chemical properties of various bitumens. The relation between temperature and physical properties is shown in a number of tables and curves without any reference to the different kinds or mixtures of bitumens, so that these data merely serve as an illustration of the range of physical properties with temperature. Other curves show the relation between certain of the physical or chemical properties—as, for example, the relation of fusion point and specific gravity, specific gravity and penetration, specific gravity and insolubility in petroleum ether, penetration and ductility, etc. The usual technical tests used in the bitumen industry are briefly described.

The book is well printed with large type, but the arrangement of references is inconvenient, all of them being in the back of the book. It contains some useful information for the chemist conversant with bituminous substances, but it can hardly be recommended to the average chemist who wishes to obtain detailed empirical information on bituminous substances, or a well-digested and well-correlated review of the present scientific knowledge of bitumens.

A. C. FIELDNER

Applied Electro-Chemistry. By A. J. ALLMAND AND H. J. T. ELLINGHAM. 2nd edition. 727 pages. Longmans, Green & Co., New York; Edward Arnold & Co., London, 1924. Price, $10.50.

The paper is good, the proof-reading careful, and the illustrations better than in many scientific books printed in England. The first 190 pages form Part I—General and Theoretical; the next 510 pages form Part II—Special and Technical. The remaining 27 pages are given to tables and indexes, both of which might well have been more extended, especially the index.

Much of Part I is unnecessarily elementary for the newly graduated electrochemical engineer, who alone will be able to read the sketchy presentations in none too clear terminology of many debatable physical-chemical theories. For example, several pages of text and footnotes are devoted to the definition of the ohm in centimeters of mercury, to Ohm's law, and examples illustrating how multiplying the number of volts and amperes results in the number of watts; also in much detail how the ampere may be determined with precision by the deposition of silver. But the actual technic of hydrogen-ion concentration measurements by electrolytic and by indicator and colorimetric methods is meager and is far from explicit. In fact, one not already familiar with the subject will find little or no exact information and one who is familiar with it will find nothing new. The writers seem to be trying to teach instead of trying to tell.

Part II is largely made up of the digested electrochemical literature of the last fifteen years. This portion of the book is its best.

Primary and storage batteries are discussed, but the sole improvement made in the dry cell in the last forty years by using flour paste is not mentioned. The wet winning and refining of the precious and base metals might have been given more space. The chapter on electroplating and electrotyping is lacking in detail of value to one specially interested. Bleaches, alkali, chlorine, hydrogen and oxygen, and miscellaneous wet electrolytic processes are well covered, as is the manufacture of sodium, aluminium, and the easily oxidizable metals from their fused salts.

The description of electric smelting and refining furnaces for ferro alloys is largely digested from foreign papers. The Northrup high-frequency induction furnace is not mentioned. Neither the Arsem vacuum furnace nor Yensen's work on vacuum purification of iron for magnetic purposes is described. Carborundum, graphite, carbon bisulfide, phosphorus, and nitrogen fixation are well discussed with illustrative data. Ozone is given the final ten pages.

The book as a whole is valuable as a digest of periodical and textbook information not readily accessible to the electrochemist remote from the great libraries, and contains a vast amount of exact data. It is lacking in references by numbers to the vast stores of information in issued patents. The fundamental purpose of a patent is to record in permanent form and in the most explicit detail each of the steps of improvement in the development of an art, and that in most cases they do, while the references in footnotes to files of technical and scientific transactions are practically unavailable to the works chemists outside the university cities.

In a word, this is a new edition of the standard work of Dr. Allmand, which appeared in 1912 and was reprinted in 1920, and is now rewritten with 200 pages added to Part II. These additions are most welcome and bring these valuable digests up to date.

BUCKNER SPEED

Medical Aspects of Chemical Warfare. By EDWARD B. VEDDER. With a chapter on **Naval Aspects of Chemical Warfare.** By DUNCAN C. WALTON. xvi + 327 pages. Williams & Wilkins Co., Baltimore, 1925. Price, $6.50.

In collecting the information contained in this book, Colonel Vedder has done a great service to the medical officers of the Army and Navy who will be called upon to treat men injured by war gases and by many of the gases which are met with through accident in civil life. The book will also enable chemists and others to gain an insight into the medical aspects of chemical warfare problems.

The treatise is a concise and accurate statement of the action of war gases. The treatment of the subject of pulmonary irritants is particularly full and excellent. The vesicants, lachrymators, irritant smokes, and miscellaneous compounds also receive adequate treatment. Emphasis is laid upon the treatment of men poisoned with gas and the morphological and functional pathology resulting from gassing.

The book is well illustrated and contains enough of the different strategic uses of gases, of meteorology, of physics, as applied to chemical warfare, to make it a well-rounded treatise.

Lt. Comm. Walton's chapter on the naval medical aspect of chemical warfare is also very timely and will be most useful to that branch of the Service.

The large number of references in the book add to its value.

A. S. LOEVENHART

A. S. T. M. Standards. Issued Triennially. 1924. 1219 pages. Published by the American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa. Price, $11.00 to nonmembers; extra copies to members, $8.00; discount to libraries 20 per cent of price to members.

This is the regular triennial publication of the American Society for Testing Materials of the standards of that society now in force.

The volume contains 220 standard specifications, methods and tests, definitions of terms, and recommended practices in effect at the time of its publication. The standards cover a very wide range. There are a total of 56 with reference to steel; 8 to wrought iron, 9 to pig iron, cast iron, and finished castings; 39 to nonferrous metals; 28 to cement, lime, gypsum, and clay products; 19 to preservative coatings; 6 to petroleum products and lubricants; 23 to road materials; 7 to coal and coke; 6 to timber and timber preservatives; 2 to insulating materials; 11 to rubber products; 1 to textile materials; and 5 to miscellaneous subjects.

The paper used in the present volume is thinner and lighter than the paper heretofore used in these publications, upon which the society is to be congratulated, since the volumes are at best large and, with the thicker paper, becoming unwieldy. This publication is of utmost value to organizations and firms interested in engineering and structural materials, and should be accessible to them.

F. P. VEITCH

Factory Practice in the Manufacture of Azo Dyes. By W. B. O'BRIEN. 176 pages. The Chemical Publishing Co., Easton, Pa., 1924. Price, $5.00.

This book is a compilation of similar processes for the manufacture of certain of the simpler monoazo dyes, including a brief description of the plant equipment and the materials needed in such processes. It is of doubtful educational value. The processes follow too closely the detailed practice of some particular factory. The plant design, the handling of raw materials, the general description of the technic employed, indicate the author's experience in the manufacture of the dyes mentioned and not necessarily the general factory practice in the United States. Although these processes serve as typical illustrations of the application of the chemical principles involved in the manufacture of the simpler azo dyes, it is regrettable that the author has said so little about the essential plant controls which safeguard the modern plant practice.

For the most part the book is well written. There are a few blemishes but they are not of a serious nature. For example, it is not clear what the author means by "dyestuffs that originate in coal-tar products." In several places in the book "metanil yellow" is written "metanile yellow." But there are few such inaccuracies.

The book was published in 1924 and yet the author gives 1919 and 1920 statistics of the production and value of dyes. It is difficult to understand why the author did not review his manuscript to present up-to-date information. Similar information was available for 1923 before the book went to press, and if the author felt it necessary to include data of this kind it is to be regretted that he did not give the latest figures, for the information presented on production and costs is misleading. Production, costs, and selling price of dyes in 1925 cannot be compared with similar data for 1919 and 1920.

M. L. CROSSLEY

Kohlenwasserstofföle und Fette, sowie die ihnen chemisch und technisch nahestehenden Stoffe. By D. HOLDE. 6th enlarged and improved edition. 179 illustrations. 196 tables. 856 pages. Verlag von Julius Springer, Berlin, 1924. Price, 45 goldmarks.

This new edition of Dr. Holde's comprehensive book on the analysis and testing of hydrocarbon oils, fats, and similar materials is greatly enlarged, the text of the 5th edition being increased from approximately 570 pages to 856 pages. With the aid of other specialists new sections have been introduced, and important revisions and additions have been made to include the advances made in Germany in recent years in research and technology relating to low-temperature tar, straw and wood tar, hydrogenated tar products, artificial resins, volt oils (Voltöle), emulsified lubricants, dynamics of lubricants, chemistry and synthesis of fats, constitution, physiology and pharmacology of fats, fatty acid anhydrides, vitamins, and edible fats.

The same convenient plan of systematic arrangement and classification for each material in question has been followed in this edition—viz., (1) discussion of industrial importance, technical use, and occurrence or preparation; (2) chemical and physical properties; (3) methods for testing; and (4) specifications. A comprehensive and detailed table of contents and index facilitates ready reference to the many tests described. Three pages of general references to the literature and numerous footnotes throughout the text permit the reader to refer to the source of the various tests and descriptions.

The first chapter is devoted to general testing methods; Chapter 2 covers petroleum and its products; Chapters 3 and 4 are on natural asphalt and mineral waxes; Chapter 5 is on tars from the pyrogenic decomposition of brown coal, bituminous coal, peat, wood, bituminous shale, etc.; Chapter 6 is on the distillation products of balsams; Chapters 7 and 8 are on vegetable and animal fats and oils, and industrial products prepared from fats; waxes, flotation oils, and physicochemical tables are the subjects of Chapters 9, 10, and 11.

The commercial specifications given under the various materials make the book more valuable to the industrial chemist, even though they are practically all German specifications. It is to be regretted that the author did not remedy the one weakness of his previous edition by including American contributions to the methods for petroleum testing—a field in which much progress has been made in recent years. No mention is made of Herschel's work on viscosity or of the American Society for Testing Materials' methods for testing petroleum and its products. The Allen and Jacobs electrically heated distillation

method (page 104), quoted from *Bureau of Mines, Bulletin* 19 (1911), has been superseded in the bureau by greatly improved methods which are fully described in *Bureau of Mines, Bulletin* 207 (1922), of which no mention is made. Likewise, the rather inadequate section on bituminous shales could have been improved by reference to American work on oil shales.

A. C. FIELDNER

Cane Sugar and Its Manufacture. By H. C. PRINSEN-GEERLIGS. 2nd edition. ix + 324 pages. Norman Rodger, London, 1924. Price, 21 s., postpaid.

Dr. Geerligs' first edition attracted the very favorable attention of workers in cane sugar. The material was presented in clear, simple language, and this is also true of the new edition. The book is addressed especially to chemists, though this is not implied in the title. Presumably, according to Dr. Geerligs' view, this justifies his omission largely of detailed descriptions of cane mills and other machinery. The chemist of the modern plant often ultimately becomes its superintendent and so should be well informed as to the mechanical devices of the industry in general.

The fact that the juice purification was formerly considered a chemical problem, but is now known to be largely one of colloids, is clearly shown and discussed. Old and largely obsolete types of continuous settlers are quite fully described and but brief mention is made of a successful and rapidly extending thickener system.

Dr. Geerligs' theory of molasses formation is probably the most important contribution yet made in the solution of this problem. His later studies are included in this edition.

This book is a very desirable addition to the library of the cane sugar factory superintendent and chemist.

GUILFORD L. SPENCER

Synthetic Organic Compounds. By S. P. SCHOTZ. 412 pages. 110 illustrations. 19 × 24 cm. Ernest Benn, Ltd., London, 1925. Price, $12.00.

This is a collection of readable descriptions of the processes of manufacture, properties, and uses of a variety of organic compounds, in the production of which chemical reactions are involved. In order to secure accuracy, first-hand information has been obtained from the industries and the proof has been submitted to technical chemists. It is avowedly written from the British standpoint, illustrations and information being drawn from British plants and references made chiefly to British and American sources. This makes it interesting to the Britisher as a record of national achievement, while to others it is valuable as a picture of British practice.

The chapters are on solvents containing chlorine, other solvents, aromatics, antiseptics and disinfectants, sweetening agents, dye intermediates, synthetic tannins, explosives, artificial silks, chemical warfare, plastics. Compounds are classified according to their uses rather than by their chemical relationships or origins. This arrangement makes some queer bed-fellows. Thus, in Chapter II we find carbon bisulfide, cracking of hydrocarbons, production of benzene, toluene, and xylene from coal tar and from petroleum, sulfite turpentine, hydrogenation of naphthalene and of phenol, catalytic nickel, promoters, manufacture of hydrogen, activated carbon, and silica gel. However, it does no harm to study compounds outside of their conventional textbook order.

"Aromatic" is used in its original sense and includes all substances which are valuable for their odors, along with some odorless ones which are employed as fixatives.

Each chapter opens with a general view of the field which it covers. The individual topics are taken up historically and the chief patents are listed. Usually several methods of manufacture are given, sometimes in general terms, but more frequently with definite directions for carrying out the process. The advantages of contrasting methods are set over against each other and an effort is made to point out which is the best practice and why. Suggestions for improvements of existing processes are often made.

The author's ideas of limits in esterification as affected by catalysts are hazy. Dr. Gibbs and several American manufacturers will be interested in the statement (page 210) that catalytic processes for oxidation of naphthalene "do not appear to have made much headway." However, one man cannot be expected to know everything, and the book does contain much interesting and valuable information about a large number of industrially important substances and will be of use to all those who wish information as to present industrial practice and suggestions for future development.

E. EMMET REID

New Books

Callinicus—A Defence of Chemical Warfare. J. B. S. HALDANE. 84 pp. E. P. Dutton & Co., New York. Price, $1.00.

Combustion in the Gas Producer and the Blast Furnace. A New Theory. A. KOREVAAR. 189 pp. D. Van Nostrand Co., New York. Price, $5.00.

Combustion in the Power Plant. A Coal Burner's Manual. THOMAS A. MARSH. 266 pp. D. Van Nostrand Co., New York. Price, $2.00.

Concentration en Ions Hydrogène et sa Mesure par la Méthode Electrométrique. MAURICE VINCENT. 101 pp. J. Hermann, Paris. Price, 8 fr.

Crushing and Grinding Machinery. HARTLAND SEYMOUR. 143 pp. D. Van Nostrand Co., New York. Price, $2.00.

Dizionario di Merceologia e di chemica Applicata. Vol. III—Naftalina-Sena. G. VITTORIO VILLAVECCHIA. 4th edition, revised and enlarged. Ulrico Hoepli, Milan. Price, 35 lire.

Employes' Representation in Coal Mines. 1924. BEN M. SELEKMAN AND MARY VAN KLEECK. 454 pp. Russell Sage Foundation, New York. Price, $2.00.

Employes' Representation in Steel Works. 1924. BEN M. SELEKMAN. 293 pp. Russell Sage Foundation, New York. Price, $1.50.

Fifth Report on Colloid Chemistry and Its General and Industrial Application with Index to the Five Reports. BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. 130 pp. H. M. Stationery Office, London. Price, 2 s. 6 d. net.

Gerbstoffe und Gerbmittel. H. GNAMM. Vol. XII of the Chemical Monograph Series, edited by JULIUS SCHMIDT. 394 pp. Wissenschaftliche Verlagsgesellschaft, Stuttgart. Price, cloth, 27 marks; paper, 24 marks.

Laboratory Manual—Direct and Alternating Current. CLARENCE E. CLEWELL. 3rd edition, revised. 112 pp. Illustrated. John Wiley & Sons, Inc. New York. Price, $1.25.

Materialprüfungswesen unter besonderer Berücksichtigung der am Staatl. Materialprüfungsamte zu Berlin-Dahlem üblichen Verfahren im Grundrisz dargestellt. 660 pp. Verlag von Ferdinand Enke, Stuttgart.

Matières Plastiques et les Textiles Artificiels. CLÉMENT AND RIVIÈRE. Encyclopedia of Chemical Industry, edited by M. MATIGNON. 450 pp. Illustrated. J.-B. Baillière et Fils, Paris. Price, paper, 55 fr., cloth, 65 fr.

Notas sobre a Industria de Oleos Vegetaes no Brasil. J. BERTINO DE M. CARVALHO. 226 pp. Imprensa Nacional, Brazil.

Notions Fondamentales d'Elément Chimique et d'Atome. GEORGES URBAIN. 179 pp. Gauthier-Villars et Cie., Paris. Price, 10 fr.

Oleos Vegetaes como combustiveis e os processos que devem ser empregados para o desenvolvimento da industria de oleos vegetaes no Brasil. J. BERTINO DE M. CARVALHO. 32 pp. Officinas Typographicas do Servico de Informacoes do Ministerio da Agricultura, Rio de Janeiro, Brazil.

Proceedings of the 27th Annual Meeting of the A. S. T. M. Parts I and II, Vol. 34, 1924. 1173 and 1133 pp. American Society for Testing Materials, Philadelphia, Pa. Price, each part, paper, $6.00; cloth, $6.50; half-leather, $8.00.

Recent Progress in Engineering Production. C. M. LINLEY. 355 pp. Illustrated. D. Van Nostrand Co., New York. Price, $10.00.

Scientific Promotion of Gas Sales. ARTHUR COE. 390 pp. D. Van Nostrand Co., New York. Price, $10.00.

Screening and Grading of Materials. J. E. LISTER. 144 pp. D. Van Nostrand Co., New York. Price, $2.00.

Sechzig Jahre Linoleumfabrikation. FELIX FRITZ. 98 pp. H. Ziolkowsky, Augsburg, Germany.

Structure of Matter. J. A. CRANSTON. 196 pp. D. VAN NOSTRAND CO., New York. Price, $4.50.

Synthèses et Catalyses Industrielles Fabrications Minerales. PAUL PASCAL. 452 pp. J. HERMANN. Paris. Price, 45 fr.

Taschenbuch für die Färberei. R. GNEHM. 2nd edition, revised. Edited by R. VON MURALT. 220 pp. Illustrated. Julius Springer. Berlin. Price, 13.50 goldmarks.

Technical Mechanics. EDWARD R. MAURER AND RAYMOND J. ROARK. 5th edition, revised and reset. 364 pp. 424 figures. John Wiley & Sons, Inc., New York. Price, $3.50.

Teinture et l'Impression Expliquées par la Chimie. ALBERT LETELLIER. 606 pp. J. Hermann, Paris. Price, 35 francs.

Text-Book of Glass Technology. F. W. HODKIN AND A. COUSEN. 550 pp. Illustrated. Constable & Co., London. Price, 42 s. net.

GOVERNMENT PUBLICATIONS

Notice—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.

Bureau of Mines

A Critical Study of the Burrell Indicator for Combustible Gases in Air. L. H. Milligan. *Technical Paper* 357. 40 pp. Paper, 10 cents.

A Test of CO_2 Recorders. J. F. Barkley. *Reports of Investigations* 2668. 3 pp. Issued March, 1925.

Coal-Mine Fatalities in February, 1925. W. W. Adams. *Reports of Investigations* 2680. 6 pp. Issued March, 1925.

Coal-Mining Problems in the State of Washington. G. W. Evans. *Bulletin* 190. 79 pp. Paper, 20 cents.

Effect of Tank Colors on Evaporation Losses of Crude Oil. Ludwig Schmidt. *Reports of Investigations* 2677. 10 pp. Issued March, 1925.

Explosives Used in February, 1925. W. W. Adams. *Reports of Investigations* 2681. 8 pp. Issued April, 1925.

Explosives Used in January, 1925. W. W. Adams. *Reports of Investigations* 2676. 7 pp. Issued March, 1925.

Friction Factors for Metal Mine Airways. G. E. McElroy and A. S. Richardson. *Reports of Investigations* 2663. 3 pp. Issued March 10, 1925.

Hazard of Unsafe Types of Gas Masks. S. H. Katz. *Reports of Investigations* 2664. 5 pp. Issued March 9, 1925.

Metal Mine Accidents in the United States, 1923. W. W. Adams. *Bulletin* 248. 90 pp. Paper, 15 cents.

Methods of Laboratory Grinding of Coke for Analysis. W. A. Selvig. *Reports of Investigations* 2679. 5 pp. Issued March, 1925.

Some Common Mistakes in Operating a Stoker-Fired Boiler. J. F. Barkley. *Reports of Investigations* 2678. 5 pp Issued March, 1925.

Subject Index of Bureau of Mines Reports of Investigations Published during the Calendar Years 1919-1924. Compiled by H. E. Tufft and E. V. Brandenburg. *Reports of Investigations* 2667. 35 pp. Issued January, 1925.

The Ignition of Firedamp by Exposed Filaments of Electric Mine-Lamp Bulbs. R. D. Leicht, A. B. Hooker, and W. P. Yant. *Reports of Investigations* 2674. 3 pp. Issued March, 1925.

The Resistance of Coal-Mine Entries to the Flow of Air. J. W. Paul, H. P. Greenwald, and G. E. McElroy. *Reports of Investigations* 2671. 4 pp. Issued March, 1925.

Bureau of Standards

A Method of Determining the Dew Points of Fuel-Air Mixtures. R. J. Kennedy. *Scientific Paper* 500. 17 pp. Paper, 10 cents. Issued February 17, 1925.

Comparative Wearing Qualities of Pima and Ordinary Cotton Used in Mail Bags. F. R. McGowan, C. W. Schoffstall, and A. A. Mercier. *Technologic Paper* 277. 11 pp. Paper, 10 cents. Issued February 2, 1925.

Effect of Twist on the Physical Properties of a Number 7s Yarn. F. R. McGowan, C. W. Schoffstall, and A. A. Mercier. *Technologic Paper* 278. 11 pp. Paper, 10 cents. Issued February 11, 1925.

Recommended Specification for Quicklime and Hydrated Lime for Use in the Manufacture of Calcium Arsenate. *Circular* 203. 4 pp. Paper, 5 cents.

United States Government Master Specifications for Gypsum Plaster. *Circular* 205. 5 pp. Paper, 5 cents.

United States Government Master Specification for Quicklime for Structural Purposes. *Circular* 201. 5 pp. Paper, 5 cents.

Department of Agriculture

Bibliography Relating to Soil Alkalies Compiled with Special Reference to Deleterious Action of Soil Alkalies and Various Other Chemical Agents on Cement and Concrete. Compiled under the direction of S. H. McCrory by F. V. King, Guy Ervin, and O. L. Evans. *Department Bulletin* 1314. 40 pp. Paper, 10 cents. Issued February 17, 1925.

Feed Cost of Milk Production as Affected by the Percentage Fat Content of the Milk. W. L. Gaines. *Journal of Agricultural Research*, 29 (December 15, 1924), 593–601.

Hot-Water Treatment of Dormant and Sprouted Seed Cane. P. A. Yoder. *Department Circular* 337. Paper, 5 cents.

Painting on the Farm. H. P. Holman. *Farmers' Bulletin* 1452. 33 pp. Paper, 5 cents. Issued April, 1925.

Relation between the Diet, the Composition of the Blood, and the Secretion of Milk of Dairy Cows. C. A. Cary and E. B. Meigs. *Journal of Agricultural Research*, 29 (December 15, 1924), 603–24.

Geological Survey

Alaska's Mineral Resources and Production in 1923. A. H. Brooks. An Early Tertiary Placer Deposit in the Yentna District. S. R. Capps. Administrative Report. A. H. Brooks. *Bulletin* 773-A. *Mineral Resources of Alaska, 1923-A*. 69 pp.

Erosion by Solution and Fill. W. T. Lee. *Bulletin* 760-C. *Contributions to the Geography of the United States 1923–24*. Pp. 107–21. Published April 4, 1925.

Gold and Silver in 1923 (General Report). J. P. Dunlop. *Mineral Resources of the United States, 1923*. Part I, pp. 549–85. Published April 6, 1925.

Gold, Silver, Copper, Lead, and Zinc in Montana in 1923. Mine Report. C. N. Gerry. *Mineral Resources of the United States, 1923*. Part I, pp. 447–79. Published March 18, 1925.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1923. Mine Report. V. C. Heikes. *Mineral Resources of the United States, 1923*. Part I, pp. 481–514. Published March 21, 1925.

Gold, Silver, Copper, Lead, and Zinc in Utah in 1923. Mine Report. V. C. Heikes. *Mineral Resources of the United States, 1923*. Part I, pp. 417–45. Published March 20, 1925.

Natural-Gas Gasoline in 1923. G. B. Richardson. *Mineral Resources of the United States, 1923*. Part II, pp. 359–64. Published March 28, 1925.

Surface Water Supply of the United States 1921. Part XI—Pacific Slope Basins in California. N. C. Grover, H. D. McGlashan, and F. F. Henshaw. *Water-Supply Paper* 531. Prepared in coöperation with the States of California and Oregon. 304 pp. Paper, 25 cents.

The Occurrence of Copper on Prince William Sound, Alaska. F. H. Moffit. *Bulletin* 773-C. *Mineral Resources of Alaska, 1923-C*. 158 pp. Paper, 5 cents.

Public Health Service

Absence of Transferable Immunizing Substances in the Blood of Morphine and Heroin Addicts. A. G. DuMez and Lawrence Kolb. *Public Health Reports*, 40 (March 20, 1925), 548–59.

A Study of the Pellagra-Preventive Action of Dried Beans, Casein, Dried Milk, and Brewers' Yeast, with a Consideration of the Essential Preventive Factors Involved. Joseph Goldberger and W. F. Tanner. *Public Health Reprint* 984. Paper, 5 cents.

Drainage Ditches Covered Economically. Concrete Pipe Manufactured and Laid Cheaply in Emporia, Va. G. S. Bote. *Public Health Reports*, 40 (March 13, 1925), 502–9.

Studies on Oxidation Reduction. VII—A Study of Dichloro Substitution Products of Phenol Indophenol. H. D. Gibbs, Barnett Cohen, and R. K. Cannan. *Public Health Reports*, 40 (April 3, 1925), 649–63.

Tariff Commission

Potassium Chlorate. A Proclamation by the President of the United States increasing the rate of duty on potassium chlorate from $1\frac{1}{2}$ to $2\frac{1}{4}$ cents per pound. 1 p. Issued April 11, 1925.

War Department

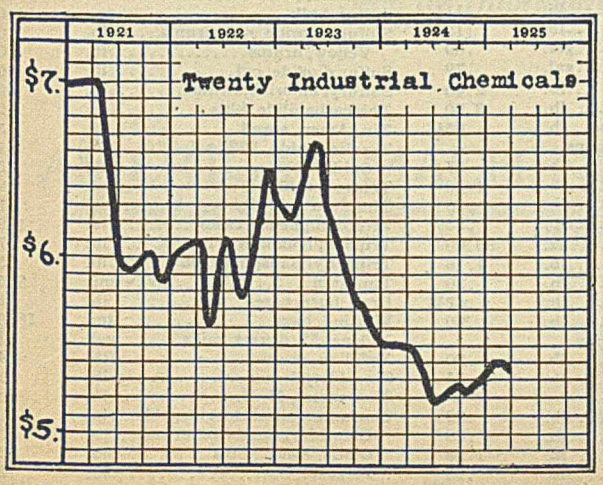
Column, Crushing, and Torsional Strength of Duralumin Tubing: Part I—Column Strength; Part II—Crushing Strength; Part III—Torsional Strength. Prepared by S. W. Thompson. *Air Service Information Circular*, Vol. 5, No. 470, 21 pp.

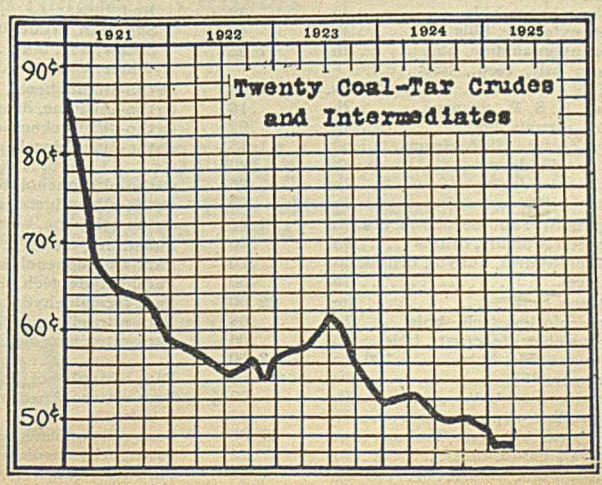
Requirements of Spar Varnish for Aircraft. Prepared by A. C. Zimmerman and E. R. Irwin. *Air Service Information Circular*, Vol. 5, No. 494, 8 pp.

MARKET REPORT—APRIL, 1925

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON APRIL 15

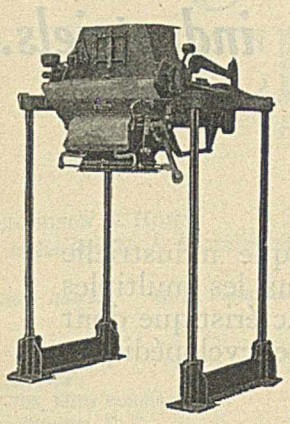
Acetanilide, tech., bbls.	lb.	.27
U. S. P., bbls.	lb.	.35
Acetic anhydride, 90–95%, cbys.	lb.	.41
Acetone, C. P., drums, wks.	lb.	.11
Acetophenetidine, bbls.	lb.	1.85
Acid, Acetic, 28%, c/l. bbls.	100 lbs.	3.12
56%, c/l. bbls.	100 lbs.	5.85
Glacial, c/l. bbls.	100 lbs.	11.01
Acetylsalicylic, bbls.	lb.	.75
Anthranilic, 99–100%, drums	lb.	1.00
Benzoic, tech., bbls.	lb.	.65
Boric, bbls.	lb.	.11
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, 85%, drums	lb.	.35
Chromotropic, bbls.	lb.	1.35
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.46
Cresylic, crude, drums	lb.	.55
Formic, 85%, cbys., N. Y.	lb.	.10
Gallic, U. S. P., bbls.	lb.	.70
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.85
H, bbls., wks.	lb.	.68
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.	.12
Hypophosphorous, 30%, U. S. P., 5 gal. demis.	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.05½
Lactic, 66%, light, bbls., wks.	lb.	.28
Metanilic, bbls.	lb.	.60
Mixed, tanks, wks.	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.35
Naphthionic, tech., bbls.	lb.	.55
Neville & Winther's, bbls.	lb.	1.00
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.10¾
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.07
Picramic, bbls.	lb.	.50
Picric, bbls.	lb.	.25
Pyrogallic, tech., bbls.	lb.	.85
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls.	lb.	.14½
Sulfanilic, 250-lb. bbls.	lb.	.16
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.25
66°, tanks, wks.	ton	14.00
60°, tanks, wks.	ton	9.50
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.	.35
Tartaric, U. S. P., cryst., bbls.	lb.	.29
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.	4.90
Cologne Spirit, bbls.	gal.	5.00
Amyl, 10%, Imp. drums	gal.	2.60
Butyl, drums, wks.	lb.	.27½
Denatured, No. 5, Comp. denat., drs.	gal.	.54½
No. 6, Comp. denat., drs.	gal.	.53½
No. 1, Spec. denat., drs.	gal.	.55½
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.	3.40
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.25
Soda, bbls., wks.	100 lbs.	3.50
Aluminium, metal, N. Y.	lb.	.27
Aluminium chloride, anhyd., drums	lb.	.22
Aluminium stearate, 100-lb. bbl.	lb.	.21½
Aluminium 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.	.30
Ammonia water, 26°, drums, wks.	lb.	.06½
Ammonium acetate, kegs	lb.	.43
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.53
Carbonate, tech., casks	lb.	.09
Chloride, gray, bbls.	lb.	.07¾
Lump, casks	lb.	.12
White, bbls.	lb.	.07
Iodide, 25-lb. jars	lb.	5.20
Lactate, bbls.	lb.	.15
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.30
Phosphate, dibasic, tech., bbls.	lb.	.18
Tribasic, bbls.	lb.	.04
Sulfate, bulk, wks.	100 lbs.	2.75
Thiocyanate, tech., kegs	lb.	.45
Amyl acetate, tech., drums	lb.	2.75
Aniline oil, drums	lb.	.16
Anthracene, 80–85%, casks, wks.	lb.	.65
Anthraquinone, subl., bbls.	lb.	1.00
Antimony, metal	lb.	.13¾
Antimony chloride, anhyd., drums	lb.	.35
Oxide, bbls.	lb.	.17
Salt, Dom., bbls.	lb.	.25
Sulfide, crimson, bbls.	lb.	.42
Golden, bbls.	lb.	.19
Vermilion, bbls.	lb.	.50
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.06
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.13½
White, cases, bbls.	lb.	.05
Asbestine, bulk, c/l.	ton	16.00
Barium carbonate, bbls., bags, wks.	ton	56.00
Chloride, bbls., bags, wks.	ton	68.00
Dioxide, bbls., wks.	lb.	.16
Hydroxide, bbls.	lb.	.04½
Nitrate, casks	lb.	.07¾
Barium sulfocyanide, 400-lb. bbls.	lb.	.30
Barytes, floated, 350-lb. bbls., wks.	ton	26.00
Benzaldehyde, tech., drums	lb.	.70
F. F. C., cbys.	lb.	1.30
U. S. P., cbys.	lb.	1.40
Benzene, pure, tanks, mills	gal.	.24
Benzidine base, bbls.	lb.	.75
Benzoyl chloride, drums	lb.	1.00
Benzyl acetate, cbys.	lb.	1.55
Alcohol, 5-liter bot.	lb.	1.45
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	2.12
Bismuth nitrate, 25-lb. jars	lb.	1.60
Oxychloride, boxes	lb.	2.90
Subnitrate, U. S. P., 25-lb. jars	lb.	2.25
Blanc fixe, dry, bbls.	ton	75.00
Bleaching powder, drums, wks.	100 lbs.	1.90
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.06
Borax, powd., bbls.	lb.	.05





Bordeaux mixture, bbls.	lb.	.11¾
British gum, com., c/l.	100 lb.	5.02
Bromine, bot.	lb.	.47
Bromobenzene, drums.	lb.	.40
Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums.	gal.	2.27
Cadmium bromide, 50-lb. jars.	lb.	1.20
Cadmium, metal, boxes.	lb.	.70
Cadmium sulfide, cs.	lb.	1.50
Caffeine, U. S. P., 5-lb. cans.	lb.	3.75
Calcium acetate, bags.	100 lbs.	3.00
Arsenate, bbls.	lb.	.06
Carbide, drums.	lb.	.04½
Chloride, drums, N. Y.	100 lbs.	24.30
Lactate, tech., bbls.	lb.	.13½
Nitrate, bbls.	ton	50.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lb.	1.10
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.84
Jap., cases.	lb.	.77½
Crude, cases	lb.	.54
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.85
Carbazole, bbls.	lb.	.50
Carbon bisulfide, drums.	lb.	.06
Carbon black, cases.	lb.	.09
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums.	lb.	.07
Casein, tech., bbls.	lb.	.12½
Cellulose acetate, cs.	lb.	1.75
Cerium oxalate, kegs.	lb.	.35
Chalk, pptd., casks.	lb.	.04¼
Charcoal, wood, powd., bbls.	lb.	.06
China clay, imp., bgs.	100 lbs.	16.00
Chloral hydrate, drums.	lb.	.60
Chloramine T., 5-lb. bot.	lb.	1.32
Chlorcosane, 5-lb. bot.	lb.	.55
Chlorohydrin, anhyd., drums.	lb.	.75
Chlorine, liq., c/l, cyl.	lb.	.05½
Chlorobenzene, mono-, drums.	lb.	.08
Chloroform, drums.	lb.	.30
Chromium acetate, 20° sol., bbls.	lb.	.05½
Sulfate, bbls.	lb.	.07
Cinchonidine sulfate, 100 oz.	oz.	.40
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs.	lb.	2.50
Cobalt oxide, bbls.	lb.	2.10
Cod-liver oil, bbls.	bbl.	29.00
Collodion, drums.	lb.	.23
Copperas, c/l, bulk.	ton	13.00
Copper, metal, elec.	lb.	.14⅜
Copper carbonate, bbls.	lb.	.16¾
Chloride, bbls.	lb.	.28
Cyanide, drums.	lb.	.50
Oxide, red, bbls.	lb.	.16½
Sulfate, bbls.	lb.	.04½
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.22
Cyanamide, bulk, N. Y.	Ammon. unit	2.05
Diaminophenol, kegs.	lb.	3.80
Dianisidine, kegs.	lb	3.50
Dichlorobenzene, drums.	lb.	.06
Diethylaniline, drums.	lb.	.64
Diethyl phthalate, drums.	lb.	.35
Diethyl sulfate, tech., drums.	lb.	.20
Dimethylaniline, drums.	lb.	.32
Dimethylsulfate, drums.	lb.	.50
Dinitrobenzene, drums.	lb.	.15
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.32
Diphenylamine, bbls.	lb.	.48
Diphenylguanidine, bbls.	lb.	1.05
Epsom salt, tech., bbls., c/l, N. Y.	100 lbs.	2.00
Ether, U. S. P., drums.	lb.	.16
Ether, nitrous, bot.	lb.	.92
Ethyl acetate, 99%, drums.	gal.	1.15
Bromide, drums.	lb.	.40
Chloride, drums.	lb.	.26
Methyl ketone, drums.	lb.	.25
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums.	lb.	.75
Glycol.	lb.	.50
Feldspar, bulk.	ton	22.00
Ferric chloride, tech., bbls.	lb.	.08
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags.	ton	25.00
Formaldehyde, bbls.	lb.	.09¼
Formaniline, drums.	lb.	.40
Fuller's earth, bags, c/l mines.	ton	17.00
Furfural, 300-lb. bbls.	lb.	.22
Glauber's salt, bbls.	100 lbs.	1.25
Glucose, 70°, bags, dry.	100 lbs.	3.89
Glycerol, C. P., drums.	lb.	.19
G salt, bbls.	lb.	.52
Hexamethylenetetramine, drums.	lb.	.65
Hydrogen peroxide, 25 vol., bbls.	lb.	.08
Hydroquinone, kegs.	lb.	1.40
Indigo, 20% paste, bbls.	lb.	.15
Iodine, crude, 200-lb. kgs.	lb.	4.10
Iodine, resubl., jars.	lb.	4.65
Iodoform, bot.	lb.	5.50
Iridium, metal.	oz.	260.00
Kieselguhr, bags.	ton	60.00
Lead, metal.	lb.	8.50
Lead acetate, bbls. white.	lb.	.15½
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.11¼
Red, bbls.	lb.	.11¾
Peroxide, drums.	lb.	.25
White, basic carb., bbls.	lb.	.10¾
Sulfate, bbls.	lb.	.10¼
Lime, live, chemical, bbls., wks.	100 lbs.	1.50
Lime, hydrated, bbls.	lb.	.01½
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.50
Lithopone, bbls.	lb.	.07
Magnesite, crude	ton	15.00
Calcined, 500-lb. bbls. wks.	ton	48.00
Magnesium, metal sticks.	lb.	1.25
Magnesium carbonate, bags.	lb.	.06¾
Chloride, drums.	ton	34.00
Fluosilicate, cryst., bbls.	lb.	.12
Oxide, U. S. P., bbls.	lb.	.42
Manganese chloride, casks.	lb.	.06½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks.	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.20
Mercury, flasks, 75 lb.	flask	83.00
Meta-nitroaniline, bbls.	lb.	.70
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.78
Methanol, 97%, tanks.	gal.	.67
Methyl acetone, drums.	gal.	.70
Salicylate, cases.	lb.	.47
Methyl chloride, cylinders.	lb.	.50
Michler's ketone, bbls.	lb.	3.75
Monoethylaniline, drums.	lb.	.90
Naphtha, solvent, tanks.	gal.	.25
Naphthalene, flake, bbls.	lb.	.05
Nickel, metal.	lb.	.31
Nickel salt, single, bbls.	lb.	.10
Double, bbls.	lb.	.11
Niter cake, bulk.	ton	5.50
Nitrobenzene, drums.	lb.	.09
Oil, castor, No. 1.	lb.	.17½
China wood, bbls.	lb.	.13¼
Coconut, Ceylon, tanks.	lb.	.09
Cod, N. F., tanks.	gal.	.55
Corn, crude, tanks.	lb.	.09
Cottonseed, crude, tanks.	lb.	.09⅝
Lard, edible, bbls.	lb.	.19⅛
Linseed, bbls.	gal.	1.06
Menhaden, crude, tanks.	gal.	.55
Neat's-foot, pure, bbls.	lb.	.14¾
Oleo, No. 1, bbls.	lb.	.13½
Olive oil, denat., bbls.	gal.	1.20
Foots, bbls.	lb.	.09⅜
Palm, Lagos, bbls.	lb.	.09½
Peanut, crude, tanks.	lb.	.10¾
Perilla, bbls.	lb.	.14¾
Rapeseed, bbls.	gal.	1.00
Red, bbls.	lb.	.11½
Soy bean, crude, bbls.	lb.	.13
Sperm, 38°, bbls.	gal.	.89
Whale, bbls.	gal.	.79
Ortho-aminophenol, kegs.	lb.	2.40
Ortho-anisidine, drums.	lb.	3.00
Ortho-dichlorobenzene, drums.	lb.	.05½
Ortho-nitrochlorobenzene, drums	lb.	.37
Ortho-nitrophenol, bbls.	lb.	1.00
Ortho-nitrotoluene, drums.	lb.	.20
Ortho-toluidine, bbls.	lb.	.25
Palladium, metal.	oz.	80.00
Para-aminophenol, kegs.	lb.	1.16
Paraldehyde, tech. drums.	lb.	.30
Para-formaldehyde, cases.	lb.	.42½
Para-nitraniline, bbls.	lb.	.60
Para-nitrochlorobenzene, drums	lb.	.20
Para-nitrophenol, bbls.	lb.	.55
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.38
Para-phenylenediamine, bbls.	lb.	1.25
Para-toluidine, bbls.	lb.	.68
Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums.	lb.	.23
Phenolphthalein, drums.	lb.	1.40
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases.	lb.	.75
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal.	oz.	119.00
Potash, caustic, drums.	lb.	.07⅛
Potassium acetate, kegs.	lb.	.29
Bicarbonate, casks.	lb.	.09½
Bichromate, casks.	lb.	.08½
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.85
Carbonate, 80–85%, calc., casks.	lb.	.06
Chlorate, kegs.	lb.	.08½
Chloride.	ton	43.55
Cyanide, cases.	lb.	.58
Meta-bisulfite, bbls.	lb.	.18
Permanganate, drums.	lb.	.14½
Prussiate, red, casks.	lb.	.37
Yellow, casks.	lb.	.18½
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums.	gal.	4.05
Quinine bisulfate, 100 oz.	oz.	.50
Sulfate, 100-oz. cans	oz.	.50
Resorcinol, tech., kegs.	lb.	1.35
Rochelle salt, bbls., U. S. P.	lb.	.19
R salt, bbls.	lb.	.45
Saccharin, cans.	lb.	1.75
Salt cake, bulk.	ton	18.00
Saltpeter, gran., bbls.	lb.	.06¼
Silica, ref., bags.	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.46½
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.	.05¾
Benzoate, bbls.	lb.	.59
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks.	lb.	.06½
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.48
Carbonate, sal soda, bbls., 100 lbs.		1.30
Chlorate, kegs.	lb.	.06¼
Chloride, bags.	ton	12.00
Cyanide, cases.	lb.	.22
Fluoride, bbls.	lb.	.08¾
Hyposulfite, bbls.	lb.	.02½
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.57
Nitrate, crude, bags, N. Y.	100 lbs.	2.64
Nitrite, bbls.	lb.	.09
Perborate, bbls.	lb.	.21
Peroxide, cases.	lb.	.22
Phosphate, trisod.	lb.	.03¾
Picramate, kegs.	lb.	.60
Prussiate, bbls.	lb.	.10
Silicate, drums, tanks.	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04¼
Stannate, drums.	lb.	.39
Sulfate, anhyd., bbls.	lb.	.02½
Sulfide, cryst., bbls.	lb.	.03
Solid, 60%.	lb.	.04
Sulfocyanide, bbls.	lb.	.45
Tungstate, kegs.	lb.	.65
Strontium carbonate, bbls.	lb.	.07
Nitrate, bbls.	lb.	.07½
Strychnine alkaloid, 100 oz., powd.	oz.	.71
Sulfate, powder.	oz.	.57½
Sulfur, bulk.	ton	14.00
Sulfur chloride, red, drums.	lb.	.05½
Yellow, drums.	lb.	.04½
Sulfur dioxide, cyl.	lb.	.08
Sulfuryl chloride, drums.	lb.	.65
Thiocarbanilide, bbls.	lb.	.25
Tin, Amer., stand.	lb.	.56¼
Tin bichloride, 50% sol., bbls.	lb.	.14¾
Oxide, bbls.	lb.	.59
Toluene, tanks.	gal.	.26
Titanium oxide, bbls., wks.	lb.	.13
Tribromophenol, cases.	lb.	1.00
Triphenylguanidine, drums.	lb.	.73
Triphenyl phosphate, bbls.	lb.	.55
Tungsten.	WO_2 unit	8.50
Urea, pure, cases.	lb.	.18
Whiting, bags.	ton	18.00
Xylene, 5°, drums, mills.	gal.	.35
Xylidine, drums.	lb.	.40
Zinc dust, drums.	lb.	.09½
Zinc, metal, N. Y.	lb.	.07½
Zinc ammonium chloride, bbls.	lb.	.07½
Chloride, granulated, drums.	lb.	.08½
Oxide, Amer., bbls.	lb.	.08½
Stearate, bbls.	lb.	.20

Automatic Weighing Machines



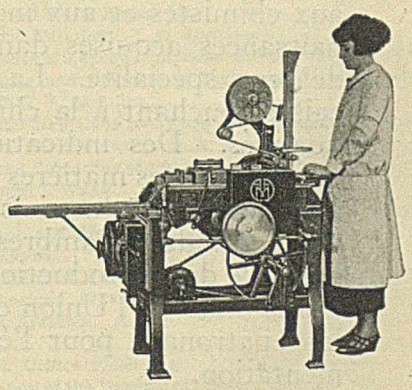
A. M. F. Machines are noted for their constant accuracy in weighing dry, free-running materials such as Flour, Fertilizer, Cement, Flaked Foods or Chemicals. We build a machine to weigh these and similiar products in quantities from ¼ oz. to 1 ton.

Write us describing your product and we will gladly furnish you with complete information and prices regarding Automatic Weighing Machines as applied to your specific product.

Power Wrapping Machines

A. M. F. Power Wrapping Machines are made to handle all types of packages in Glassine, Waxed Paper or Tinfoil. Considered by many as the fastest and best made machines on the market and will wrap packages from 1" x ½" x ¼" to 8" x 6" x 6".

A. M. F. Wrapping Machines assure your product the highest degree of sanitation, preserving and entirely excluding moisture, dust, insects and other spoilage elements.



We also manufacture Rotary Pumps, Tobacco Machinery, etc., and contract for Special Machinery. Our plant is one of the largest and best equipped in the country and can solve your particular problem.

Send for Information and Illustrated Circulars

AMERICAN MACHINE & FOUNDRY COMPANY

Main Office and Works: 5520 Second Avenue, Brooklyn, New York, U. S. A. Cable Address "Cigmach" Brooklyn.
New York Office: 511 Fifth Avenue, New York City, U. S. A.