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EDITORIALS

FUTURE CHEMISTS. Among the record of cycles should be recorded that which seems to demand periodically an increased supply of the best trained men. The rapid expansion of the chemical industry at the close of the World War found so many of the promising men leaving the academic halls as to lead the Rockefeller Foundation to supply funds through the National Research Council for a series of fellowships, the primary purpose of which was to save for science and research some of those graduate students who might otherwise immediately enter the employ of industry. Some of these fellows chose research careers in educational institutions as their life's work, but many have since found their way into industry.

The result of that increased demand for scientific personnel is recognized to have had another effect upon American chemistry, being in a large measure responsible for the decrease in the number of those really qualified now to assume the duties and direct the activities of the departments of chemistry in educational institutions. This dearth of material unfortunately comes concurrently with the retirement through age limitation of a considerable number of those whose names have become synonymous with progress in American chemistry.

It is not at all surprising that many men look to industry as the proper outlet for their scientific talents. The chemical industry may be proud of its depression record. This is not only a splendid showing as regards earnings, but with respect to employment as well. A survey made by the Chemical Alliance, Inc., comparing the statistics for two dates representing periods respectively about three months before the expiration of a code for the chemical manufacturing industry and six months after its annulment—a period that marks slow progress—indicates a good record. There have been slightly increased hours in factory occupations but they have not advanced beyond the average permitted by the former code and in nonfactory occupations they have not increased and are still considerably below the code maximum. In both classifications the workers are paid at higher rates than the code minimum and this proportion tends to increase. There are also indications of higher average rates, while the income of workers, their average and weekly earnings, have increased.

But what of the future? The demand is always for the best trained men. Some of those who will take their doctorate in 1937 are already employed as of the date of their degree. If this sort of thing continues, how are we to be sure that the graduates of the future will really be adequately trained and up to the standard? Is it wise to leave to anyone but the very best among our scientists the task and responsibility of training successive classes of the younger men? How can anyone less qualified be expected to train men of ever increasing capability which the situation demands? Might it not be in the interest of both industry and education to work out some coöperative plan to make it attractive to selected men to remain in research and teaching and give leadership where it will actually do the greatest good over a period of time—namely, the academic institutions which can be certified by the AMERICAN CHEMICAL SOCIETY's Committee on Accrediting Institutions Offering Instruction in Chemistry as places where men are really trained?

PUBLICATION POLICY. Here and there in the field of chemistry and the industry we find those who continue to pursue a very conservative policy regarding publication. Many reasons are advanced and when these are debated by the technical editor he is likely to be accused of selfish motives and insufficient regard for trade property. The technical editor, however, has seen so many examples of benefit derived from adequate publication at the right time that he continues to urge it.

Many great organizations have their own experience in publication to guide them, and we are pleased to quote here from the *Review of Scientific Instruments* for March, 1936, the remarks of Dr. Buckley in the report of the Conference on Applied Physics, who discussed the liberal policy of the Bell Telephone Laboratories toward publication:

> We publish extensively in the engineering and scientific journals, in our own journals, always, of course, using care lest

publication be premature from the business standpoint. Why have we made this change from little to liberal? We have found that it pays. We do not publish merely to be charitable or to advertise. One reason for publishing is that the man who is doing a research is forced to round out the job in a technical way because the results are going to be read by his scientific peers. Another special benefit in a large industry is this: Although a good research job is respected in the laboratory its publication in a journal gives it a standing demanding attention throughout the rest of the organization. It is often the best way of making the work of the research people effectively available to other departments. Moreover, publication gives a personal satisfaction to the scientific worker in the public esteem which he gains. The result is usually to stimulate him to further effort and to make of him a more valuable employee. Still another benefit from publication is the effect on the problem of employment of high-grade men for scientific work. The prospective employee welcomes association with others of his own type and the opportunity for maintaining his place in the scientific world. On the basis of some 20 years of experience I can recommend the policy of liberal publication very wholeheartedly.

This liberal attitude is shared by most of our great industrial units whose success is definitely bound up with scientific progress. They have found that profits increase for all as the literature is made richer by such contributions.

THE INSTITUTE OF CHEMISTRY. A few years ago the AMERICAN CHEMICAL SOCIETY held two sessions of an Institute of Chemistry, with a view to giving any who could attend the opportunity to bring himself quickly up to date on a number of subjects, to meet leaders in various fields, and to combine such a stimulating period with activities characteristic of vacations. The plan could not be continued for want of financial assistance, since, like everything of its type, the institute could not be run on a strictly self-supporting basis. Some argued that the number of those who took advantage of what the program offered was out of proportion to total costs. Others thought the idea was ahead of its time. All these factors, together, cut short the experiment.

We wonder if the project should not be revived. It is the common experience in educational institutions and industrial plants that the depression has added to the load carried by the chemist. The necessity for more work to be done in the discharge of one's regular duties has served to decrease time for accessory reading, while concurrently the literature has grown and has increased in its specialization. This situation makes it more desirable than ever to give men and women who are becoming more and more specialized the opportunity which the Institute of Chemistry was designed to afford. The specialty will not suffer, but will be advanced by programs like this of the institute. It is quite likely that, if attempted again, still larger numbers can find it possible to attend and the venture might be more nearly self-supporting. Nothing can be done about 1936, but it is none too early to consider the project with the summer of 1937 a possibility.

INDUSTRY AND THE PROFESSOR. The several problems involved in establishing coöperation between gown and overalls have long had expert consideration. The educator interested in research of value to industry obviously can do his best work if his own information is kept up to date. The industrialist hesitates to reveal trade secrets, even in the patent literature, and too often leaves his professorial colleague so much in the dark that the value of his work suffers. On several occasions papers of academic origin submitted for publication have had to be rejected on the basis that those who had conducted the research were obviously unfamiliar with the latest industrial practice, though it was admitted that the details such as are expected in a technical paper had not been published. Rely on the patent literature as an adequate source of information? Well, hardly.

And so we are often confronted with the question, how can the abilities of our professors be utilized to the best advantage? Might not industry at least suggest from time to time the problems in pure science, the solution of which would be of considerable interest, and with the knowledge that the results obtained would appear promptly in the chemical literature? Should not such programs of work be accompanied with enough data to serve reliably as a guide to ensure really useful work? There ought to be a satisfactory method for guiding this research effort.

PLAIN RESPONSIBILITY. Several cases of physical handicaps, which under state laws and regulations make it practically impossible for men to enter industrial employment, have come to our notice recently. While it is easy to say that the teacher should make plain to a pupil what he may expect to encounter in pursuing a certain line of work under a physical handicap, it is unquestionably difficult and embarrassing to do so. In the long run, however, a discussion of the limitations confronting one so unfortunate is a humanitarian act and the duty of the teacher.

These instructors, who appreciate such difficulties in the career of one pursuing a profession, are therefore faced with the performance of an act which, while unwelcome, is nevertheless kindly.

What we urge must not be confused with scholarship. It is seldom safe to guide a man into other activity because his early record in the subject of his choice is not satisfactory. There are many examples to condemn such practice, but personalities, physical handicaps, and obvious inaptitude could form the basis of beneficial conferences. Far better to help those who might find places elsewhere to change the direction of their work early than to graduate them as chemists and chemical engineers, only to have them find no employment.

THE FURANS

HERCULES POWDER COMPANY, BRUNSWICK, GA.

Fifteen Years of Progress

FREDUS N. PETERS, JR.
The Quaker Oats Company, Chicago, Ill.

ALMOST fifteen years have passed since furfural entered the industrial chemical field, and it may be of interest to review the rise of the furans to more or less industrial prominence and see what promises made for these products in 1922 have reached fruition. To the casual reader, achievements are more interesting than failures but to the student the latter are often more instructive. Hence this paper takes the unconventional course of recording the failures as well as the triumphs of furfural and its derivatives.

Probably no chemical product has ever received kinder treatment in the technical press during its infancy or has created more widespread interest and speculation than furfural. This was probably due to a number of circumstances. Furfural came on the industrial stage in the early days of America's rise to eminence in the chemical field. Its production was one of the Government's earliest ventures into the field of the industrial utilization of agricultural products. Early in the twenties, LaForge and Mains of the Bureau of Chemistry did some excellent pioneer work on the commercial production of furfural from corncobs (*19*). Mains's work on the distillation of furfural-water mixtures is still the standard reference in this field (*21*). About the same time The Quaker Oats Company through its consultants, The Miner Laboratories, independently developed the production of furfural from oat hulls and for many years the plant at Cedar Rapids, Iowa, was the world's sole source of furfural in commercial quantities. Although this American plant is still the largest producer of furfural, a plant in Sweden is reported to be making furfural from tanbark. Still smaller plants are located in various parts of Russia, but data regarding these latter units are very meager. Aside from acetic acid, alcohol, and sugars, this compound was one of the first chemicals to be made in large quantities from agricultural products, although butyl alcohol from corn was being developed at the same time. Last and by no means least responsible for its favorable publicity was the unusual heterocyclic ring structure which characterizes all furan compounds.

A Thousand-Pound Order

In 1922 a drum of furfural was shipped to the Exposition of Chemical Industries to prove to skeptics that at least 500 pounds of the aldehyde were available if anyone wished to buy it. At that time most shipments were 5-gallon lots, but within a few months larger orders were received and those responsible for furfural sales have not yet forgotten the thrill they had late that year when an order for 1000 pounds was received. Although it is not a matter of record, the manager of the mill at Cedar Rapids probably supervised the loading of those two precious drums.

Although it was almost invariably referred to as a "recent laboratory curiosity," furfural had been discovered in 1832 (*11*), and hence enough was known of its general properties to enable those interested in it to predict that it might be useful in the then infant resin industry. It was sold for one dollar a pound. Formaldehyde was quoted at about the same price, and optimists predicted that soon millions of pounds of furfural would be consumed annually in the manufacture of phenolic resins. While this prediction was not immediately realized, it was not long before drum cars of furfural were regularly shipped to the makers of resins, and these eventually grew into tank car shipments. During this steady increase in furfural consumption there were frequent price reductions until today 98.5 per cent furfural is quoted at 9 cents a pound. However, the pioneers made the mistake of assuming that furfural was merely another aldehyde which could be substituted for formaldehyde with no changes or modifications. The large number of patents issued on furfural resins is presumptive evidence that the manufacture of such products involves more than mere substitution. A consideration of the facts to follow will show that the manufacture of these products is a distinct and separate art; in the words of a manufacturer of furfural resins, "it is not obvious but rather unexpected that the resins resulting from the furfural reactions with phenol should be as similar as they are to those obtained by condensation of formaldehyde with phenol."

Furfural in Resins

Since little concerning furfural resins has appeared outside of the patent literature, the following summary of some of the properties making furfural valuable in this field is given. In the first place, its boiling point is above the normal reaction temperature of furfural and phenol; hence during the reaction great precautions against the loss of aldehyde are not necessary. This high boiling point also simplifies the removal of water formed in the reaction, and thus a substantially anhydrous product of uniform character is formed, free from cracking and blistering. In connection with this question of water formation is a factor seldom fully appreciated even by those most familiar with resin manufacture. This is the high molecular weight of furfural. If it is assumed that in a finished resin, equimolecular quantities of aldehyde and phenol have reacted with the liberation of one molecule of water, then for each 96 pounds of furfural reacting, only 18 pounds of water are liberated. In the case of formaldehyde, this same amount of water is formed for each 30 pounds of anhydrous aldehyde consumed. Obviously the result is that furfural resins contain a proportionately larger quantity of the aldehyde residue than is present in the older type of resin.

In the second place, furfural is a solvent for phenolic bodies and for resinous condensation products; hence throughout the reaction process the mixture is substantially homogeneous. The resulting product is uniform; the chances for one portion of the mixture to react to a greater extent than another are practically eliminated. Further, this function of furfural is extremely important since thereby liquid products of various viscosities can be produced, wherein substantially all of the aldehyde and phenol have combined.

Phenol-furfural resins sold under the trade name "Durite" react rapidly in heated molds to an exact replica of the mold cavity with respect not only to dimension, but also finish and polish of the cavity. These resins react most completely at the temperature of the mold, forming solid products which do not distort and lose little or no polish when ejected from the cavity at full mold temperature. The resins produced have a permanent black or brown color without the addition of pigments.

While pure furfural resin made in glassware absorbs no moisture after 100-hour immersion in distilled water, the commercial grade of resin which includes certain impurities will absorb approximately 0.18 per cent of water after 100-hour immersion. The moisture absorption of a molding compound depends on its resin content and the type of filler used; a one-inch cube of the usual wood floor-resin composition, after being heated for 24 hours at 100° C. (212° F.), will lose approximately 0.48 per cent of its weight, and, when submerged in distilled water for 48 hours, will show a gain of 0.59 per cent. Oil absorption determined in a similar manner is extremely low. More complete data on the properties of Durite resins and molding compounds have been published previously (*1*).

These advantages were not all discernible in 1922. Thus, since at that time it was found that furfural reacted more slowly than formaldehyde and the demand for greater production speeds became more insistent, the use of formaldehyde was favored by some producers. Also it was not long before the age-long demand for color made itself felt and dark-colored furfural resins were ruled out of the purely decorative and esthetic fields. Undoubtedly the patent situation contributed to the preference for formaldehyde by some manufacturers. The basic formaldehyde patents were well along in years by that time, whereas the first U. S. furfural-resin patent was not issued until late in 1921 (*26*). This was followed by many more; a few of the typical ones are listed (*8*, *14*, *23*, *27*).

During these years The Quaker Oats Company was the sole American source for furfural, and possibly the lack of alternative suppliers of the raw material deterred some from giving more than scant attention to the new product. Nevertheless, the resin manufacturers immediately became the largest customers of the infant industry and held that position for five or six years. Although more furfural is being converted into resins now than ever before, other uses have greatly eclipsed the importance of resins as an outlet for it.

Just as the formaldehyde resins of 1936 are far superior to those of 1922, so progress has occurred in the manufacture of furfural resins. They can now be made to react as rapidly as modern production methods require, and there is little doubt but that, if this subject should receive the same amount of intensive research as has been accorded other resins, furfural products would assume a still more important place in the field of plastics.

Within three or four years after the manufacture of furfural resins began, it was found that furfural was an excellent solvent for potentially reactive phenolic resins as well as for many naturally occurring gums. This discovery (*6*, *22*) resulted in its widespread adoption as a solvent in the manufacture of resin-bonded abrasive wheels. For years furfural has enjoyed preëminence in this field, and no solvent has yet been equally suitable from all points of view. The importance of this type of grinding wheel can be appreciated from the fact that the grinding costs incident to the manufacture of a moderate-priced automobile have been reduced 80 per cent during the past ten years, and wheels in which furfural was used have been largely responsible for this saving.

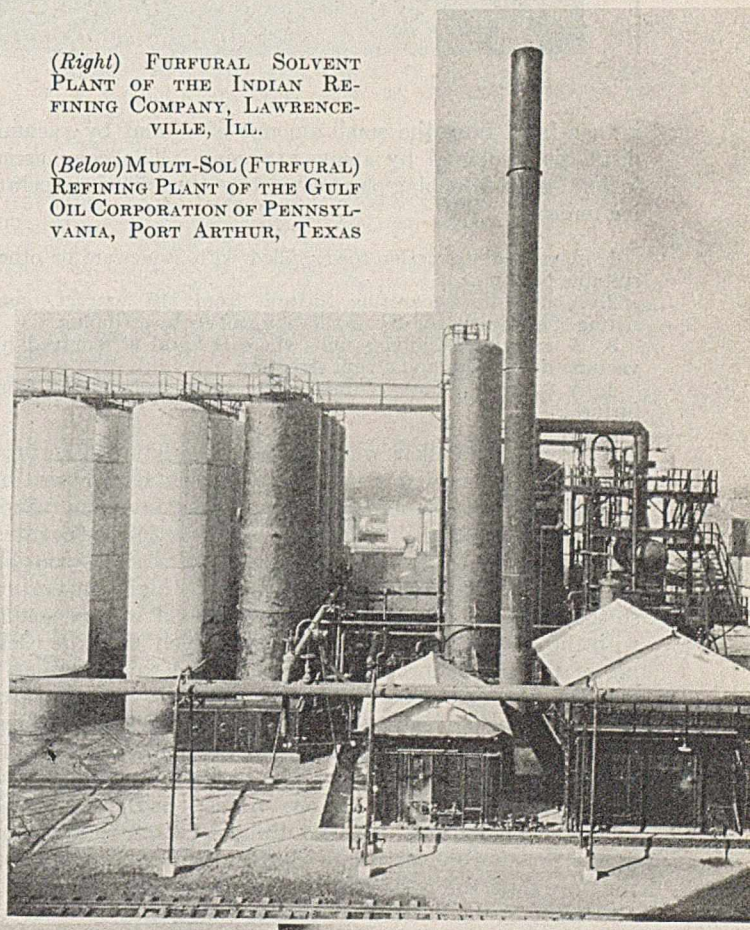
Aside from the resin-forming ability of furfural, the most easily recognized property of commercial significance is its solvent power. Some years ago it was predicted that this solvent would be used in the preparation of varnishes and lacquers and that it would find application as a paint and varnish remover. Had the rest of the chemical industry remained static, that prophecy would have been fulfilled, but, with the introduction of colorless and almost odorless solvents with a wide range of boiling points, the use of furfural in this field constantly decreased until today it is small. A few special types of lacquers and varnishes are made with furfural, and, where the utmost in water resistance is required, it is used because it has a very definite effect on the water resistivity of films. This may be due to an adsorbed film of the solvent which always remains in the finished product. It is interesting to note, however, that within the past year there has been a renewal of interest in furfural as a solvent, and possibly some of the recently initiated experimental projects will eventually assume industrial importance.

Furfural as a Refining Agent

A new type of solvent application arose, however, and in 1927 the Hercules Powder Company revolutionized the wood rosin industry by beginning the manufacture of pale rosins from the pine stumps of Georgia. Their plant was located at Brunswick, Georgia. This process has already been described (*15*, *16*), so it will suffice to say that a dark-colored (FF) rosin is dissolved in gasoline, and the resulting solution is then washed with furfural at a temperature at which the two liquids are miscible. Upon cooling, the solution separates into two phases with the furfural layer containing a substantial portion of the color bodies originally associated with the rosin. A very light colored product of WW grade can be made by this process. In 1933 another furfural plant was erected by the same company at Hattiesburg, Miss. This process allowed wood rosins to enter fields previously reserved exclusively for gum rosin—namely, paper sizing, soaps, etc.

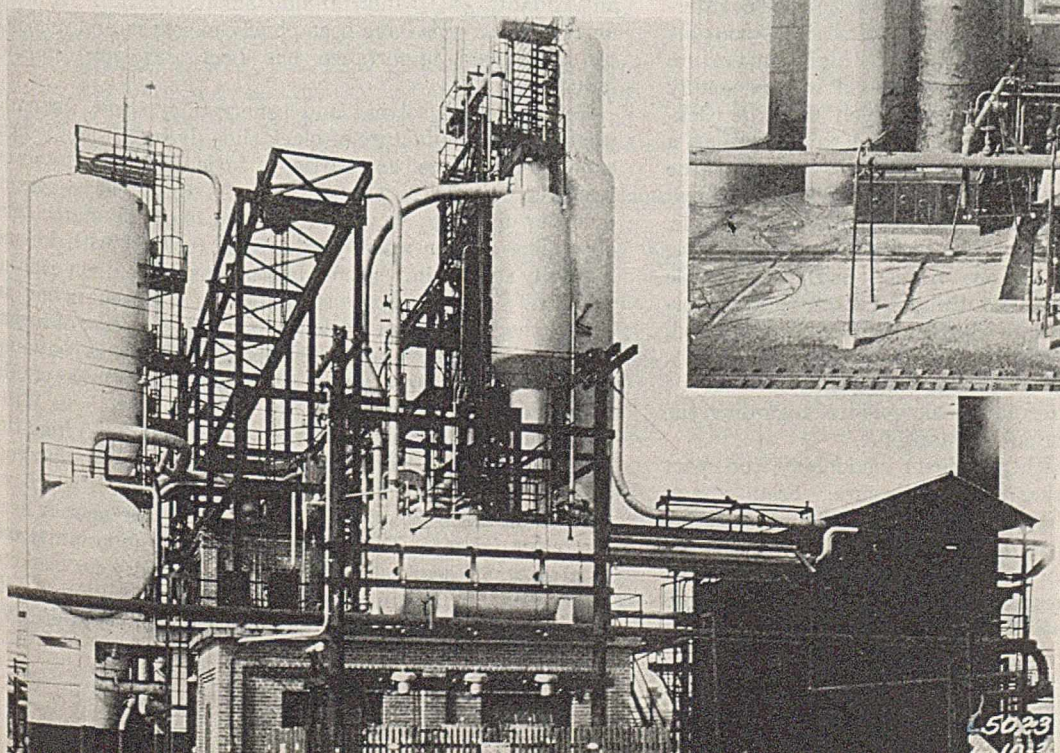
In 1925 a U. S. Patent appeared (*13*) describing the removal of sulfur compounds from petroleum hydrocarbons by the selective solvent action of furfural. This was several years before the erection of the first furfural-oil refining plant in 1933. It is an interesting bit of history that in 1929 the writer attempted to interest one of the large oil companies in a furfural solvent process and was told that solvent refining was of no interest to that company, and, even if it were, furfural could never be used. In 1933 the Indian Refining Company began the treatment of all its Havoline oil with furfural, and for the first time in history readers of advertisements in the *Saturday Evening Post*, *Time*, and other national magazines could read about the remarkable solvent action of furfural without recourse to a scientific publication. In 1935 The Texas Company built a 4500-barrel-per-day furfural-solvent plant at Port Arthur, Texas, and the Gulf Oil Corporation started operation of a 5000-barrel plant of similar design at the same city; the Shell interests in England began construction of a furfural unit, and similar plants are in operation in Roumania and Germany.

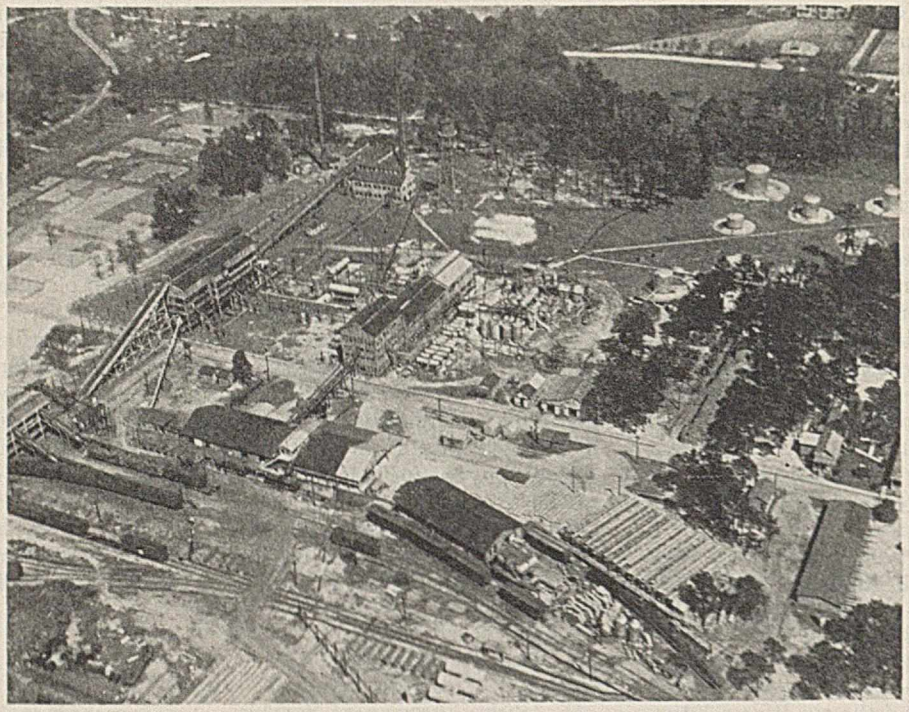
The action of furfural in oil refining is fully described by Bryant, Manley, and McCarty (*7*), but for those not familiar with the process it may be said that by countercurrent washing of oil with furfural, at temperatures in the neighborhood of 200° F., certain undesirable constituents of the oil are dissolved by the furfural which is then drawn from the bottom of the tower. The portion of the oil dissolved is called the "extract." Since the more highly paraffinic hydrocarbons (called the "raffinate") are insoluble and lighter than furfural, they are removed from the top of the tower. This raffinate



(*Right*) Furfural Solvent Plant of the Indian Refining Company, Lawrenceville, Ill.

(*Below*) Multi-Sol (Furfural) Refining Plant of the Gulf Oil Corporation of Pennsylvania, Port Arthur, Texas





NAVAL STORES PLANT OF THE HERCULES POWDER COMPANY, HATTIESBURG, MISS.

is then freed from the small amount of solvent by vacuum distillation followed by steam stripping. The commercial furfural-solvent refining plant consists of the following operating units:

1. A vertical extraction tower, filled with stoneware or other suitable packing.
2. A unit for separating furfural from the extract, consisting of apparatus for dry distillation and steam stripping.
3. A raffinate stripping unit where furfural is removed by vacuum distillation and steam stripping.
4. A furfural recovery unit where water is removed from furfural.

To those unfamiliar with the characteristics of furfural it might seem surprising that adequate contact followed by a simple gravity separation of the furfural extract and refined oil fractions could be obtained in a single, continuous, counterflow extraction tower. A number of factors are responsible for this. Furfural may be applied at a fairly high temperature so that even viscous oils are sufficiently fluid to mix readily with the solvent. Second, furfural selectively wets the packing of the tower, forming a thin film and thus exposing a greatly increased area to contact with oil. Finally, the density of furfural is so much greater than oil that a rapid separation of the hydrocarbon from the solvent is possible. One of the most startling facts, however, about this process, aside from the high quality of oils produced, is the remarkable economy of operation. The plant may be operated at atmospheric pressure except where vacuum distillation is desired, thus avoiding the costs and hazards of pressure equipment, and recovery of furfural in commercial operation is about 99.975 per cent. Such results speak volumes regarding the stability of furfural under such conditions.

To those unfamiliar with petroleum technology, the exact purpose of solvent refining may be obscure. From a nontechnical point of view it may be said that solvent refining of motor oils was developed to overcome the two most easily recognized faults of such lubricants: first, instability under extreme conditions of heat and oxidation, and secondly, an objectionably high viscosity-temperature coefficient. To the average motor car driver the first fault means excessive sludge formation in the crankcase and the second, a motor hard to start in cold weather. Solvent refining removes much of the less stable hydrocarbon fractions; hence less sludge is formed when solvent-treated oils are used. At the same time the solvent improves the viscosity characteristics of oil so that even in very cold weather the oil will flow relatively easily and yet at high temperatures will possess sufficient "body" to make it a satisfactory lubricant.

Uses of the Furans

Because of its similarity in many respects to both benzaldehyde and formaldehyde, furfural has been proposed for use in the manufacture of dyes (*10*, *30*), fungicides (*24*, *29*), antioxidants (*34*), and tanning agents (*2*, *33*). However, most of these uses have been chiefly on paper, and very little of commercial importance has been developed in these industries.

Because of its solvent and penetrating power, furfural is used in the manufacture of black shoe dyes (*25*) and is being experimentally tried as a carrier of toxic substances into wood for telegraph poles, pilings, etc. A small but continuous quantity finds its way into preservatives for starch, glue, etc. The condensation products of furfural with ketones, normally soluble in benzene, become insoluble upon exposure to light. This property is applied in photoengraving and photolithography (*3*). Although the consumption of furfural by these industries is small, it has been steady and continuous for a number of years and has actually surpassed that of other larger but short-lived outlets.

A number of furfural derivatives have appeared from time to time. Among the earliest of these was hydrofuramide, the ammonia condensation product of furfural, which was used as an antioxidant, rubber accelerator (*31*), curing agent for resins (*9*), etc. None of these uses is important today. The zinc and lead salts of dithiofuroic acid were marketed under the trade names of "Furac II" and "Furac III," respectively, and had some popularity as rubber accelerators

for a time (*20*). Furfuryl alcohol made by the catalytic hydrogenation of furfural (*28*) is used in the manufacture of resins and as a solvent for resins (*18*) as well as for the preparation of certain textile dyes (*12*). This alcohol has the property of resinifying with minute quantities of mineral acids, and for a number of years laboratory table tops have been coated with the alcohol followed by the application of a 15 per cent solution of sulfuric acid. The resin, formed *in situ*, is highly water and acid resistant. A resin varnish based on this general principle is now being marketed.

The recent unlamented depression was responsible for wrecking a promising outlet for furfuryl alcohol. By treating it with carbon disulfide and sodium hydroxide, furfuryl xanthate (*17*) is formed and exhaustive tests showed this substance to be an effective flotation compound, particularly for copper ores. About the time the new product was ready, most of the copper mines in this country ceased production, thus almost eliminating the demand for flotation agents. Of all the furfural derivatives which have appeared, furfuryl alcohol has enjoyed the greatest demand but its volume of sales compared to that of furfural leaves much to be desired. This may be due to the comparatively high cost, unfamiliarity with its properties, and the abundance of other products which confront the chemist on every side.

Tetrahydrofurfuryl alcohol has been offered at a comparatively high price but has found industrial application chiefly in Germany where it is used for the preparation of wetting and dispersing agents for use in textile printing. Bertsch (*4*) states that a solution of 2 kg. of grain soap and 10 kg. of tetrahydrofurfuryl alcohol in 100 liters of water is suitable "for the removal of oil filaments containing mineral oil from textiles." Recently articles have appeared describing the preparation of esters of this alcohol which are said to be plasticizers for cellulose derivatives (*5*). Furoyl chloride and furoic acid are other furans commercially available, but neither has found application in more than semi-commercial quantities.

What of the Future?

Several years passed after the first furfural-resin patent was issued before such products were accepted by industry. The furfural-oil refining patent of 1925 was not translated into commercial operation until late in 1933. Recent patents dealing with furfural-lignin resins (*32*), maleic acid from furfural (*35*), the furans as wetting agents (*4*), as well as the other fifty-odd patents issued during 1935, may indicate some of the future outlets for these products.

But regardless of what is in store, it may be said in conclusion that for fifteen years furfural has proved of absorbing interest to its sponsors, it has fulfilled and exceeded their fondest dreams in some repects, it has cruelly disappointed them in others, it has grown from a "laboratory curiosity" to a tank car commodity, it has merited over three thousand literature references, and yet its possibilities in many fields are almost unexplored. In these respects furfural is probably not unique among synthetic organic chemicals but at least it has earned an enviable position among the chemical achievements of the last fifteen years.

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Solvent Extraction

The July, 1935, issue of Industrial and Engineering Chemistry included a comprehensive paper by T. G. Hunter and A. W. Nash on "Liquid-Liquid Extraction Systems." On page 837 a scheme is described for separation by fractional distribution, employing the multiple-contact method, and it is stated that "computations for processes of this type have not been specially described in the literature."

May I call attention to my paper entitled "Beitrag zur Theorie des Ausschüttelns [*Z. angew. Chem.*, *38*, 323 (1925)]? The process described (although on a laboratory scale) is very much the same as the multiple-contact method of Hunter and Nash, and is even less complicated than the method shown in their Figure 2.

The opinion about the comparative efficiency of the multiple-contact and the countercurrent methods (page 838) is true only when applied to the relative amounts of solvent, not when both high purity and high yields of both products are required. That is probably the principal reason why the multiple-contact method finds its widest application in the laboratory where these two requirements are of the utmost importance for the analytical results.

Ploieşti, Roumania M. Frenc

April 3, 1936

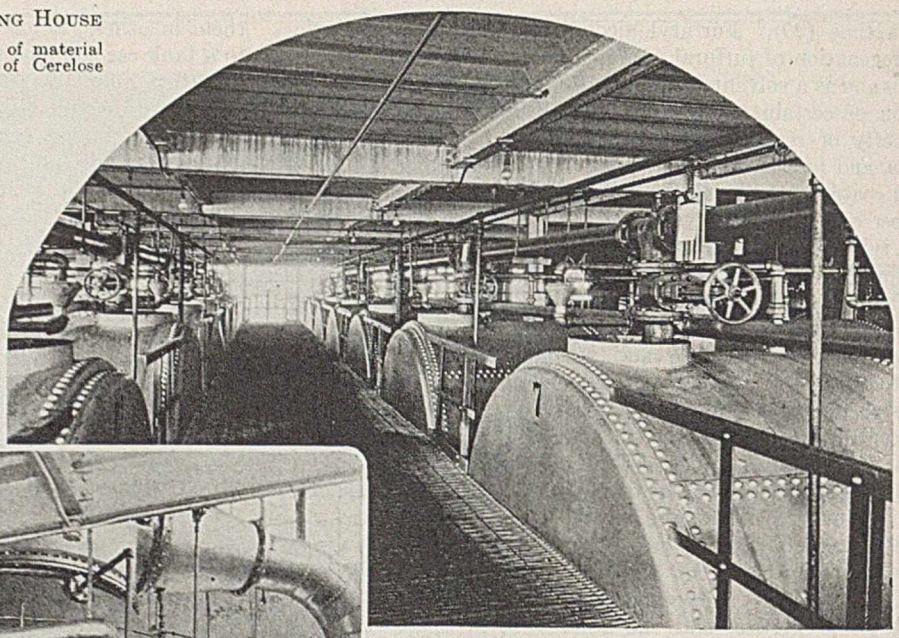
(*Right*) Working Aisle in Crystallizing House

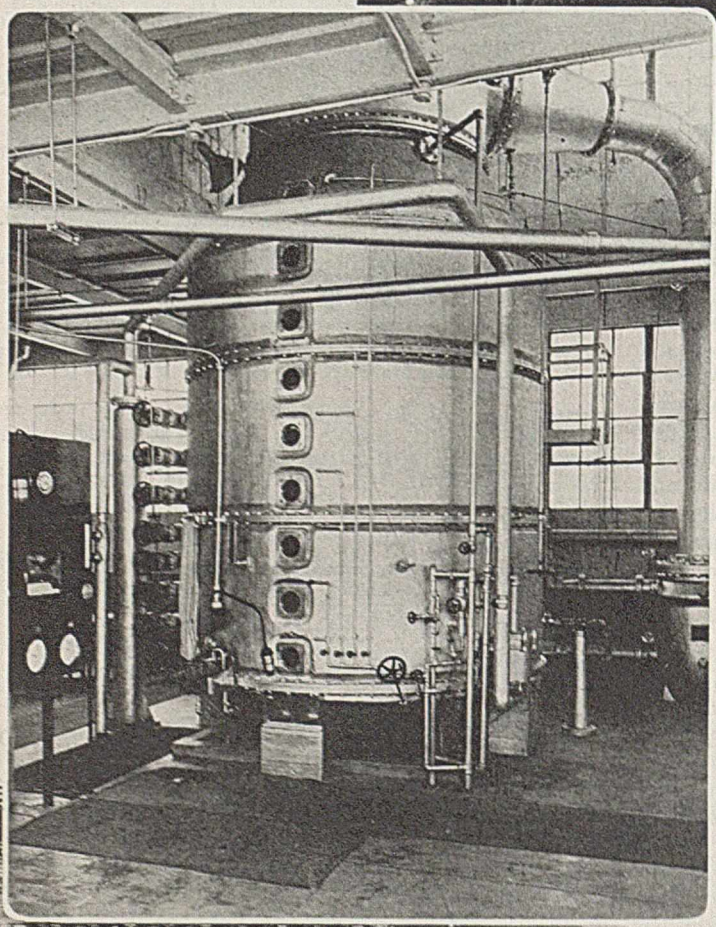
Here 160 crystallizers hold over 100,000 pounds of material in service, with a capacity of 600,000 pounds of Cerelose hydrate per day.

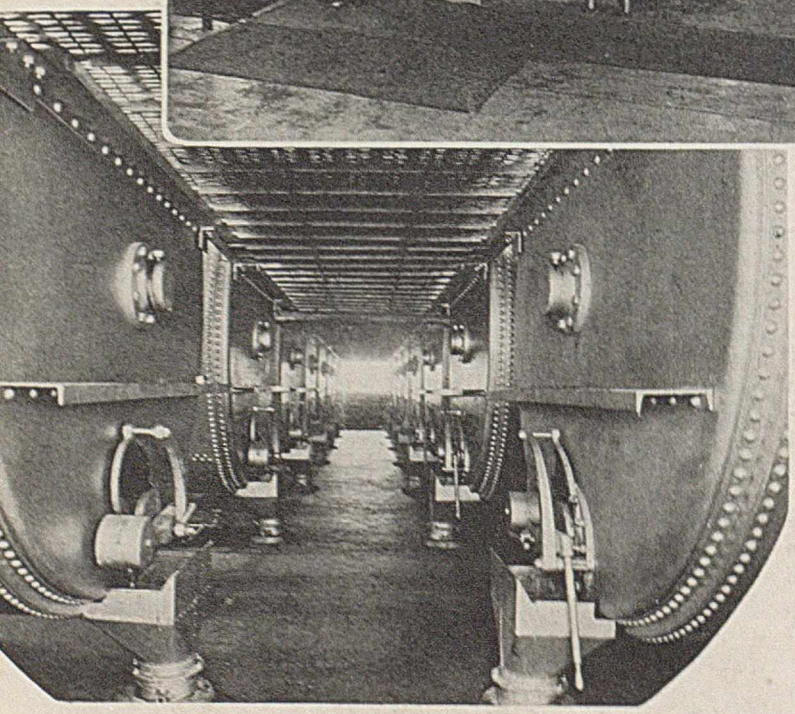
(*Center*) Brass Crystallizing Pan for the Production of c. p. Anhydrous Dextrose

Capacity, 2000 bags per day.

(*Bottom*) Discharge Aisle Which Delivers the Cured Sugar Magma to the Mixer Box Feeding the Centrifugals on the Floors Below







DEVELOPMENT AND PRODUCTION OF ANHYDROUS DEXTROSE

W. B. NEWKIRK
Corn Products Refining Company, Argo, Ill.

Crystallographic reasons for choosing anhydrous dextrose as the form required to produce a chemically pure dextrose are given. Photomicrographs illustrate the crystalline characteristics of alpha-hydrate and anhydrous dextrose under various operating conditions. The process finally evolved is described in detail.

AFTER the industrial methods of manufacturing high-purity dextrose hydrate (*4*) had been developed, the problem of improving the method of Porst and Mumford (*5*) was undertaken. Their procedure was being used for the production of chemically pure dextrose.

This method was open to many objections. The principal drawback was that the crystallization was carried out in a quiescent state in stone crocks to form a semi-solid mass. This mass was puddled to form a mushy magma from which the mother liquor was unsuccessfully removed in high-speed centrifugals produced by the International Equipment Company. The spinning time was long, the difficulties of purging were great; the sugar product leaving the centrifugal machine contained between 10 and 20 per cent free water. From this sugar it was almost impossible to obtain C. P. dextrose without alcoholic washings and numerous recrystallizations.

The successful production of a purgeable dextrose hydrate from converter liquors led first to attempts along the lines similar to those commercially used. The reason for abandoning this procedure can best be developed by a brief survey of hydrate crystallization.

Hydrate Crystallization

The first recorded pentagonal leaflet was reported by Becke (*2*). Drawings based on Becke's data are shown in the article by the writer (*4*).

Figure 1 shows a photomicrograph of the pentagonal leaflet as found in hydrol, the final molasses of the process. This is an exceedingly thin, fragile, leaflike structure that will not lend itself to commercial separations in any shape or manner. These are not fragmentary crystals. Although they are extremely thin, the edges are perfectly straight. This type of crystal shows strikingly the hemimorph habitus of the dextrose hydrate, which in other crystal forms of this sugar is more or less concealed.

Becke (*2*) evidently obtained his crystals from honey, for they are typically hemimorph. Figure 2 shows a photomicrograph of dextrose crystals as they exist in honey. They are obviously of the same type as those of Figure 1. The shingle-like arrangement of these dextrose crystals from honey is due to the habit of parallel growth.

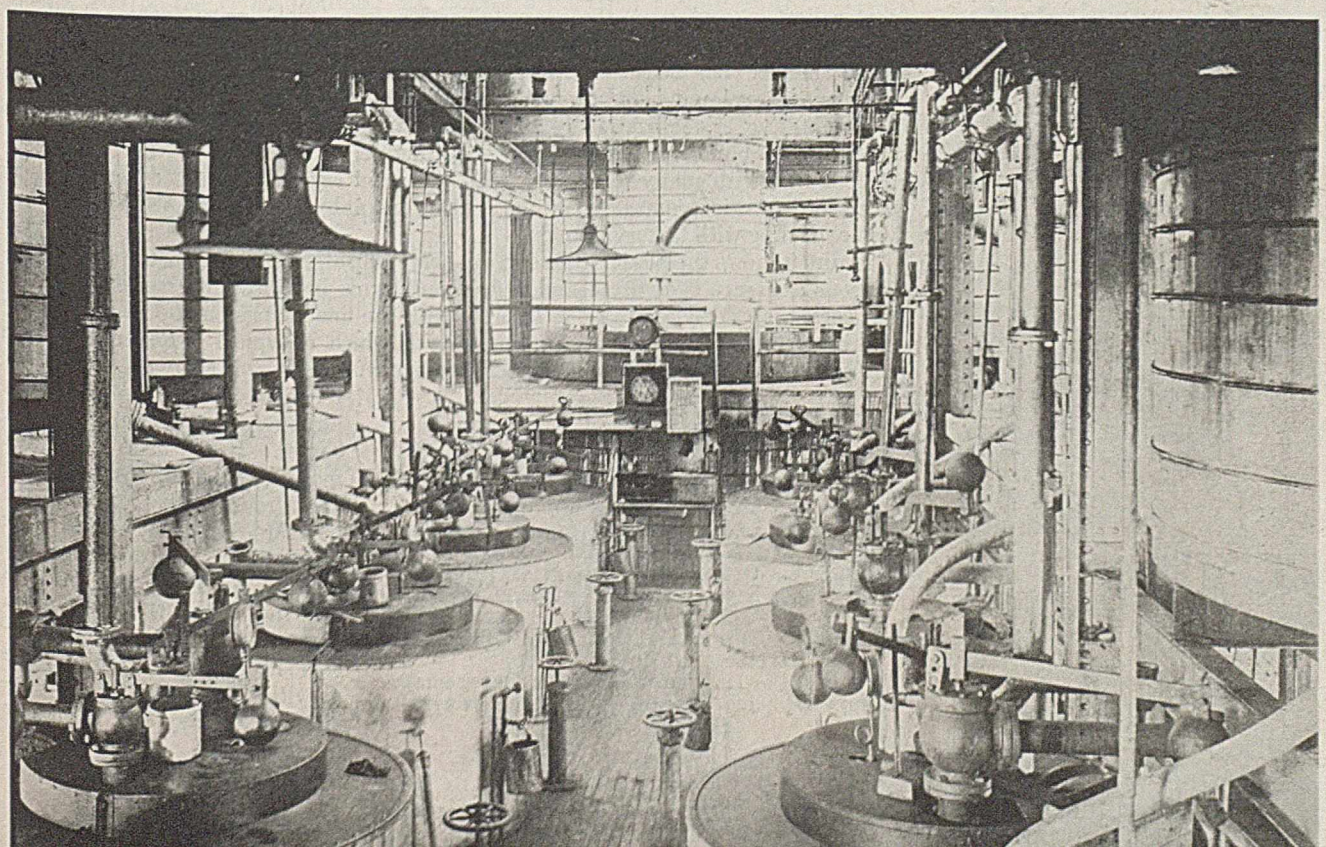
Dextrose hydrate naturally occurs as the hemimorph form. However, the form which is commercially possible to purge is produced by the twinning of two of these hemimorph forms after a rotation of 180°. In order to picture this phase, a single, well-formed hydrate was produced in the laboratory. Figure 3 is a photomicrograph of this crystal type, which is close to ideal. The development of the individual surfaces are uniform. The longitudinal prismatic surfaces are well developed. The edges of the vertical prism are very sharp. Owing to the difficulties in properly focusing an object of definite thickness, it is impossible to determine by Figure 3 whether the edges formed by the vertical prism are inclined in the same or opposite directions.

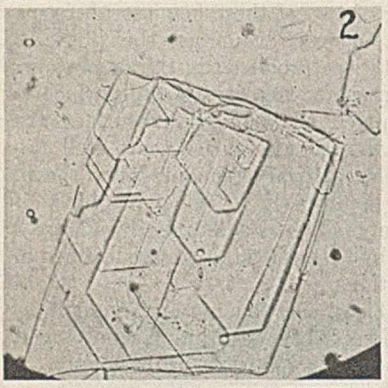
The shape of this crystal is subject to a number of modifications; under some conditions it becomes thinner and longer, under other conditions shorter and thicker. For example, if dextrose hydrate is allowed to crystallize without motion in normal factory liquors, according to Soxhlet (*6*) "wart-like aggregations" are obtained. They resemble more closely the forms of the sea urchin; i. e., spicules grow in all directions from a common nucleus, very much like a sea urchin. These spicules are easily broken so that, when the mass is centrifuged, it becomes a rather tight, compact mat which cannot be washed thoroughly without a great waste of sugar. Figure 4 is a photomicrograph of this type of dextrose crystallization; only part of the cluster was selected in order to obtain a more detailed picture. It would be impossible to remove the mother liquor from the small capillary spaces toward the center of this aggregation. Also, the aggregation would be easily broken into small fragments by any reasonable pressures exerted upon it. Figure 4 also shows the incomplete development of any of the normal faces.

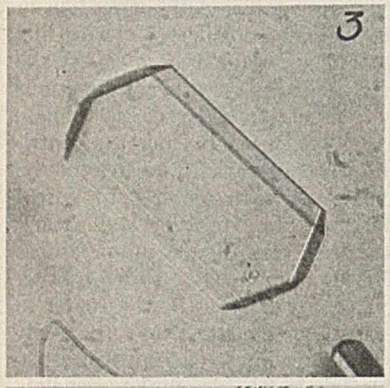
The developed process of crystallizing dextrose hydrate from normal refinery liquors in a manner which permitted it to be separated from the mother liquor by centrifugal processes, gave good yields of a washable sugar (close to 100

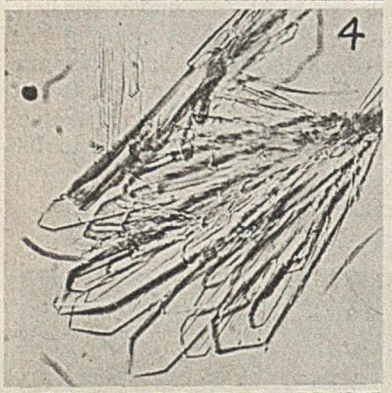
CONVERTER FLOOR WHERE STARCH IS CONVERTED TO SUGAR LIQUOR FROM WHICH HYDRATE CERELOSE IS PRODUCED

Capacity, 40,000 bushels of corn per day.









purity, *4*). Figure 5 is a photomicrograph of the typical hexagonal tablet produced by this crystallizing procedure. These crystals are approximately hexagonal in shape but have very few unaltered faces. The delineation of these faces is irregular because the crystals are of a composite type. The form is apparently symmetrical in so far as it shows a hexagonal contour. The composite structure is the result of parallel growth oriented along the *b* axis. No pentagonal structures are visible, but there are indications of hemimorph development in the form of markings parallel to the *a* axis. It is evident that, in regard to centrifugal separating characteristics, these crystals show a decided improvement over any of the crystals previously shown. Centrifugal separation is the only commercially profitable method. It was hoped that a continuation of the development of this process would give the desired chemically pure product.

The effect of colloidal impurities is startlingly demonstrated by Figure 6, a photomicrograph of dextrose resulting from the reconversion and crystallization of hydrol produced from a starch conversion. The impurities present have shortened the growth along the *b* axis so that the crystal is almost a perfect hexagon in shape and of good thickness in comparison to those just described. The top and bottom faces of the tablet are lenticular instead of flat, which prevents the formation of aggregates. There are also no indications of parallel growth but there are some indications of penetration twins. Dextrose sodium chloride is similar to these crystals.

On the other hand, if a pure dextrose sirup is crystallized under conditions necessary for the crystallization in motion of dextrose hydrate, we obtain a crystal of poorer shape. Figure 7 is a photomicrograph of dextrose hydrate from high-purity solutions. The crystals grow considerably longer and are markedly thinner. This long thin crystal is mechanically weak, and, although the mother liquors are light in gravity and of low viscosity so that they should readily purge from the crystal mass, the crystals do not thoroughly release the mother liquor. The tendency toward aggregate clusters, similar to Soxhlet's aggregations, is indicated by the grouping of these crystals on one side of Figure 7.

Another objection to the use of hydrate crystallization which developed during this work is that the low-gravity liquors, if not completely and thoroughly refined, carry with them soluble impurities from the bone black which deposit as a haze in the crystallizers so that the sugar, although it would finish with an acceptable purity and color, was not of a quality sufficient to warrant its production as a chemically pure product.

Anhydrous Crystallization

In early experiments some success was obtained with anhydrous crystallization in crystallizers. It was thought advisable to make a resurvey of these data in connection with the production of chemically pure anhydrous dextrose from high-purity liquors.

Behr (*3*) in 1882 specifically demanded that the anhydrous crystallization from converter liquors, and even the recrystallization from high-purity sugars, should be carried out under absolutely quiescent conditions. Even building vibrations were objectionable. His belief was rather well founded, when taken in conjunction with the gravities recommended by him at that time. Figure 8 is a photomicrograph of a representative crystallization of Behr's anhydrous dextrose. The crystals are rod shaped with blunt ends and are very refractive.

Behr met with many difficulties with quiescent crystallization because there is no clear-cut transition point between the hydrate and anhydrous ranges, particularly when we are dealing with factory liquors.

Figure 9 shows the possibilities of a dual crystallization and demonstrates the simultaneous existence of hydrate and anhydrous forms in quiescent crystallization. In one corner is a dark aggregate of hydrate with the fine lacings on the edges, showing the interlacing and clustering of this growth which is typical of quiescent hydrate crystallization. The sea-urchin cluster of anhydrous dextrose is also seen. The heavy refractive rods with blunt ends again radiate from a common center. If this mass were given motion, either the hydrate or the anhydrous form would be the ultimate result, but neither phase would be properly developed.

Many attempts were made to use the Behr (*3*) crystallization data and apply them to crystallization in motion. However, the gravities recommended were entirely too heavy and viscous for

FIGURE 1. PENTAGONAL LEAFLETS OF α-DEXTROSE HYDRATE CRYSTALS (× 400)
FIGURE 2. α-DEXTROSE HYDRATE CRYSTALS FROM HONEY (× 45)
FIGURE 3. IDEAL CRYSTAL OF α-DEXTROSE HYDRATE (× 200)
FIGURE 4. QUIESCENT CRYSTALLIZATION OF α-DEXTROSE HYDRATE FROM CONVERTED STARCH LIQUOR (× 90)
FIGURE 5. CRYSTALLIZATION OF α-DEXTROSE HYDRATE IN MOTION (× 90)
FIGURE 6. α-DEXTROSE HYDRATE CRYSTALLIZATION OUT OF HYDROL FROM RECONVERTED HYDROL (× 90)

crystallization in motion. The crystals were of such shape that they disintegrated easily. Figure 10 shows this characteristic crystal of anhydrous dextrose grown from high-gravity liquors in motion. The crystals represented here were produced under the conditions of rather strenuous motion in order to accentuate the peculiarities shown. Once again we see the radial grouping of these crystals. The striking characteristic of the crystals is the deep indentation in the outer ends which leaves a weak, easily broken structure. The resulting crystal members could be easily mistaken for poorly developed hydrate crystals if it were not for the refractive character of the anhydrous crystal. One of the crystals of this cluster shows the ragged end from which these weak fragments have already broken off.

Figure 11 visualizes the true anhydrous crystal structure when grown from a water solution. The four normal tetrahedral surfaces on top and bottom of the crystal are well marked. In addition, four facets are visible which represent a tetrahedral of opposite sign and of different surface index. These facets appear on crystals grown from water but never on crystals grown from alcoholic solutions.

With the proper gravities for slow motion there are conditions between the anhydrous dextrose crystals of Behr and those in Figure 11. When working with high purities we are able to obtain proper purging crystals, but another difficulty was met. Figure 13 is the phase diagram of dextrose, based partly on data from the Bureau of Standards and from the Geophysical Laboratory, and partly on data from this laboratory.

The slope of the solubility curve of anhydrous alpha-dextrose is quite steep. If any real yield is to be obtained, we must either enter the crystallizer with extremely heavy gravities, in which case we have to contend with the tendency of the anhydrous crystals to grow as shown in Figure 10 (demonstrating the tendency of the crystals to break off at the ends), or we must enter the crystallizer with reasonable gravities and reduce the final temperature until there is great danger from the development of hydrate crystals.

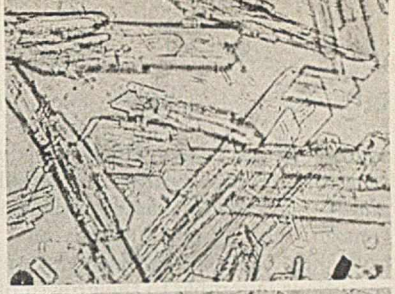
The normal tendency for high-purity solutions is to produce anhydrous crystals, but, when the mother liquor becomes light owing to the crystallization of dextrose, and the temperatures become low because of the forced cooling of the crystallizer, we arrive at an unstable condition in which the trend of crystallization is easily affected by accidental factors such as spontaneous seeding from the air or infections from the mixer box. This condition becomes dangerous if hydrate is manufactured in the same building. When this infection takes place, the material may change over rapidly to the hydrate crystal, stopping proper purging and eventually causing the mass in the equipment to solidify.

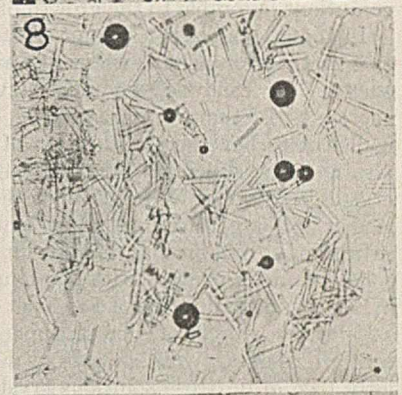
This same change might take place readily in the centrifugal basket with slow-purging magmas when we attempt to wash the centrifugal cake.

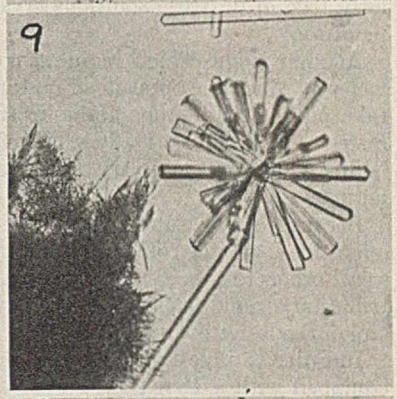
To fulfill the requirements for the formation of ideal purging of anhydrous crystals, the crystallization should be carried out in relatively light-gravity liquors of low viscosity. To avoid hydrate difficulties, we should avoid low-temperature conditions at the end of the crystallization. To obtain a reasonable yield, some withdrawal of water should be made during the crystallizing process. These conditions can best be fulfilled by crystallizing in a vacuum pan during evaporation. The crystals grown under these conditions are close to the ideal for the production of a chemically pure sugar. Figure 12 is a photomicrograph of the anhydrous dextrose as produced in vacuum-pan operations. The crystals are short, stocky, and almost cubical, and form a porous cake from which the mother liquor is easily drained and through which the wash water passes rapidly. The general tendency of dextrose to form composite crystals is apparent even from the best anhydrous dextrose commercially possible. They often display a superficial similarity to hydrate dextrose, in so far as crystals of approximately pentagonal outline are common. However, they are easily differentiated from the hydrate on account of their great refractiveness and structural compactness.

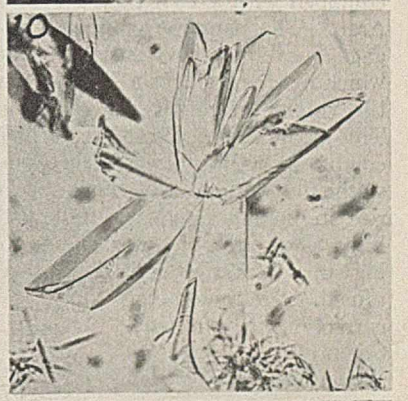
Crystallization Process

The development of a method of crystallizing dextrose in strike pans was not easy. Several conditions offered stumbling blocks. In addition to the two alpha-dextrose crystals with their various troublesome habits, the anhydrous beta-dextrose is also present and can be crystallized. When we dissolve any of these isomers in water, we first make a









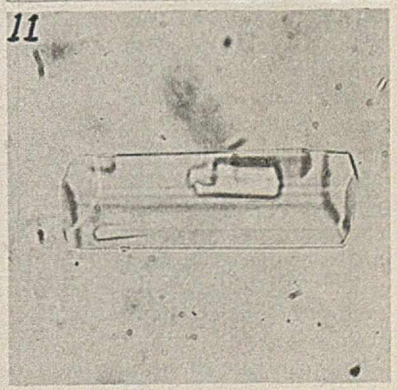


FIGURE 7. CRYSTALLIZATION OF α-DEXTROSE HYDRATE IN MOTION FROM PURE SOLUTION (× 45)

FIGURE 8. QUIESCENT CRYSTALLIZATION OF ANHYDROUS α-DEXTROSE (× 90)

FIGURE 9. MIXED CRYSTALS FROM QUIESCENT CRYSTALLIZATION OF α-DEXTROSE (× 400)

FIGURE 10. MOVING CRYSTALLIZATION OF ANHYDROUS α-DEXTROSE FROM IMPURE SOLUTIONS (× 90)

FIGURE 11. IDEAL CRYSTAL OF ANHYDROUS α-DEXTROSE FROM PURE WATER SOLUTIONS (× 200)

FIGURE 12. ANHYDROUS α-DEXTROSE FROM PAN-BOILED PURE SOLUTIONS (× 45)

solution of that isomer which immediately starts the process of mutarotation and results in an equilibrium between the alpha and beta isomerides; data on their numbers and descriptions contain only meager information. When we attempt to crystallize any of these isomers, we must have crystallizing conditions favorable to the growth of that isomer.

In the crystallization of any crystalline body from a solution of that compound, we must have supersaturation. (In sucrose, for example, we must have a supersaturation of sucrose.) In the crystallization of dextrose it is not alone sufficient to have supersaturation of a dextrose solution but also to have supersaturation of the isomer which is to be crystallized. In order to establish the supersaturation of this isomer, we are forced to carry comparatively high supersaturations compared to equilibrium mixtures of a specific solid isomer in contact with the equilibrated mother liquor. Where a supersaturation of 1 to 3 per cent will cause rapid and satisfactory growth of sucrose, supersaturations of 5 to 8 per cent are necessary with anhydrous dextrose. This is particularly true of dextrose solutions crystallized at elevated temperatures.

Another point which required consideration was the velocity at which the opposite of mutarotation could be made to take place. Anhydrous alpha-dextrose cannot be deposited faster than it can be made. Therefore, considerably longer boiling times are necessary than are common to the sucrose industry.

Because of the supersaturations required for commercial operations, greater control of the crystallizing mass is necessary both as to gravity, temperature, and the amount and distribution of solid nuclei inducted at the graining stage. Control of the latter is quite important.

In order to investigate this problem, a 5-gallon brass pan equipped with a Pyrex glass belt was built and installed at Argo. The pan was equipped with thermometer, vacuum gage, feed lines, and surface condenser, the condensate of which discharged into a container with a sight glass so that the volume of condensate could be measured at any time. This arrangement allowed the control of gravities and boiling conditions with sufficient accuracy to establish necessary data as the foundation for the final development. The commercial rise in boiling point was established for various dextrose liquors over that of water. The proper evaluation of operating supersaturation at various stages in the boiling were obtained. A refractometer correction curve for various concentrations within the range required for boiling operations was developed. A method of boiling to grain was finally developed which could be successfully repeated and from which it was possible to manufacture chemically pure dextrose at reasonable costs.

The Edgewater, N. J., factory of this company was equipped with a small plant for the production of chemically pure dextrose. This consists of stoneware melting and treating vessels, brass filter press, stoneware receiving equipment, glass vacuum pan, 14-inch American Tool basket centrifugal, and vacuum drying equipment.

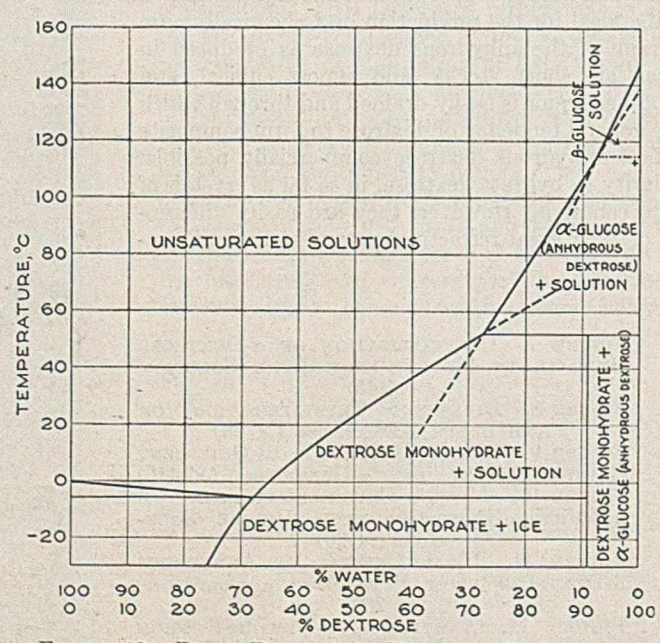


FIGURE 13. PHASE DIAGRAM OF DEXTROSE SOLUBILITY

A man was taught the art of boiling dextrose, and the production of chemically pure dextrose was started. This equipment made it possible to deliver about 300 pounds per week and at the same time reduce the selling price of the product. After less than 6 months, the increase in sales forced the erection of a larger plant.

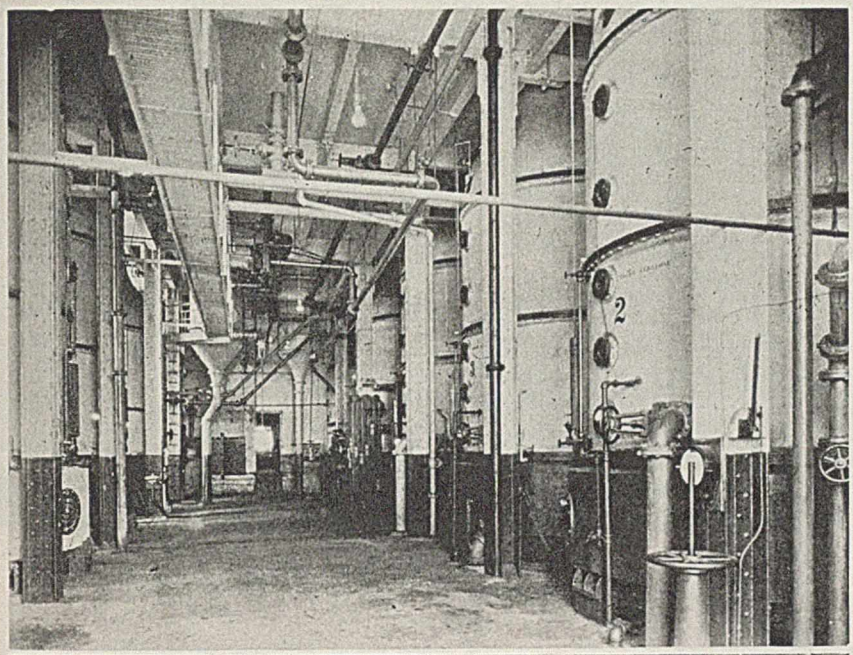
The next factory was built at Kansas City. This consisted of melting equipment in the Cerelose building, carbon presses of wood construction, pan receiving tanks, one 5-foot vacuum pan, two 40-inch centrifugals, and a 3-foot Hershey granulator. This unit had a capacity of about fifty 100-pound bags of chemically pure dextrose per day. The operations were scarcely started before the reduced price resulting from the improvement in manufacturing conditions forced an increase, and a second 5-foot pan was installed. A relatively short period later, enlarged equipment was again found necessary. The new unit was installed at Argo. In designing and building this equipment, the ideal plant was desired, and cost of apparatus was given little or no consideration. In describing this layout, the flow sheet of the process now in use will be followed.

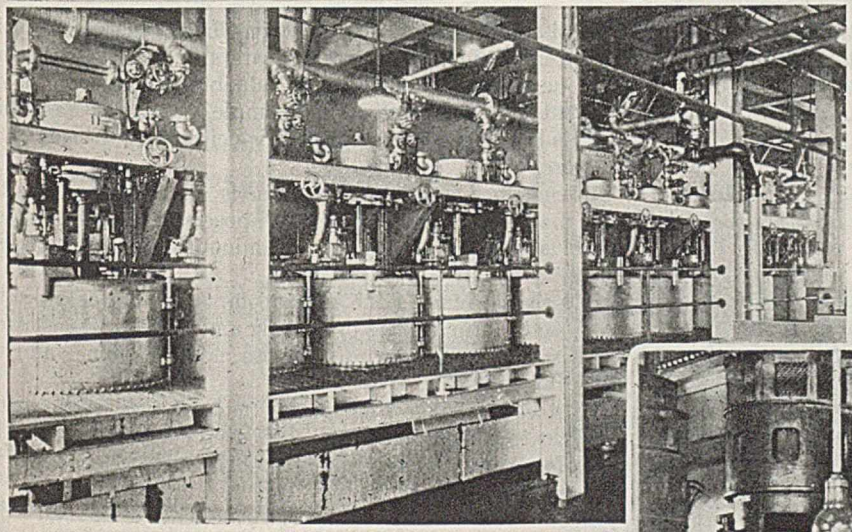
Steps in the Process

Centrifugally washed white hydrate (Cerelose) instead of going through the driers is delivered wet to a melt tank. The water used for melting is condensate from boiler steam used on the finishing pan. The condensate is filtered over Hydro-Darco water filter. The carbon bed of this filter is renewed annually. The melt at 28° to 30° Bé. is delivered to the carbon treating system situated in the anhydrous building. There are no connecting doors between the refining and the boiling systems. This arrangement prevents the tracking of carbon into the boiling building and keeps out the carbon dust.

The containers for carbon are set into a turntable located inside a tank containing approximately 100 gallons of liquor to be treated. The tank is closed and the carbon containers are turned upside down. After about 3 minutes all of the carbon dust has settled and been mixed into the carbon slurry. The slurry is discharged into the treating tank. The carbon treatment consists in the addition of about 0.8 per cent Darco on the dry substance treated. The treating temperature is 160° F. The time of contact is 30 minutes.

The carbon-treated liquor is delivered to a Sweetland press, dressed with a 12-ounce, chain-weave cotton cloth. No filter aid is used in the filtration. The cloudy liquor is returned to the treating system until 20 minutes after the operator decides that only clear liquor is being delivered by the filter. At this time the clear liquor is delivered from the Sweetland press to two streamline filters which, in turn, deliver almost optically void liquors to the pan floor. All pipe lines and containers leaving the Sweetland press are either brass, copper, or suitably protected steel. The reason is that, if the pH of dextrose goes much above 5.0, alkaline decomposition products of





(*Left*) Aisle on the Evaporator Floor Where Both Light and Heavy Evaporation in Hydrate Cerelose Takes Place

Triple pans are used for light evaporation and single pans for heavy evaporation.

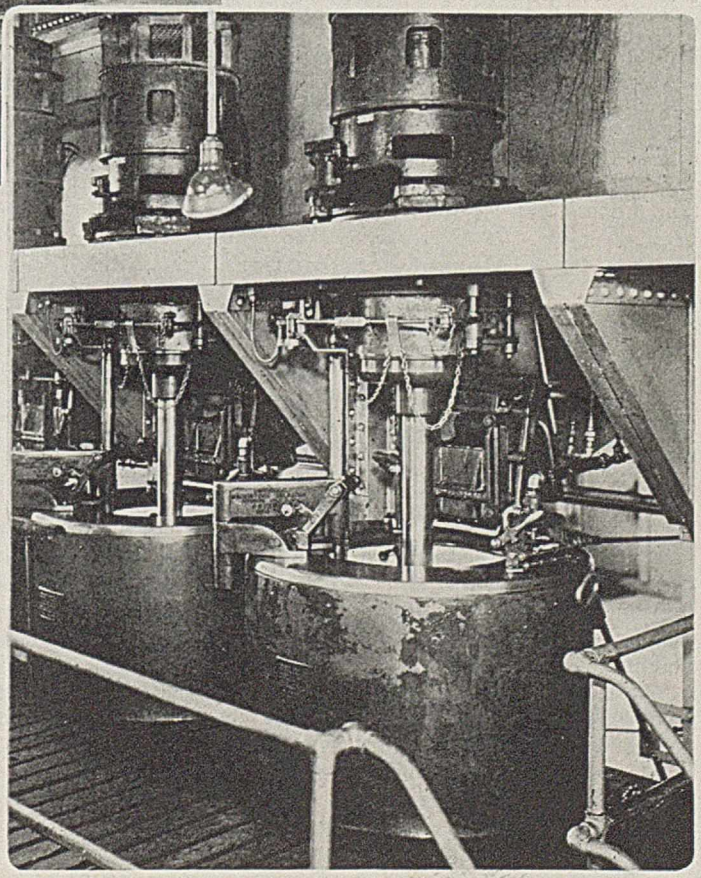
(*Center*) Working Platform of One of the Batteries of Hydrolytic Centrifugals

There are 115 of these machines.

(*Bottom*) Electric High-Speed Centrifugals for the Production of C. P. Anhydrous Dextrose, of Bronze and Monel Metal Construction

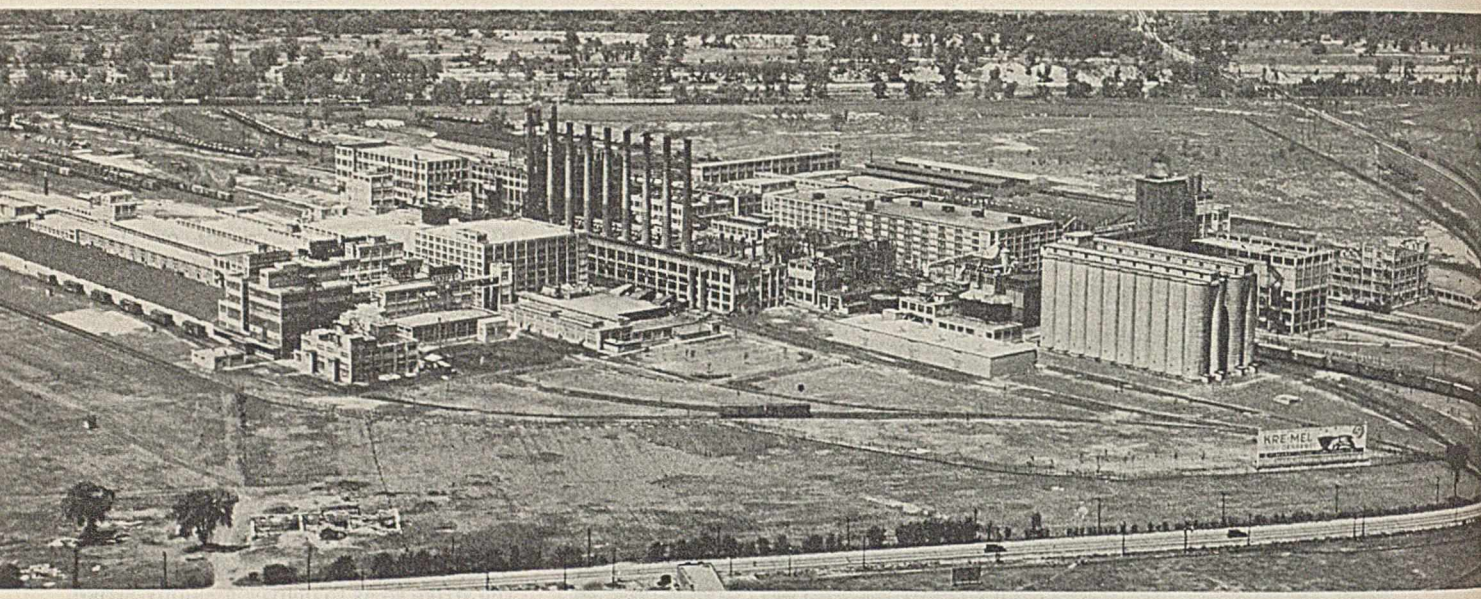
false grain will not develop in the mixer box, although it is not desirable to thin the strike so as to deliver a sloppy strike to the centrifugal.

The finished strike is dropped into a copper mixer box which feeds brass Hepworth electrical centrifugals. The mixer box is covered to prevent the induction of hydrate dust from the adjoining Cerelose sugarhouse, or any other dust material. The mixer box is warmed before the introduction of the strike in order to prevent surface chilling with its attendant induction of hydrate seed. After the purging of the mother liquor, the sugar is washed with hot condensate which has been carbon-filtered, as previously stated. Hot water is used to prevent the retained



dextrose are produced. The condition of the liquors is favorable, therefore, for the corrosion of steel and iron equipment, although the acidity is not sufficient to keep the iron in solution permanently. The major portion is precipitated upon concentration of the liquors and causes an iron haze in the sugar.

The liquors are drawn into an ordinary strike pan common to all sugarhouses, with the exception that it is made entirely of copper and brass. Sufficient liquor is drawn in so that we have between 15 and 20 per cent of the volume of finished strike at the time the charge has reached graining conditions. The grain is taken in without seeding, being induced by gravities alone. Concentration at grain point corresponds closely to 90 per cent dry substance. After the induction of grain, supersaturation is reduced by the introduction of a relatively large charge of 30 Bé. liquor. The mother liquor, during the growing stage of the strike, runs approximately 82 per cent dry substance. When the pan is approximately full and ready to be "brought together," one of two procedures is used; the preferred one is to boil the strike on water. Rather high supersaturations have been used here in order to force the opposite of mutarotation to take place; therefore the supersaturation must be reduced so that



Aërial View, Argo Plant of the Corn Products Refining Company

Capacity, 85,000 bushels of corn per day.

mother liquor from becoming cooled by a cold water wash and thus becoming highly supersaturated and at the same time definitely within the hydrate crystallizing range. The sugar scrolls are covered to prevent the intake of dust and dirt, and delivered to a tandem granulating system.

The granulating equipment consists of Hershey driers. The top drier is supplied with hot air which has been filtered through glass filter mats. The fibers of these mats are coated with a permanently sticky material so as to retain any dust particles which strike the coating material. The top drier discharges into a cold-air drier to cool the sugar to proper packing temperatures. This drier is also equipped with glass wool air-filter mats. The dried sugar is elevated to Hummer screens and delivered into packing hoppers.

The packing hoppers and packing spouts are equipped with a vacuum pickup device to remove any dust which may have accidentally entered the finished sugar stream. The sugar, as it leaves the packing hopper, contains not over 0.05 per cent moisture. The total known impurities, as far as we can ascertain, are less than 10 parts per million.

Market Possibilities

With the successful development of a technical method for the manufacture of chemically pure dextrose which makes this product available at reasonable prices, the question arises as to the market possibilities. Not a single use to be described enters the food field but is strictly new business which will increase the use of corn and will compete with products which in the past were not derived from corn.

There is no wish to slight the food field. Dextrose is entering this field extensively and on its own merits. In the food field, however, the competition is with other carbohydrates, the total consumption of which depends entirely upon population and can increase only as population increases. In the manufacturing chemical field its use will be on its own merits and limited only by its merits.

Through oxidation methods dextrose can be converted into a whole series of carboxylic acids with carbon chains up to six, such as glutaric, saccharic, propionic, etc.; when their development follows the same course as that of C. P. dextrose, they can be sold at prices which make them attractive to the manufacturing chemist as raw materials.

A whole series of polyvalent alcohols can be produced. For example, the Atlas Powder Company is now manufacturing sorbitol and mannitol. These longer chained alcohols are finding extensive industrial uses and are also the starting point for a new series of industrially valuable esters and acids of different configurations. For example, vitamin C (ascorbic acid) is being made from sorbitol, which in turn is made from dextrose.

Arsenates, mercurials, and phenols can be introduced to form many toxic compounds which possess germicidal and insecticidal properties, such as aminobenzoic acid glucose esters.

In a similar manner the amino compounds can be added to dextrose to form a series of wetting and dispersing agents for textiles and rubber, such as glucose naphthylamine and glucose alkylamine.

Most of the active principles of materia medica are naturally dextrose derivatives. There is now available a starting point for the synthetic production of these active principles in a pure state.

The diversified character of the glucosides is the best indication of the great variety of compounds which can be made from dextrose (*1*). Armstrong lists glucose phenol compounds, glucose alcohol compounds, glucose aldehyde compounds, glucose acid compounds, glucose oxycumarin derivatives, oxyanthraquinone derivatives, oxyflavone derivatives, mustard oil derivatives, anthocyanin derivatives, digitalis derivatives, sapogenin derivatives, benzyl derivatives, and indican derivatives. Dextrose can be introduced into and be made a part of practically every type of organic compound and can be handled through a great number of organic reactions.

Acknowledgment

The photomicrographs shown in Figures 1 to 12 were made by Otto A. Sjostrom of this company.

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TANTALUM CARBIDE

ITS RELATION TO OTHER HARD REFRACTORY COMPOUNDS

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IN RECENT years tool materials harder than any tool steel have been increasingly used in metal-working industries. Examples are tungsten carbide cemented with cobalt, compositions of tantalum carbide with tungsten and nickel, and the same compositions with titanium carbide. These compositions have comprised as major ingredients certain refractory elements or their compounds with metalloids, together with minor percentages of a metal of the iron group. The commercial success of these new tool materials has stimulated study of these high-melting metals and compounds. This article discloses new observations of the compounds of tantalum and of columbium with the metalloids carbon and boron, including new figures for densities and crystalline form as disclosed by x-ray methods and pycnometric measurements. For purposes of comparison, it is enlightening to compare this new information with other data in the group of compounds of titanium, vanadium, chromium, zirconium, columbium, molybdenum, hafnium, tantalum, and tungsten, with the metalloids boron, carbon, and nitrogen. Table I shows this information (including new observations marked with asterisks). Important information is still lacking, and the author is not responsible for the data in cases not marked with asterisks. However, the best available information has been given.

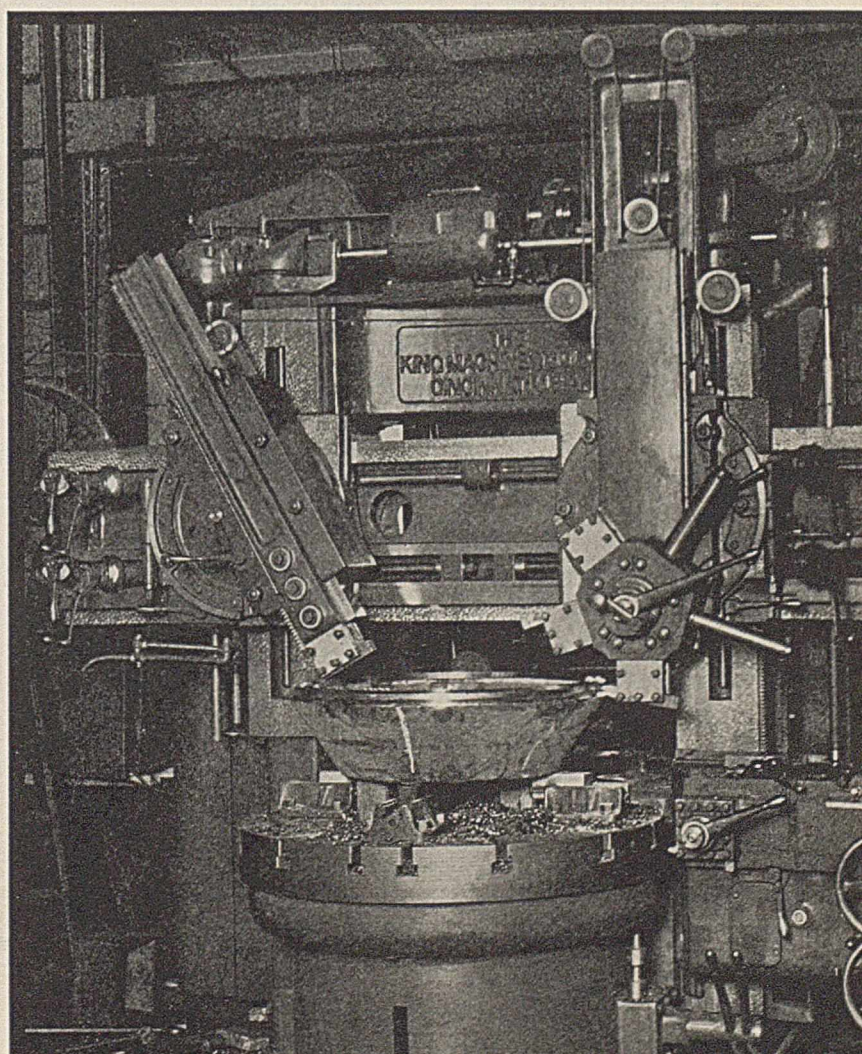
A high melting point seems to be the requisite for the chief ingredient of a successful hard tool material. Substances at present commercially useful include the following: tungsten carbide (melting point approximately 2867° C.), tantalum carbide (melting point approximately 3875° C.), columbium carbide (melting point approximately 3500° C.), and titanium carbide (melting point approximately 3140° C.). This requisite is not of itself so important a factor, for these cutting tools rarely attain a temperature above 850° C., but resistance to wear, or what is commonly called "hardness," seems to be a concomitant of high melting point. The word "hardness" requires special definition to be useful to physico-chemical reasoning, for crystalline form or arrangement of the atoms in the lattices as disclosed by x-ray crystallographic analysis affects the ease with which solids may be dislocated by shearing forces. The well-known difference between graphite and the diamond is a case in point. For present purposes, hardness will be considered as a function of chemical attraction between atoms, specifically in the sodium chloride type lattice as the square of the valence divided by the atomic volume to the two-thirds power.

A second requisite is a simple crystalline structure which will permit slippage without breaking—in common words, to avoid brittleness. Crystalline structures with a high order of symmetry are more ductile than crystalline bodies of unequal or inclined axes of symmetry.

A third requisite is that connoted by the term "metal"—namely, high thermal and electrical conductivity—and other properties such as are associated with metallic luster.

A forth requisite is chemical stability under conditions of use.

Referring to the first requisite of high melting point and its associated properties of hardness, Friederich attempted



A MACHINING OPERATION ON 13 PER CENT MANGANESE STEEL WITH TANTALUM CARBIDE TOOLS

to correlate the physical properties of solid bodies as a consequence of chemical bond. Table II gives the calculations with new data on tantalum carbide and columbium carbide following Friederich (*11*). Included for comparison purposes are the figures for some other well-known compounds crystallizing in the sodium chloride type system. The true densities and lattice dimensions of titanium carbide and vanadium carbide are not known with sufficient accuracy to compare with tantalum carbide and columbium carbide.

The densities, crystalline form, and lattice dimensions of tantalum and columbium carbides were determined (for TaC, d = 14.48, a = 4.445 Å.; for CbC, d = 7.82, a = 4.4578 Å.); both crystallize in the sodium chloride type. The results are in good agreement with the calculated densities using these lattice dimensions and the new (1936) atomic weights for tantalum and columbium of 180.89 and 92.91. The heat of formation of tantalum carbide is 38 ± 5 kilocalories; tungsten carbide (WC) has no perceptible heat of formation. The melting points of carbides of chromium, molybdenum, and tungsten are lower than those of

Tantalum and Columbium Carbides

Densities. A new physical form of both tantalum carbide and of columbium carbide was prepared, and the purities were checked by chemical and spectrographic tests. The densities of these substances were determined by pycnometric methods. The density of different samples of this tantalum carbide was observed to be 14.51, 14.46, 14.49, and 14.47 grams per cc. compared to water at 20° C. The average is 14.48 at 20° C. This figure is considerably higher than the result of 14.05 reported by others (*8*). The new form of tantalum carbide has a typical golden metallic luster.

The density of the new form of columbium carbide, with a lavender-gray luster, was found to be 7.82, compared to water at 20° C. This value compares with previous reports of 7.56 for the density of columbium carbide (*6*).

Lattice Dimensions. The lattice dimension of tantalum carbide was determined by back-reflection precision methods, and was found to be a = 4.445 ± 0.0005 Å., compared to previous reports of figures varying from a = 4.427

Table I. Compilation of Data on

Titanium	Vanadium	Chromium	Zirconium	Columbium
		Borides		
Ti boride H + 9 (*6*) Electrical resistance, 0.152 × 10^{-4} (*6*); temp. liquid air, 0.037 × 10^{-4} (*6*)	V boride H + 9 (*12*) Elec. res., 0.16 × 10^{-4} (room temp.), temp. liquid air, 0.035 × 10^{-4} (*6*)	Cr_3B_2 (*9*) d = 6.7 (*9*) CrB (*9*) d = 5.4, 5.5, 6.1 (*9*) H 8 (*9*)	Zr boride H + 9 (*6*) M. p. 2990° C. ± 50° (*6*) Elec. res., 0.092 × 10^{-4} (*6*) ZrB_2* d = 5.64 approx. Hex. a = 3.15 c = 3.53 $\frac{c}{a}$ = 1.12 ± 0.02	CbB_2 (*3*) d = 6.4 H + 9 (*3*)
		Carbides		
TiC H + 8 (+9) (*6*) NaCl type, a = 4.60 (*6*) d = 4.25 (*6*) M. p. 3140° C. ± 90° (*6*)	VC H 9–10 (*6*) d = 5.36 (*6*) NaCl type, a = 4.30 (*6*) Elec. res., 1.56 10^{-6} (?) M. p. 2830° C. (?) (*15*)	Cr_4C d = 6.97 (*18*) cfc a = 10.638 (*18*) Cr_3C_2 d = 6.683 (*18*) Rhombic (*18*) a = 2.821 b = 5.52 c = 11.46 H > quartz M. p. 1890° C. (*15*) Cr_7C_3 (*18*) Hex. a = 13.98 c = 4.523 $\frac{c}{a}$ = 0.324	ZrC H 8–9 (*6*) d = 6.90 (*6*) NaCl type a = 4.76 (*6*) M. p. 3530° C. (*1*) Elec. res., 0.634 × 10^{-4} (*5*); temp. liquid air, 0.378 × 10^{-4} (*5*)	CbC d = 7.82* (d = 7.56) (*6*) M. p. 3500° C. ± 125° (*1*) Color, lavender-gray* NaCl type a = 4.46* (a = 4.40) (*5, 13*)
		Nitrides		
TiN H 8–9 (*6*) NaCl type (*6*) a = 4.40 (*6*) M. p. 2950° C. ± 50° (*6*) d = 5.18 (*5*)	VN d = 5.63 (*15*) M. p. 2050° C. (*15*) NaCl type a = 4.28 (*18*)	CrN Decomposes at 1400° C. NaCl type a = 4.140 (*18*)	ZrN H + 8 d = 6.93 (*5*) NaCl type a = 4.63 (*14*) Elec. res., 0.136 × 10^{-4} (*6*); temp. liquid air, 0.0397 × 10^{-4} (*6*) M. p. 2983° C. ± 50 (*6*)	CbN d = 8.40 (*5*) NaCl type a = 4.41 (*5*) H + 8 (*5*)

either carbon or the metal; carbides of tantalum, columbium, vanadium, hafnium, zirconium, and titanium have higher melting points than the respective metals. ZrB_2, TaB_2, CbB_2 were subjected to x-ray crystallographic examination and yielded definite patterns, but no evidence of a compound TaB was found. Uses of hard carbides of tungsten and tantalum as constituents of tool materials are discussed. Compositions containing 80 per cent tantalum carbide are little affected by acids such as sulfuric and hydrochloric; they are harder than steel, and have a strength of 275,000 pounds per square inch on cross rupture tests.

(*19*) to $a = 4.49$ (*6*). The lattice dimension of columbium carbide was found to be $a = 4.4578 \pm 0.0003$ Å., compared to a previous report of 4.40 (*6*).

Reconciliation of Density and Lattice Dimensions. According to Becker (*6*) columbium carbide has a calculated density (from $a = 4.40$) of 8.20 against his observation of 7.56. Likewise tantalum carbide is recalculated (from $a = 4.49$) to have a density of 13.95 against his observation of 14.05. With the new data, much closer checks are obtained between densities calculated from the x-ray observations and the pycnometric determinations.

Calculating the density of tantalum carbide from the figure obtained in this laboratory as the average of four determinations ($a = 4.445$), we obtain

$$\frac{4 \times 192.88 \times 1.6489 \times 10^{-24}}{(4.445 \times 10^{-8})^3} = 14.47$$

which is in excellent agreement with the average pycnometric density figure, 14.48. The old atomic weight of tantalum accepted prior to 1936 was 181.4, which gives a molecular weight of 193.4 instead of 192.88, and would give a calculated density of 14.525. Hence, the new atomic weight for tantalum is more consistent with observations made here.

Recalculating the density of columbium carbide from the new observed lattice dimension of $a = 4.4578$, we find

$$\frac{4 \times 104.91 \times 1.6489 \times 10^{-24}}{(4.4578 \times 10^{-8})^3} = 7.81$$

This compares with the observed density of 7.82 for the new form of columbium carbide. The old atomic weight for columbium (93.1) would yield a higher density than when the new (1936) atomic weight of 92.91 is employed in the calculation (*16*).

Table III shows the observations reported to date on the density and lattice parameters of columbium and tantalum carbides.

High-Melting Compounds[a]

Molybdenum	Hafnium	Tantalum	Tungsten
Borides			
Mo_3B_4 (*20*) d = 7.1 (*20*) H + 9 (*20*) MoB_2	Hf boride M. p. 3062° C. Elec. res., 0.10 × 10^{-4} (room temp.)	TaB_2 (*3*) H + 9 (*3*) d = 11.0 (*3*)	WB_2 d = 10.77 (*21*) H + 9
Carbides			
Mo_2C H 7–9 (*6*) d = 8.9 (*6*) M. p. 2687° C. ± 50° (*1*) Hex. close-packed $a = 2.99$ (*6*) $c = 4.72$ (*6*) $\frac{c}{a} = 1.58$ (*6*)	HfC d = 12.20 (*5*) M. p. 3887° C. ± 150° (*5*) Elec. res., 1.09 × 10^{-4} (*5*)	TaC H + 9 d = 14.49* M. p. 3875° C. ± 150° (*1*) Elec. res., 0.17 × 10^{-4} (*2*) [1 × 10^{-4} (*1, 5*)] NaCl type $a = 4.445$* Color, golden metallic	W_2C H 9–10 (*6*) d = 17.20 (*6*) Hex close-packed (*6*) $a = 2.99$ $c = 4.72$ $\frac{c}{a} = 1.578$ M. p. 2857° C. ±50° (*1*) WC H + 9 (*6*) d = 15.50 (*6*) Hex. close-packed (*6*) $a = 2.94$ $c = 2.86$ $\frac{c}{a} = 0.973$ M. p. 2867° C. ± 50°
MoC H 7–8 (*6*) d = 8.40 (*6*) M. p. 2692° C. ± 50° (*1*) Hex. close-packed (*6*) $a = 4.88$ $c = 6.54$ $\frac{c}{a} = 1.34$			
Nitrides			
		TaN H + 8 (*6*) d = 14.1 (calcd., *6*) M. p. 3090° C. ± 50° (*6*) Hex. $a = 3.05$ $c = 4.95$ $\frac{c}{a} = 1.62$	

[a] Hardness (H) is given on Mohs' scale (diamond = 10); electrical resistance is given in ohms per cm. An asterisk indicates that the datum is new.

Zirconium Boride

A compound of zirconium, boron, and a small amount of carbon was prepared by heating zirconium dioxide and carbon with an excess of boron oxide at about 2000° C.:

$$ZrO_2 + B_2O_3 + 5C \longrightarrow ZrB_2 + 5CO$$

Three times as much boron oxide as indicated in the above equation was employed. The heating was done in an Acheson graphite crucible with 492 grams zirconium dioxide, 840 grams boron oxide, and

TABLE II. FIGURES OBTAINED BY CONSIDERING THE VALENCE SQUARED DIVIDED BY THE ATOMIC VOLUME TO THE TWO-THIRDS POWER IN A SERIES OF COMPOUNDS OF SODIUM CHLORIDE TYPE CRYSTALLINE ARRANGEMENT

Compound[a]	NaCl	AgCl	NaF	PbS	CaO	MgO	TiN	ScN	VN	CbN	TiC	ZrC	HfC	VC	CbC	TaC
Valence	1	1	1	2	2	2	3	3	3	3	4	4	4	4	4	4
Density	2.2	5.56	2.83	7.42	3.37	3.65	5.18	4.46	5.63	8.40	4.25	6.90	12.20	5.36	7.82	14.47
Lattice a	5.628	5.54	4.62	5.97	4.79	4.20	4.40	4.44	4.28	4.41	4.60	4.76	...	4.30	4.46	4.445
Atomic vol.	13.53	12.8	7.42	16.1	8.39	5.57	6.17	6.65	5.77	6.42	7.05	7.48	7.81	5.87	6.708	6.67
$100 \times \frac{W^2}{V_A^{2/3}}$*	18	19	26	63	97	127	268	255	280	260	435	418	406	491	450	452

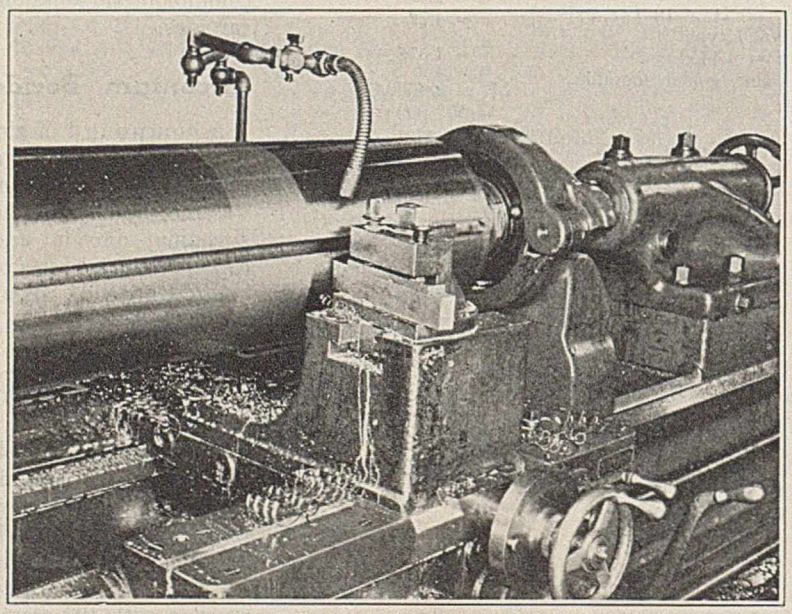
[a] These compounds are all of the same crystalline form—NaCl type cubic. The distance a is the number of Ångström units between similar kinds of atoms.
* W = valence; V_A = atomic volume = atomic weight/density.

TABLE III. LATTICE PARAMETERS AND DENSITIES FOR TANTALUM AND COLUMBIUM CARBIDE

Investigator	a_0, Å.	Calcd. Density Grams/cc.
TaC		
Arkel (*4*)	4.56	...
Goldschmidt (*14*)	4.427	...
Becker and Ebert (*7*)	4.49	13.95, 14.05
Schwarz and Summa (*19*)	4.4460	...
Burgers and Basart (*10*)	4.445	...
McKenna, Smith, and Walters	4.4450	14.47, 14.48
CbC		
Becker and Ebert (*7*)	4.40	8.20, 7.56
McKenna, Smith, and Walters	4.4578	7.81, 7.82

120 grams carbon black. After cooling, a gray friable mass was obtained in the lower part of the crucible, weighing 446 grams. Boiling with hydrochloric or with nitric acid had no effect. Chemical analysis showed (in per cent) zirconium, 78.55; boron, 18.15; carbon, 1.89; silicon, 0.03; total, 98.62. Spectrum analysis showed the presence of some iron in this product. The density was 5.64 compared to water at 25° C. On the assumption that a compound ZrB_2 exists, it would contain about 19.2 per cent boron. Therefore this material is probably ZrB_2, with impurities.

A portion, 170 grams, was heated with 8.5 grams boron oxide in a vacuum electric furnace at 1530° C. and resulted in a carbon content of 1.09 per cent. Two x-ray spectrograms of the purified product were made. When the sin θ values for the various lines of the two photograms were fitted on a series of Davey-Hull charts, an exact agreement was found between the structure indicated by the two films. There were just the exact number of lines of the correct relative intensities to place the zirconium atoms on the lattice points of a simple hexagonal cell with an axial ratio of c/a 1.12 ± 0.02. This leads to values of c and of a of 3.53 and 3.15, respectively. The zirconium atoms in the pure metal are on the lattice points of a close-packed structure with an axial ratio of $c = 1.59$. This seems to be a logical variation in arrangement inasmuch as there is 66.66 a for each per cent of boron present, which must be included somewhere. The more open simple hexagonal lattice would allow this.



MACHINING STEEL WITH TANTALUM CARBIDE TOOLS
(Note the interrupted cut.)

Thermal Properties of Carbides and of Two-Component Systems

Of the materials used in modern hard-tool compositions, (1) tantalum carbide and (2) tungsten with carbon differ fundamentally. As to crystalline form, the tungsten-carbon system is of close-packed hexagonal form, whereas tantalum carbide, columbium carbide, and titanium carbide definitely crystallize in the sodium chloride type cubic system. It should be noted that according to the best available data the tungsten-carbon systems and the molybdenum-carbon systems melt at temperatures below the melting points of their respective metals; on the contrary, the melting points of the other carbides mentioned which are in the IV and V groups of the periodic table, have melting points higher than those of their respective metals. This is shown in Table IV.

Since a definite and sudden increase in melting point of a two-component system is interpreted by physical metallurgists to mean the formation of a compound, it was believed that the compounds of tantalum, columbium, vanadium, hafnium, zirconium, and titanium with carbon are of a more definite and stable nature than those of tungsten and molybdenum with carbon, if indeed these latter two systems may be said to be chemical compounds at all.

Accordingly, determinations of the heats of combustion of tantalum carbide and tungsten carbide were made with a view to establishing the heats of formation of the alleged compounds. In confirmation of this, tantalum carbide was found to have a positive heat of formation of 38 kilocalories per gram molecular weight, while the tungsten-carbon system gave a zero heat of formation. The determination of the heat of formation of tantalum carbide was as follows:

OBSERVATION. The value 1590 calories was obtained by burning 1.000 gram tantalum which contained 6.31 per cent carbon in a bomb calorimeter of the Berthelot type in oxygen of 25 atmospheres pressure.

KNOWN DATA. Tantalum plus oxygen gives 498.3 kilocalories per gram molecular weight of tantalum pentoxide (*17*). Carbon plus oxygen gives 94.4 kilocalories per gram molecular weight carbon dioxide.

CALCULATIONS. A 1.000-gram sample of tantalum carbide containing 6.31 per cent carbon contains 0.9369 gram tantalum and 0.0631 gram carbon, which gives 0.005165 mole tantalum and 0.005258 mole carbon, using the atomic weights given in International Critical Tables (tantalum = 181.4, carbon = 12.00). (If the atomic weight of tantalum is taken as equal to 180.89, the new value, then the amount of tantalum becomes 0.005179 mole.)

	Kilocal.
Heat from burning 0.005165 gram mol. wt. of Ta	1.287
Heat from burning 0.005165 gram mol. wt. of C	0.488
Heat from burning 0.000093 gram mol. wt. of C	0.009
Total heat if elements were uncombined	1.784
Heat of combustion actually observed	1.590
For 0.005165 TaC	0.194
For 1 mole TaC	38 ± 5

The uncertainty is about ±5 kilocalories. Therefore we should write:

$$Ta(c) + C(c) = TaC(c), Q = 38 \pm 5 \text{ kilocal.}$$

Likewise the heat of formation of tungsten carbide was investigated by combustion in oxygen in a bomb calorimeter, obtaining a value of practically zero for the heat of formation of tungsten carbide. One gram of tungsten carbide gave 1461 calories or 286.3 kilocalories per gram molecular weight of 196 grams compared to the total heat of 286 kilocalories which would have been obtained from burning the equivalent amounts of tungsten and carbon separately, using the data in International Critical Tables for the heats of formation of tungsten trioxide and carbon dioxide.

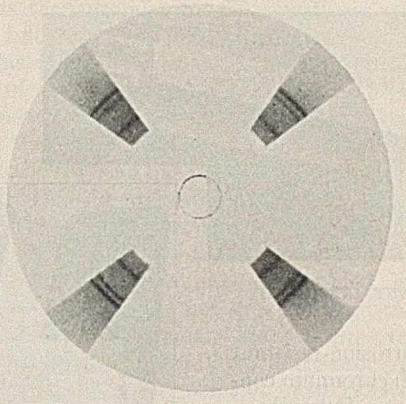


FIGURE 1. BACK-REFLECTION PHOTOGRAM FOR DETERMINING LATTICE PARAMETER OF COLUMBIUM CARBIDE

Inner diffraction circle	Cu K_β (026)
Intermediate diffraction circle	Cu K_{α_2} (044)
Outer diffraction circle	Cu K_{α_1} (044)

found for these compounds is a mixture of hydrofluoric and nitric acids.

Technical uses of compositions of tantalum carbide in the chemical industry have included spray nozzles for chemicals. Here we have a hard metallic material with a hardness much greater than steel and with noncorrosive properties which approach platinum. Tests in various corrosive substances of composition comprising 80 per cent tantalum carbide and the balance tungsten metal and nickel are shown in Table V. This tantalum carbide alloy has a strength of 275,000 pounds per square inch in transverse rupture test and a Rockwell hardness of 88.4A, which is much harder than the hardest steel. That a metal composition possessing this combination of physical and chemical properties is destined to play a large part in chemical industry seems obvious.

TABLE IV. PERIODIC ARRANGEMENT OF HIGH-MELTING-POINT METALS AND THEIR SIMPLER CARBIDES

Group IV, Column I					Group V, Column I					Group VI, Column I				
Element	Atomic wt.	M. p. °C.	Carbide	M. p. °C.	Element	Atomic wt.	M. p. °C.	Carbide	M. p. °C.	Element	Atomic wt.	M. p. °C.	Carbide	M. p. °C.
Ti	47.9	1800	TiC	3146	V	50.95	1710	VC	2830	Cr	52.01	1615	C_3Cr_2	1890
Zr	91.22	1700	ZrC	3530	Cb	92.91	1950	CbC	3500	Mo	96.0	2620	MoC	2692
Hf	178.6	1700	HfC	3887	Ta	180.89	2850	TaC	3875	W	184.0	3370	WC	2867

The products of the combustions were carefully examined, showing them to be pure oxides, and the carbon dioxide gas was weighed, checking the completeness of the reactions.

Borides of Tantalum and Columbium

Of the compounds of tantalum and of columbium with boron, TaB_2 and CbB_2 were made corresponding to the formulas of Andrieux (*3*). These compounds yielded definite x-ray diffraction spectra but were not identifiable here as any of the simpler forms. Some of the literature hesitates to supply a formula for tantalum boride or columbium boride. Substances were also prepared here corresponding to the rough composition TaB, but x-ray diffraction patterns of these were not obtained, the rays being entirely scattered; this behavior indicates that they were not compounds but mixtures in a fine degree of dispersion. Hence no corroboration of a compound TaB was obtained.

Technical Uses

The technical use of such hard compounds as are discussed in this article requires that compositions containing them as ingredients be capable of resisting mechanical stresses. Therefore, compounds with unsymmetrical structures—that is, other than cubic or hexagonal—are generally not so well adapted to these uses, for it is a general rule that such solids are brittle in aggregates.

The chemical properties of compounds given in Table I are largely influenced by the character of the metal atom in each compound.

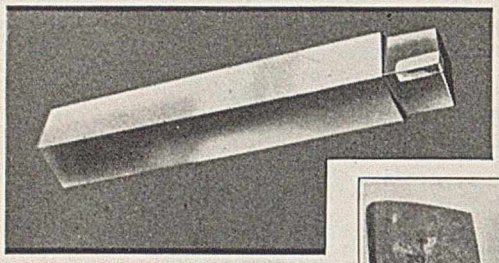
Carbides and borides of tantalum, for instance, may be boiled with nitric acid solutions, with hydrochloric acid, or with mixtures of the two without effect. The only acid solvent

TABLE V. CORROSION RESISTANCE TESTS

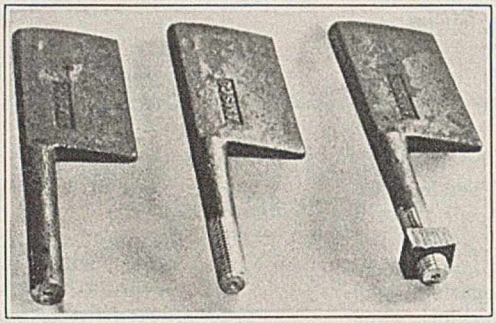
(Losses in mg. from 24-hour immersion at room temperature; pieces of approximately equal area (3.2 sq. cm.) weighing about 5 grams each)

Reagent (Aqueous Solns.)	Typical TaC Alloy 80% TaC, 20% NiW	Typical WC Alloys 87% WC, 13% Co	Typical WC Alloys 94.5% WC, 5.5% Co and Fe
HCl, 1:1	1.0	3.8	2.9
HCl, concd.	0.2	29.2	1.2
HCl, 10%	0.4	2.4	3.8
H_2SO_4, 10%	0.3	4.3	5.6
H_2SO_4, concd.	Nil	3.8	2.1
NaOH, 10%	0.3	1.3	0.4
KOH, 10%	0.2	0.3	0.4
SO_2, satd.	0.1	4.0	2.1
$K_3Fe_3(CN)_6$	0.2	0.4	Nil
$K_3Fe_3(CN)_6$ + 10% KOH	4.8	95.5	138.6
HNO_3, concd.	0.4	Decomposed	1.6
HNO_3, 10%	0.6	Decomposed	83.0

Its influence as a tool material in the chemical industry has already been felt, for tantalum carbide compositions are used to tip lathe and boring tools with which we may cut such hard and corrosion-resistant materials as stainless steels (both in the annealed and in the hardened condition), stellites,



Tool of Tantalum Alloy



Paddles for Clay-Mixing Machines, Which Must Withstand Considerable Abrasive Wear, Are Made of 13 Per Cent Manganese Steel, Ordinarily Considered Unmachinable

and other corrosion-resistant alloys of high chromium content, such as Duralloy, Sillichrome, Illium, and others. Hadfield's 12 per cent manganese steel used in abrasion-resisting grinding machinery in the chemical industries is commercially machinable with tantalum carbide tools. These alloys are therefore made more available to use in chemical industry in finished machined forms.

Tantalum carbide possesses the highest melting point of all substances (with the possible exception of hafnium carbide). Since other valuable physical and chemical properties are associated with it as required by physico-chemical theories, the increasing technical use of tantalum carbide for high-duty services of all kinds appears to be inevitable.

Acknowledgment

Grateful acknowledgment is hereby made to F. M. Walters, Jr., H. A. Smith, D. R. Harper, 3rd, C. W. Balke, and William E. Newcomer.

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THE SOYBEAN

A Plant Immigrant Makes Good

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THE soybean is one of the oldest crops grown. It was described in a Chinese book on materia medica, "Ben Tsao Gang Mu," written by Emperor Shen-Nung about 4800 years ago. In China and Japan the soybean has been of prime importance since ancient times, and in value and variety of uses is still the outstanding legume grown in those countries.

Production of soybeans in Asia is concentrated in Japan, Korea, and two regions in the eastern part of China. Previous to 1908 the trade in soybeans was confined almost altogether to oriental countries, particularly China and Japan. Since then the usefulness of the soybean has been more generally appreciated in other countries, and an important international trade has developed.

Soybeans were introduced into the United States in 1804, yet a hundred years later there were very few grown outside the southern states. By 1919 the crop had reached a fairly uniform development in the area east of the Mississippi River and considerable prominence in New England and certain southern and western states. However, the total acreage of soybeans in the United States fluctuated noticeably, and by 1924 had decreased in the eastern part of the country, particularly in New England and New York. In 1924, twenty-two states produced the bulk of soybeans in the United States, the total crop of gathered beans being slightly above 5,000,000 bushels.

From 1924 to 1935, inclusive, production increased rapidly, figures for 1935 indicating a total of nearly 39,637,000 bushels of gathered beans. The more rapid increase of production has occurred in the corn-belt states, particularly in Illinois, Missouri, Indiana, and Iowa. In 1935 Illinois produced about one-half of all the beans crushed in America.

Description of the Bean

The soybean (*Soja max*) is a summer leguminous annual. Pods are from 1 to 2.5 inches long and contain from two to four seeds. The stems, leaves, and seed pods are covered with short reddish brown or gray hairs. The root tubercles are large and abundant. There are many varieties of soy-

The soybean, established for many centuries in the Orient, is now rapidly coming into prominence as a farm crop in this country. Nearly 40,000,000 bushels of soybeans were grown in the United States in 1935. The soybean grain is by far the richest in protein and oil of any of our common crops. Besides furnishing excellent feed and fodder on the farm, the soybean is finding a wide use in the industries. Various edible products of high nutritive value are becoming available on the market. Besides its use in the paint industry, the oil has a prominent place in the fabrication of a long list of important commercial commodities. The residue from the oil is now receiving much attention as a raw material for the preparation of plastics and paper sizing.

beans and literally hundreds of types and strains. Figure 1 shows the plant at time of active growth or about the flowering stage. The flowers are small and inconspicuous, either white or purple, and are clustered in the axils of the leaves. The stems are branched and rather woody, and grow from 2 to 3.5 feet or more in height. Figure 2 shows a mature plant about ready to harvest for seed after the leaves have fallen.

Soybean Culture

The soybean has a wide adaptation and is grown in many sections of the United States. With the exception of cowpeas and lespedeza, the soybean is more acid-tolerant than any other legume crop grown in the corn belt where most of the commercial beans are produced. Cultivation of the crop is not complicated and is similar to that of corn. Soybeans can be grown on the average corn-belt farm with the tools already in use for other crops. The combine, which threshes out the beans and leaves the straw on the land, has been a boon to the soybean grower as well as to the wheat producer; in Illinois there are about three thousand of these machines. Illinois averaged 18 bushels of soybeans per acre in 1935. Cost records reported by the Illinois Agricultural Experiment Station (*19*) show that soybeans can be produced for 63 cents per bushel as an average for the three-year period, 1931–33. These were low-cost years because of high yields and the advantages of harvesting with the combine.

Industrial Uses

Two decades ago the soybean was only a substitute in American agriculture. Today there are few, if any, crops that outrank it in interest and future possibilities. The need in 1920 was for more legumes in the rotation, more home-grown high-protein feeds in the feed bin, and substitutes in the rotation for red clover and oats. For these purposes the soybean was then promising. This early promise has been more than fulfilled. The real preëminence of the soybean, however, was to come later with the trend toward the development of industrial uses for agricultural products, the finding of new uses for old crops, and the creation of new markets for the farmer. It is with this new outlook for agriculture that the soybean has become the "wonder bean."

For many years the utilization of the increasing acreage of soybeans did not worry the producer for there was a steady demand for seed with which to plant the expanding acreage. As the harvest of beans doubled and trebled, however, the demand for seed alone was not great enough to provide an outlet for all threshed beans. Marked progress has been made in the development of industrial uses for soybeans during the past few years. It was not until 1929 that the absorption by soybean crushing mills began to be a potent factor in influencing production of the crop. Since 1929 the number of mills crushing beans has grown rapidly. At present about thirty-five soybean mills and a number of cottonseed oil mills are crushing soybeans for oil and oil meal, twenty concerns are manufacturing soybean food products, fifteen mills are making soybean flour, and more than fifty factories are turning out various industrial products.

Imports

Imports of soybeans and soybean products into the United States have not been extensive, with the exception of imports of oil during the World War. Nevertheless, the amounts imported have represented sufficiently large proportions of the total supply to have an effect on the market.

The amount of soybeans imported has been fairly constant from year to year but at no time particularly significant. The range for ten years, 1922–31, was from about 59,000 in

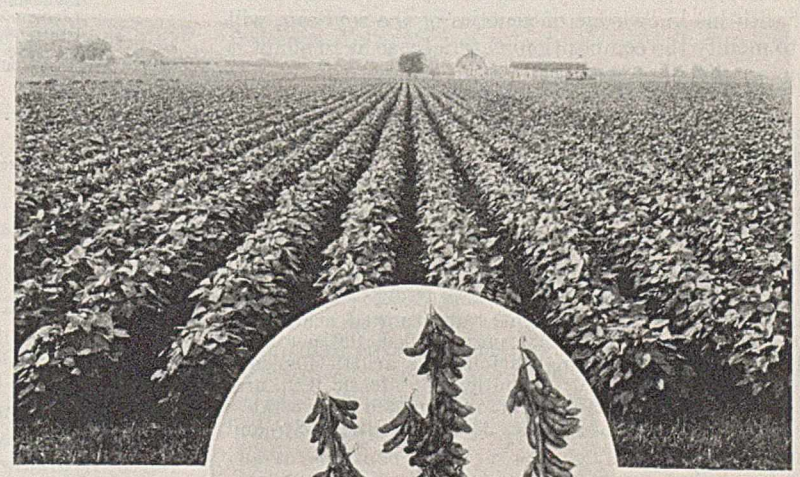

Figure 1. (*Above*) A Beautiful Field of Illini Soybeans, a Variety Extensively Used for Industrial Purposes

Figure 2. (*Below*) A Soybean Plant Loaded with Pods and Ready for the Harvest

1922 to over 72,000 bushels in 1929. In 1931 the amount of beans imported returned to about the 1922 figure.

For a considerable period beginning in 1915, imports of soybean-oil meal and cake were somewhat irregular. Upward trends seemed apparent, however, from 1925 until 1930 when tariff duties were levied on these two products for the first time. Imports of meal and cake reached approximately 86,000 tons in 1929; in 1931 they represented only 20,000 tons which is the amount of meal obtainable from 825,000 bushels of beans.

Imports of soybean oil into the United States were greatly stimulated during the World War, when there was a shortage of vegetable oils and when some of the normal outlets in Europe were closed. Imports reached a total of nearly 336 million pounds in 1918. Since that time they have declined irregularly but continually. The first marked drop occurred in 1921 when the emergency tariff measure of that year took effect. As the increased tariff duties of 1930 became effective, further reduction in imports became apparent.

Composition of Soybean Seed

Extensive studies have been made by agricultural experiment stations in this country on the chemical composition of the soybean. The soybean differs from other legumes in nitrogen, oil, and starch content. The following table shows the approximate percentage composition of the soybean compared with that of the navy bean (*18*):

Legume	Moisture	Protein	Fat	N-Free Extract	Fiber	Ash
Soybean	9.9	36.5	17.5	26.5	4.3	5.3
Navy bean	13.4	22.7	1.5	53.0	5.8	3.6

The differences in protein and fat between soybeans and navy beans are especially outstanding. There is a rather wide difference in the composition of different varieties of soybeans due no doubt to variety, soil, and climate. The plant breeder, with his knowledge of genetics of the soybean, will be able to modify the composition materially so as to adapt it to various specific purposes.

Composition of Soybean Oil

Baughman and Jamieson (*10*) have done valuable work on the composition of soybean oil. They have characterized an oil expressed with an Anderson expeller from a large late variety known as Mammoth Yellow as follows:

Specific gravity, 25°/25° C., 0.9203; n_D^{25}, 1.4736; iodine number (Hanus), 128.0; saponification value, 189.5; acid value, 0.5; saturated acids, 11.5 per cent; unsaturated acids, 83.5 per cent (iodine number, 148.7); unsaponified, 0.6 per cent. This oil was found to contain the following acids: linolenic, 2.2; linoleic, 49.3; oleic, 32.0; palmitic, 6.5; stearic, 4.2; arachidic 0.7; and lignoceric, 0.1 per cent. Calculated as glycerides: linolenic, 2.3; linoleic, 51.5; oleic, 33.4; palmitic, 6.8; and stearic, 4.4 per cent.

Smith's data (*21*) indicate that soybean oil, with an iodine number of 134, contains approximately 2 to 3 per cent linolenic, 55 to 57 per cent linoleic, and 26 to 27 per cent oleic, with 9 to 10 per cent saturated acids.

Composition of Soybean-Oil Meal

The composition (*14*) of soybean-oil meal varies somewhat, depending on the kind of beans and method of extraction. The following figures are based on analyses of six to sixteen samples and were secured from mills using different processes of extraction:

	Percentage Compn.	No. of Samples
Dry substance	91.85	12
Crude protein	41.41	16
Ether extract	5.05	16
Ash	5.70	16
Crude fiber	7.50	12
Total nitrogen	6.63	16
Calcium	0.273	8
Phosphorus	0.454	6

It is interesting to note the rather high calcium and phosphorus content of soybean-oil meal.

Methods of Processing Soybeans for Consumption

Expeller Method. The most widely adopted method of oil extraction is a continuous-pressure process in which use is made of expellers. The beans are crushed, dried to a moisture content of about 3 per cent, and passed through a steam-jacketed trough which heats the beans to about 150° F. before they reach the pressing cage of the expeller. This treatment renders the product more mobile without injuring the resulting oil for use in the manufacture of varnishes or impairing the digestibility of the nutrients in the meal. The expeller operates on the same principle as a household meat grinder. The ordinary working pressure is about 6 tons a square inch. The oil is pumped through a rotary strainer on its way to storage; the cake emerges in thin sheets that are broken up on a revolving cake breaker at the discharge end.

Table I. Utilization of Soybeans and Soybean Products in 1930

Utilization of Soy Product	Amount
	1000 bu.
Beans:	
Feed	2,750
Seed	4,025
Ground:	
Food	200
Feed	200
Crushed	4,800
Total	11,975
Oil:	*1000 lb.*
Edible purposes:	
Oleomargarine	750
Lard substitutes	500
Other food products	4,750
Paint and other industries:	
Paint and varnish	9,000
Linoleum and oilcloth	4,000
Other uses	3,500
Soap kettle	8,500
Increased stocks, including oil equivalent	6,200
Total	37,200
Meal:	*Tons*
Feed:	
Commercial	84,100
Other	15,000
Food:	
Flour	850
Infant and diabetic foods	50
Other uses, including glue	10,000
Total	110,000

Hydraulic-Press Method. The most ancient method of extracting oil is by expression, which has been used in Manchuria for centuries (*15*). In recent years the hydraulic press has been utilized for the process. Beans are prepared for the hydraulic press in practically the same way as for the expellers except that the beans have to be heated to a higher temperature before being pressed. This process is not continuous and requires considerable hand labor for loading and unloading the presses.

Solvent-Extraction Process. The oil from the flaked or ground beans is dissolved with benzene or a special high-test gasoline, usually after the beans have been thoroughly cleaned. The oil is then separated from the solvent by distilling off the latter. The solvent is used again and again. Objection has been made that some of the solvent remains in the meal. While efficiently operated modern plants can remove the last trace of the solvent, mills in the United States have not yet pushed the process to that stage of perfection. Oil obtained by this method possesses superior bleaching qualities and shows less refining loss. Likewise the meal is less susceptible to rancidity and shows better adhesive properties for utilization in the glue industry.

Disposition of the Domestic Crop

The demand for soybeans is largely determined by three main uses: seed, livestock feed, and crushing. Distribution of gathered beans by uses is shown in Table I. Complete figures are not available for 1935. Doubtless considerable shifts in the amounts used for different purposes will be noted when final tabulations are made.

Particular attention is called to the amount of beans crushed in 1930—namely, 4,800,000 bushels—and the quantity of the oil produced from this reasonably large supply of beans, totaling more than 37,000,000 pounds of oil (*22*). Most of the 110,000 tons of meal was used for commercial feed. The two products of the soybean which are attracting most attention are the oil and the meal.

Out of a total factory consumption (*2*) of 22,958,000 pounds of soybean oil in 1933, 489,000 pounds were used in compounds and shortening, 7000 pounds in oleomargarine, 460,000 pounds in other edible products, 4,233,000 pounds in soap, 8,568,000 pounds in paint and varnish, 5,641,000 pounds in linoleum and oilcloth, 65,000 pounds in printing inks, and 2,626,000 pounds in miscellaneous products. Eight hundred sixty-seven thousand pounds represented "loss including foots." In 1933 the paint and varnish, linoleum, and oilcloth industries consumed 61.88 per cent of the total.

Two years later in 1935, out of a total factory consumption (*3*) of 91,166,000 pounds of soybean oil, 52,452,000 pounds were used in compounds and vegetable shortenings, 1,740,000 pounds in oleomargarine, 9,421,000 pounds in other edible products, 2,549,000 pounds in soap, 13,003,000 pounds in paint and varnish, 4,816,000 pounds in linoleum and oilcloth, 52,000 pounds in printing ink, and 1,665,000 pounds in miscellaneous products. About 5,000,000 pounds were accounted for by "loss including foots."

Products Derived from Soybeans

Products derived from soybeans grown in the United States are many. The list of products actually being placed on the market in the United States and Canada, compiled from letters received by the University of Illinois during the latter part of 1931, is given in Table II.

This list is increasing from month to month. Only the remarkable versatility of the soybean crop can explain the far-reaching development in its utilization, and the real development seems to have just begun.

Table II. Commodities in Which Soybeans or Soybean Products Are Used[a]

	Food Products	
Soybean flour	Macaroni (20% soybean flour)	Soya cream biscuits
Soybean-meal flour	Soybean muffins	La Choy soy sauce
Refined edible soybean oil	Soybean cookies	Zoybeans (cooked beans)
Soybean salad oil	Soybean doughnuts	Bacon and Zoybeans
Chocolate bars (30% soybean flour)	Vegetable shortening	Zoy bouillon
Cocoa (up to 60% soybean flour)	Infant foods	Casein gluten flour
	Diabetic foods	No-fat mayonnaise
Sausages (up to 50% soybean flour)	Oleomargarine	Fatless spread
	Lard substitutes	Soyex-malt-cocoa drink
Bread (7.5% soybean flour)	Filled sweets	
	Soybean sprouts	Soybean milk
Rolls (10% soybean flour)	Soybean cheese	Soybean ice cream
	Feed Products	
Cake or meal	Poultry chow	Rabbit chow
Commercial feed	Dog chow	34% protein chow chow
Dairy feed	Calf chow	
Hog chow		Chick Startena
	Industrial Products	
Paint	Printers' ink	Lauxein emulsifier
Varnish	Glycerol	Soap
Enamels	Celluloid	Core binders
Oilcloth	Lauxtex plastic wall coat	Rubber substitutes
Linoleum		Plastics
	Lauxein waterproof soybean glue	

[a] This list includes a number of products for which only trade names are available.

Industrial Use of Soybean Oil

Soybean oil was apparently first produced in the United States in North Carolina in 1910 and later in 1920 at Chicago Heights, Ill. The quantity produced in this country at that time was not sufficient to be noted in the U. S. Census. However, such marked advances have been made that in 1935 there were produced in this country more than 91,000,000 pounds of high-grade soybean oil.

The quality of soybean oil has varied so widely in the past that many users have been prejudiced against it. However, developments in processing and refining have been rapid in recent years, and today the product is fairly uniform in quality and is usually superior to imported oil. The standard for raw soybean oil as promulgated by the National Soybean Oil Manufacturers' Association is as follows:

Tentative Specifications for Raw Soybean Oil (*9*); A. S. T. M. Designation D 124-33T, Issued 1922, Revised 1933

	Maximum	*Minimum*
Foots, per cent	2.5	...
Loss on heating at 105–110° C., per cent	0.1	...
Sp. gr. at 15.5°/15.5° C.	...	0.924
Acid No.	3.0	...
Saponification No.	...	190.00
Iodine No. (Wijs)	...	131.00

Color, not darker than a freshly prepared solution of 1.0 gram potassium dichromate in 100 ml. pure H_2SO_4 (sp. gr., 1.84) or its equivalent in iron-cobalt solution

Soybean oil is adapted to a wide range of uses, as shown briefly in Table III.

Soybean Oil in the Paint Industry

No phase in the utilization of soybeans has been more striking than the development of methods for using the oil in paints and varnishes. Since Illinois was the leading soybean-producing state in 1924, it was natural for the Illinois Agricultural Experiment Station to do what it could to promote the wider industrial utilization of soybean products.

Six years ago, in 1930, the experiment station launched this project. At the outset of the work it was found that paint companies were cautious in matters pertaining to the use of soybean oil. In fact, as Toch (*23*) reported, soybean oil as a paint oil was practically unknown as recently as 1909. "Since that time," Toch stated in 1921, "many investigators have published more or less conflicting articles concerning soya bean oil, and even the physical and chemical constants of soya bean oil vary to some extent. Owing to the fact that discordant results were continually obtained, it is only within the last year that it has been possible to state with some degree of certainty whether soya bean oil is a substitute for linseed oil, an adjunct to it, or neither." Written less than twenty-five years ago, this was one of the earlier statements in this country on the question of the use of soybean oil in paints and varnishes. Between that time and the start of the Illinois experiments, successes and failures as this new development progressed were reported and discussed in a number of papers (*5, 6, 8, 17*).

With this record as a background, the first of the Illinois station's studies on the use of soybean oil for paint purposes was begun in August, 1930. Paints were tested in which soybean oil constituted varying proportions up to 50 per cent of the total vehicle (liquids) used in the paint. Direct com-

TABLE III. ADAPTABILITY OF SOYBEAN OIL TO USE IN VARIOUS PRODUCTS

Use	Probable Adaptation	Inferior Adaptation	Satisfactory Adaptation	Superior Adaptation
Drying products:				
Paint	To 50%	.....	To 25–40%	To prevent yellowing
Varnish	To 20%	.....	To add luster	.....
Linoleum and oilcloth	To 20%	.....	To give elasticity	.....
Waterproof goods	To 25%	.....	To prevent cracking	.....
Soap products:				
Hard soaps:				
Toilet	If hydrogenated, to 25%	In any amount	.....	.....
Household	If hydrogenated, to 20%	In any amount	.....	.....
Laundry	Depends on price	.....	In considerable amounts	.....
Soft soaps:				
Shampoos, etc.	Limited	In any amount	.....	.....
Automobile soaps, etc.	Depends on price	.....	.....	Very good
Edible products:				
Lard compounds	Depends on elimination of odor and rancidity	.....	If properly refined	.....
Cooking oils	If odor is permanently eliminated	.....	To some extent	.....
Salad oils	In small amounts	In any amount	.....	.....
Fountain drinks	Excellent	.....	In increasing amounts	.....
Candy	Fair	In large amounts	.....	.....
Mayonnaise	In small amounts	In any amount	.....	.....
Margarine	In small amounts if properly treated	.....	In small amounts	.....
Miscellaneous:				
Foundry core oil	In large amounts	.....	If properly treated	.....
Printers' ink	Little change from present use	.....	In small amounts	.....

parisons were made with standard linseed oil paints. After five years of exposure the paints made with soybean oil formulas are very satisfactory.

A large number of test panels were put out during the spring of 1931 for the first time. The purpose was to study the behavior of paints differing primarily in their content of raw and treated soybean oil and in addition to compare the effectiveness of different driers. Interior paints, as well as exterior ones, were studied. The results on the set of panels coated with interior paints containing soybean oil have been highly pleasing, and the work was extended even further. Rooms in the agricultural buildings on the University of Illinois campus were painted with soybean oil paint. Today, after three years, the paint in these rooms is in excellent condition. A number of buildings on the campus were also painted with soybean-oil paints[1] three years ago. These were inspected in July, 1935, and found to be in good condition. The University of Illinois is now making liberal use of soybean paint.

Results of the exposure and other tests indicate that soybean oil has a permanent place in the manufacture of paint. The condition of the panels supports the findings of other workers to the effect that 30 per cent and more of the oil used in the paint can consist of soybean oil when properly treated and when driers suited to this kind of oil are used.

This conviction is supported by results obtained in the field. Many farm buildings in Illinois painted with soybean oil paint were inspected recently by the writer. This paint is giving satisfaction when properly handled and applied. A number of organizations and paint manufacturers are interested in soybean oil for paint purposes and are doing much to promote its intelligent use.

Gardner (*7*), a pioneer in the study of the use of soybean oil for paint purposes, writes as follows:

> I have been working on soybean oil for about twenty-five years, and on many occasions I have suggested its possibilities in exterior and interior paints for certain formulations, provided it was properly reinforced with other oils to give the desired physical properties. Proper treatment with other oils, in my opinion, will do away with the defects which otherwise might be encountered, such as "after softening" and mildew accumulation. It is believed, therefore, that soybean oil will occupy a most important position in the paint industry during the coming years.

[1] The term "soybean-oil paint" is used when the paint contains any soybean oil.

Soybean Oil as a Core Binder

The use of soybean oil as a core binder has been under investigation for some years. Sefing and Surls (*20*) report as follows on the use of soybean oil as a core binder: "Soybean oil can be used satisfactorily as a core binder for foundry work. It produces cores that are on a par with those made from linseed oil." Casberg and Schubert (*4*) present similar data on the suitability of soybean oil for core oil as follows: "Raw soybean oil produced cores with an average tensile strength slightly higher than the average tensile strength of cores made from semi-refined or varnish soybean oil and compares favorably with the core oils now on the market."

Other Uses for Soybean Oil

Joyce (*11*) has written:

> In treating the soybean oil our company operates a lecithin plant in which the lecithin or vegetable phosphatides are extracted from the oil. This lecithin is not only used in the medical profession as a nerve food, but is used in the confectionery trade as a means of properly distributing icings and cake coatings.

Other uses where soybean oil may serve are suggested by Kishlar (*12*):

> Millions of pounds of sulfonated castor oils are used each year in sprays, leather processing, cloth printing, and similar uses. A new sulfonated soy oil has been developed which is proving to be of equal value at materially less cost. . .
>
> Several years ago attention was called to a young man who had had eczema for many years. He was allergic to almost every form of protein. At the request of a famous New York physician, a specially refined soybean oil was prepared. The trouble in a few weeks cleared up. Many of the allergies disappeared. The physician prescribed soybeans to scores more, with equally successful results. This oil need not be taken like medicine, but is used in mayonnaise, French dressing, Russian dressing, or in any other way the usual cooking oils may be used.

Plastic Industry

During the last six years there has been a dramatic rise of a new industry—plastics. It is said that the total value of

plastics sold to the consumer amounted to approximately 200,000,000 dollars last year. This development seems to be a modern miracle. Plastics are found in furniture, wall panels, builders' hardware, electric fixtures, ash trays, clocks, toilet articles, decorative stair fronts, automobile parts, light switches, distributor cases, window frames, safety glass, buttons, buckles, costume jewelry for clothing, and literally hundreds of other little gadgets. The list is growing month by month.

The soybean is a source of raw material for the plastic industry. From a ton of soybeans are produced about 250 pounds of oil and 1600 pounds of meal, containing approximately 40 per cent protein. This raw material is proving to be an excellent source of material for the plastic industry. Last year America produced about 40,000,000 bushels of soybeans. If 40 per cent of this is protein, it is evident that the soybean is an extensive source of plastic material. One automobile company has been reported to be constructing a plant for plastic manufacture costing $5,000,000.

O'Brien (*16*) reports as follows on products derived from soybean meal:

> The protein is extracted from the soybean meal at a high degree of purity. We have developed certain uses of protein in sizing of paper and in certain wax emulsions for paper in waterproofing. The use of protein in sizing has developed new possibilities in paper and paper manufacture and has permitted the use of certain types of pulp which could not be used before for the manufacture of paper that was to be sized. An extensive research program has been carried on in the paper industry on the use of protein and in all, I would say, 2000 tons of paper have been made. We have also done some work on the use of protein as a coating material instead of casein and also in replacing starch in beaters, and because of the improvement in the paper by the use of protein instead of starch there are good possibilities in this direction. We have also done considerable research on the use of protein or modified forms of protein as a resin, and this field looks rather encouraging. . .
>
> In the making of vegetable proteins there is a finely divided residue which is practically in colloidal form which is sold to manufacturers of dog foods, rabbit foods, etc., and there is also a coarser material which consists largely of the hulls of beans which is supplied to plastic manufacturers to take the place of wood flour in making various plastic articles such as telephone instruments, automobile instrument parts, cigar lighters, etc.

Boyer (*1*) makes the following comment concerning certain research problems now under way in the Edison Institute laboratory:

> Another problem that we are investigating at present is the use of solvents other than the hydrocarbon type in the extraction process. We have produced extracted meal in this manner that has very unique and interesting properties. Although we are not now at the point where we can safely predict anything, we believe that an entirely new field can be opened up in this way for the soybean meal. One of our aims is to produce a synthetic fiber similar perhaps to the one now being produced in Italy from milk casein.

Soybean Glue

Soybean glue (*13*), although a newcomer in the plywood field, has found many uses in the last eight years. The tonnage approximates that of all other plywood glues combined. It is used for many forms of plywood, with the chief exception of gluing fancy veneers where stain is an important factor. The chief uses at present are for Pacific Coast fir and pine plywood, where it is used exclusively; box shooks in eastern and southern states; drawer bottoms, glass backs, etc., in the furniture field, and for laminating fiber boards. Joyce (*11*) states:

> When the flour is taken from the meal, the residue may be used as a stock food. The extracted meal is also used by our company as a source of vegetable protein. This protein, known as Beta protein, is used by the paper manufacturing trade as a sizing and a coating. The soybean protein is also used as a vegetable glue and is of particular interest to furniture manufacturers in the preparation of veneer work and by airplane manufacturers in making airplane propellers, etc. The glue, being waterproof and of very great tensile strength, is in great demand in the industry.

Soybean-oil meal has not been used for fertilizer purposes in this country to any extent. It has been reported that Japan used, from 1917 to 1932, one to one and a half million tons of soybean-oil meal a year in fertilizers. There may come a time when it will serve the American farmer in the conservation and improvement of his soil.

Further Investigation Needed

Much valuable research has been done in certain foreign countries and the United States, particularly in the fields of agronomy, genetics, and animal nutrition. However, only within the last few years have the chemist and industrialists become deeply interested in the great possibilities of the soybean. The following are only a few of the many lines of study which need thorough and prompt investigation:

To study the composition of the soybean as affected by climate, soil, and varietal differences.

To determine the effect of different methods of processing on the quality of the meal and oil.

To study in further detail the characteristics and composition of soybean oil.

To discover new industrial uses for the soybean and soybean products, and to improve the products now utilized by the industries.

To investigate methods of improving soybean oil with special reference to its use in the paint and varnish industry.

To investigate further the use of soybean-oil meal in the manufacture of plastics.

To produce, by breeding, varieties better suited to the needs of industry.

To determine the economic place of the soybean in our agricultural and industrial program.

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Fermentative Utilization of Cellulosic Materials

Especially the Pentosans

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The production of industrial chemicals by fermentation is a specialized application of the principles of catalysis in heterogeneous system. The catalysts, the enzymes, are produced during the course of the reaction accompanying the increase in numbers of the microörganism employed. The process is therefore one of autocatalysis. The general approach is the same as that for other industrial catalyses—that is, to determine the conditions under which the appropriate catalyst will produce the maximum yields of the desired chemicals in a minimum time at the least cost. Typical examples are discussed illustrating the application of the principles to the production of chemicals by the fermentation of cellulosic materials, especially the pentosans. It is evident that only a few of the industrial possibilities have been explored in detail.

THE production of chemicals by fermentation is a case of catalysis, or rather autocatalysis, in heterogeneous system. Zymotechnical syntheses differ from other catalytic processes in that in the latter case the catalyst, usually a simple type of chemical, is manufactured outside the reaction mixture and then added to the reaction mixture under controlled conditions. In the fermentation process the catalysts, the enzymes, are manufactured during the course of the reaction. The handling of the fermentation must involve a specialized knowledge of the nutrition of the organism employed and of the conditions under which it will produce, in the highest degree, the particular catalysts desired.

Different organisms bring about different chemical transformations in the same medium, and the chemism of a given organism on a given substrate varies with alteration of nutritional and of physical-chemical environment. Moreover, instances are known in which two different organisms growing together bring about chemical changes which neither one alone could effect. In fermentation processes we are dealing with a series of products in various stages of oxidation and reduction. The fact that the organisms do not completely transform the substrate into water and carbon dioxide provides the basis for a fermentation industry.

There is a voluminous literature on the products formed by the action of microörganisms, especially on the carbohydrates and other nonnitrogenous compounds. Figure 1 gives the fermentative interrelationships of the microbiological dissimilation products of the carbohydrates as previously published by the author (*6*). These include products identified as being formed by the action of bacteria, yeasts, or molds. The dissimilation products are listed alphabetically in the left-hand column as substrates. In the right-hand column the same materials are classed as products. The lines connecting a member of the left-hand column with certain members of the right-hand column represent products formed by the action of microöganisms on the given substrate. Conversely, the lines connecting a given product with various substrates show the different substrates from which the products may be produced. Not all of the forty-eight compounds listed are simple decomposition products; there are many instances of synthesis into more complex materials.

It is evident that the microörganisms present unique tools as catalysts in the production of chemicals. Only a few items in the chart have been commercially exploited. The problem resolves itself into the bringing together of the appropriate catalysts—that is, microörganism or microörganisms—and the appropriate substrate under conditions giving optimum yields of the desired chemicals in minimum time with least expense. This, then, is the chemical approach to the problems of the production of chemicals by fermentation.

The purpose of this paper is to present material illustrating the application of the principles outlined, as typical examples of the chemical approach to the problem. This objective is most easily met by discussing for the most part the work done and in progress in this laboratory as illustrative material. References to the literature are given in the papers cited.

"Cellulose" is here used in the broad sense to include plant structural tissues which, upon hydrolysis, yield dextrose. Under the term "pentosans" are included those plant structural tissues yielding pentoses, usually xylose, upon hydrolysis. The sources of cellulose fall into two classes. The plants from which cellulose is a main product include especially the trees from which pulp and paper are made; the second class includes those plants for which cellulose is a by-product, and the main product is food materials. In this connection it might be well to distinguish between agricultural or farm wastes and trade wastes. Cornstalks, straws, corncobs, etc., belong to the first class. They are really farm wastes in the sense that they remain on the farm. On the other hand, materials such as oat hulls, cottonseed hulls, hemp hurds, and sawdust are trade wastes. They are concentrated at the factory with transportation charges amortized by the sale of the various main products.

Cellulose Fermentation

Direct Fermentation to Produce Fuel Gas. The production of fuel gas by the anaërobic fermentation of farm wastes has been studied in this country especially by Buswell, Boruff, and co-workers (*1*, *4*, *5*). According to these workers, as early as 1897 a waste-disposal tank at Bombay was equipped with gas collectors and the gas used to drive gas engines; at about the same time gas so produced was used for heating and lighting purposes in England. In 1925 Imhoff in Germany equipped a sludge digestion tank with gas collectors and connected them to the city mains; the gas was found to be satisfactory for general municipal use. The gas is principally methane with small amounts of hydrogen. Their studies show the process to be directly applicable to farm wastes. They calculate that a ton of cornstalks yields 10,000 to 20,000 cubic feet of gas. Using the lower figure, a ton of cornstalks would furnish gas for 400 people daily, allowing 25 cubic feet per capita. On this basis in a region in which 30 per cent

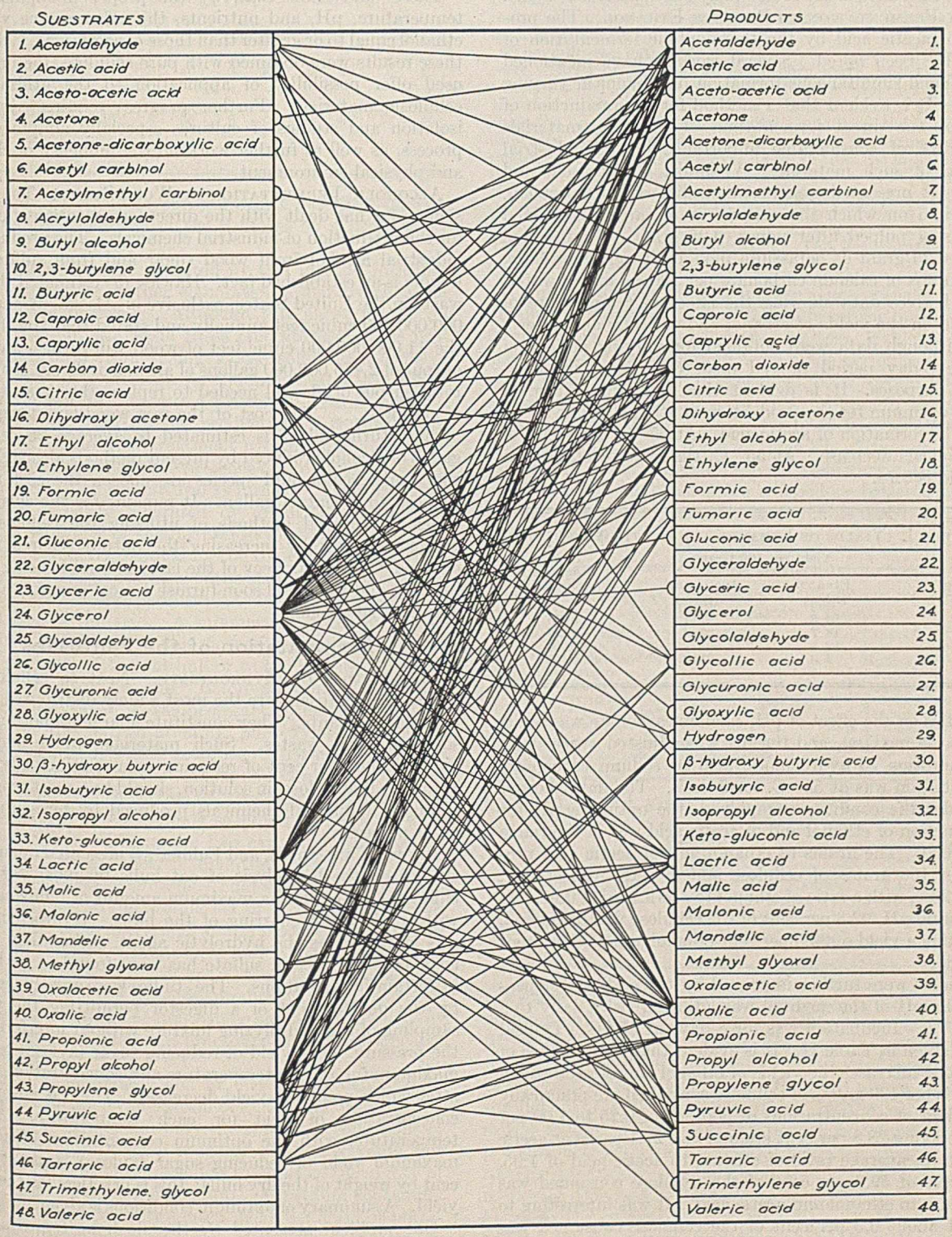

Figure 1. Fermentative Interrelationships of Microbiological Dissimilation Products of Carbohydrates (*6*)

of the land is planted to corn, a circle within an 8-mile radius would produce enough cornstalks to supply a city of 80,000 inhabitants with gas. The cost of collection of the raw material is at present a limiting factor in the development of this process. The Ames Field Station of the U. S. Department of Agriculture is studying various phases of this problem.

Direct Fermentation to Produce Acetic Acid. This procedure is so well known, as the Langwell process, as to require little discussion in this paper. The process has been applied in this country especially to corncobs as the raw material. The subject of the production of acids by fermentation has been adequately reviewed by May and Herrick (*10*).

Direct Fermentation to Produce Ethanol. The production of acetic acid by the thermophilic fermentation of cellulose has been noted. Several workers have mentioned the occasional simultaneous formation of ethanol in varying amounts. It is evident that a method for the production of ethanol by the direct fermentation of cellulosic materials would prove of considerable importance in the industrial utilization of such materials. Veldhuis, Christensen, and Fulmer (*12*) presented systematic studies on this problem. The medium on which the cultures were carried contained 3.0 grams of pulped filter paper, 0.25 gram of ammonium chloride, 0.25 gram of potassium monohydrogen phosphate, and 4.0 grams of calcium carbonate per 100 cc. of tap water.

Table I gives data showing the effect of temperature of incubation on the yields of ethanol and of acetic acid after 8 days. Although data were obtained for varying periods of time, the 8-day period proved most convenient for comparative purposes. It is evident that the temperature of 55° C. is optimum for the production of ethanol, while 60° is best for the formation of acetic acid. At 65° C. the yields of both chemicals decrease. At 55° C. the ratio of ethanol to acetic acid is 0.74.

Table I. Yields of Ethanol and Acetic Acid

Temp.	Yield per 100 Grams Cellulose Added		Ratio, Ethanol to Acetic Acid
	Ethanol	Acetic acid	
° C.	*Grams*	*Grams*	
50	13.8	17.1	0.80
55	18.7	25.4	0.74
60	12.8	31.7	0.40
65	3.3	28.3	0.12

In studies on the effect of pH, calcium carbonate was omitted from the medium, and the pH was adjusted twice daily by the addition of hydrochloric acid or sodium carbonate. The incubation was at 55° C. for 8 days. The data showed that, under the conditions employed, the optimum pH for the production of ethanol and of acetic acid was in the range of 7.50–8.00. The grams of ethanol and of acetic acid produced per 100 grams of cellulose added were, respectively, 21.5 and 23.5, with a ratio of ethanol to acetic acid of 0.91. At the optimum pH, 92.3 per cent of the cellulose was consumed, representing a yield of 23.3 per cent ethanol and 25.5 per cent acetic acid.

The yields were further improved by the addition of peptone. The pH of the medium was adjusted twice daily to a value of 7.5. Incubation was for 8 days at 55° C. Typical data are given in Table II. It is evident that the presence of the peptone increases the yields of ethanol and of acetic acid. The yields per 100 grams of cellulose consumed are practically independent of concentrations of peptone of 0.25 to 1.00 per cent, averaging 28.8 per cent ethanol and 27.1 per cent acetic acid with an average ratio of ethanol to acetic acid of 1.05. An average of 59.9 per cent of the cellulose consumed was converted into ethanol and acetic acid. It was interesting to find that about 0.5 per cent of the cellulose consumed was converted to *n*-butanol.

Table II. Effect of Peptone on Yields of Acetic Acid and Ethanol at 55° C.

Peptone	Cellulose Consumed	Yield per 100 Grams Cellulose Added		Yield per 100 Grams Cellulose Consumed		Ratio, Ethanol to Acetic Acid
		Ethanol	Acetic acid	Ethanol	Acetic acid	
%	%	*Grams*	*Grams*	*Grams*	*Grams*	
0	71.0	19.7	17.7	27.7	24.7	1.11
0.25	78.0	23.3	21.7	29.8	27.8	1.07
0.50	90.0	25.3	23.7	28.1	26.3	1.07
1.00	91.0	26.0	26.7	28.6	29.3	0.97

These data show that, by the proper manipulation of temperature, pH, and nutrients, the culture gave yields of ethanol equal to or greater than those of acetic acid. Although these results were obtained with pure cellulose, the principles used offer possibility of application to the utilization of cellulosic materials. Further progress requires systematic isolation and studies of cultures especially adapted to the process, as well as further work on the influence of chemical and physical environment.

Alcoholic Fermentation of Wood Sugar. The discussion so far has dealt with the direct fermentation of cellulose for the production of industrial chemicals. The production of industrial alcohol from wood sugar and from sulfite waste liquors is an established fact. Hawley (*9*) estimated the wood waste in the United States, exclusive of Alaska, at about 11,000,000,000 cubic feet annually and stated that "on this basis the 11,000,000,000 cubic feet of wood will furnish an annual output of 2,476,000,000 gallons of alcohol or 33 per cent of the total output of alcohol needed to replace the present output of gasoline.... The cost of the raw wood laid down at the manufacturing plant is estimated to average 25 cents per gallon of alcohol produced by present methods although where the proper region and species are chosen the cost may be reduced to 7 cents a gallon. It remains for the chemists to develop improved methods of utilizing the cellulose more completely, thereby increasing the output secured per ton of wood." The prophecy of the last sentence is being rapidly fulfilled, and wood will soon furnish a most economical source of industrial alcohol.

Fermentation of the Pentosans

Preparation of Hydrolyzate. Next to cellulose and lignin, the pentosans are the most widely distributed organic materials in plants. They constitute a large proportion of the so-called farm wastes. Such materials, upon hydrolysis, give up to 40 per cent of reducing sugars, principally xylose. It follows that xylose, in solution, should be a most economical source of industrial chemicals produced by fermentative or other processes.

Bryner, Christensen, and Fulmer (*3*) presented quantitative studies on the hydrolysis of oat hulls by means of hydrochloric acid to obtain a maximum amount of reducing sugars with a minimum charring of the hulls. Hydrochloric acid was employed as the hydrolytic agent, rather than sulfuric acid, because calcium sulfate has been found to be harmful in certain fermentations. The studies were greatly facilitated by the development of a digestor permitting the periodic sampling of the hydrolyzing mixture without interfering with the pressure. The yield of reducing sugar (xylose) reaches a maximum for a given temperature and concentration of acid, after which point the yield decreases. There is an optimum concentration of acid for each temperature. At each temperature, with the optimum concentration of acid, the maximum yield of reducing sugar (xylose) is about 40 per cent by weight of the dry hulls; this is practically a theoretical yield. A summary of optimum conditions is given in Table III.

One problem presented by the alcoholic fermentation of wood hydrolyzate is the presence of pentoses which are not

TABLE III. OPTIMUM CONDITIONS FOR HYDROLYSIS OF OAT HULLS WITH HYDROCHLORIC ACID

Steam Pressure	Normality of HCl	Time	Yield of Xylose per 100 Grams of Hulls
Lb./sq. in. (kg./sq. cm.)		*Min.*	*Grams*
0 (0)	1.49	240	38.8
20 (1.4)	0.090	120	40.0
40 (2.8)	0.050	90	40.0
60 (4.2)	0.042	75	39.5
80 (5.6)	0.042	60	39.9
100 (7.0)	0.042	30	40.5

TABLE IV. OPTIMUM CONDITIONS FOR YIELD OF FURFURAL PER 100 GRAMS OF XYLOSE IN 20 PER CENT SOLUTION

	HCl Concentration:											
	0.25 *N*		0.50 *N*		0.75 *N*		1.00 *N*		1.50 *N*		2.00 *N*	
	Per Cent NaCl:											
Time *Hours*	0	40	0	40	0	40	0	40	0	40	0	40
2	0	12	2	19	4	25	3	27	4	33	13	36
4	3	19	5	30	6	35	9	38	14	39	17	36
6	2	24	5	39	10	37	20	35				
8	5	26	6	36	11	40						

fermented by yeast. The procedure just described offers a method for the separation of the pentoses by a preliminary hydrolysis.

The solution of xylose prepared by this method furnishes the raw material for further elaboration either by chemical or fermentative processes. Although this paper has to do with fermentation, studies in these laboratories on the production of furfural from strong xylose solutions will be of interest as part of a program for the industrial utilization of agricultural materials. Fulmer, Christensen, Hixon, and Foster (*7*) presented data on the production of furfural from strong xylose solutions by treatment with hydrochloric acid–sodium chloride systems in the presence of the solvent toluene. The toluene removed the furfural as formed. The furfural so concentrated is easily separated by distillation. The salt lowered the solubility of the furfural in the reaction mixture, thereby facilitating its removal by the toluene. The salt also increased the chemical potential of the acid, thereby increasing the rate of reaction and permitting the use of relatively low concentrations of the acid. A summary of optimum conditions is given in Table IV. This method is directly applicable to the hydrolyzate of the oat hull or to the hull itself.

FERMENTATION OF XYLOSE. Before studying the fermentation of hydrolyzates, it was necessary to gain detailed information on the fermentation of pure xylose. Table V lists sixteen chemicals which have been reported as produced by the action of bacteria and molds on xylose. Breden and Fulmer (*2*) compared the action of *Aerobacter faeni* on sucrose and on xylose. The compounds so noted in Table V were identified as produced from the two carbohydrates, and all but hydrogen were followed quantitatively, both under aërobic and anaërobic conditions. That work was undertaken with a special view to the production of 2, 3-butyleneglycol; the yields were, respectively, 18.2 and 21.0 per cent from xylose and sucrose. Fulmer, Christensen, and Kendall (*8*) studied the influence of the composition of the medium, especially with reference to sucrose, upon the production of 2,3-butyleneglycol by various species of Aerobacter and obtained yields as high as 47 per cent. The same procedure should be applicable to xylose solutions.

Underkofler, Christensen, and Fulmer (*11*) presented data on the butyl-acetonic fermentation of xylose and other sugars. This research illustrates not only the studies of conditions of the medium optimum for the production of the solvents, but also the development of a procedure to improve the ability of the organism to ferment the medium. A medium containing per 100 cc., 1.0 gram of corn-gluten meal, 0.2 gram of potassium monohydrogen phosphate, and about 6 grams of carbohydrate proved to be entirely satisfactory for subsequent studies.

The original culture was isolated in 1931 from wheat and was chosen because of its ability to ferment sugars somewhat better than did other cultures tested. The usual procedure for preparing cultures for the fermentation of corn mash is:

Sterile corn mash, in long fermentation tubes, is inoculated from a spore culture and heated for 1 or 2 minutes in boiling water to kill vegetative cells and to ensure a start from resistant spores. This procedure is known as "heat shocking." The tubes are promptly cooled and incubated. The active cultures are transferred daily into fresh sterile corn mash. The fifth transfer is allowed to complete the fermentation and is set aside for several days for sporulation to take place. Using this spore culture, the process is repeated several times. The procedure described materially increases the ability of the culture to bring about the desired fermentation.

The cultures employed for the fermentation of the sugars were treated by this procedure in corn mash, and the one was selected which gave the most active fermentation in sugar media. However, the cycles could not be carried out in the sugar media since the organism did not sporulate readily in the tubes. This difficulty was finally overcome by pouring the fermented sugar medium into sterile Erlenmeyer flasks so that the liquid formed a thin layer. Under these conditions sporulation took place readily. By the introduction of this method into the cycle, a culture was obtained by means of which the fermentation of xylose was completed in half the time required for the culture not so treated. The solvent yields were increased. The fermentation of corn mash remained normal.

Using the derived culture and the semi-synthetic medium, detailed studies were made of the course of the butyl-acetonic fermentation of starch, dextrose, maltose, levulose, sucrose, and xylose. Determinations were made periodically of total acidity, pH, carbohydrate consumed, total solvent yield, and the proportion of the three solvents, *n*-butanol, acetone, and ethanol. Data for the times required to reach maximum solvent production are given in Table VI. Although the times required to attain maximum solvent yield vary with the sugar employed, the final yields are as good or better than those obtained with corn meal or with starch as based on the dextrose equivalent.

TABLE V. CHEMICALS REPORTED AS PRODUCED BY ACTION OF MICROÖRGANISMS ON XYLOSE

Acetic acid[a]	Ethanol[a]
Acetone	Formic acid[a]
Acetylmethylcarbinol[a]	Hydrogen[a]
n-Butanol	Lactic acid[a]
2,3-Butyleneglycol[a]	Oxalic acid
Butyric acid[a]	Propionic acid
Carbon dioxide[a]	Succinic acid[a]
Citric acid	Xylonic acid[a]

[a] Identified by Breden and Fulmer (1931) as produced by the action of *Aerobacter faeni* on xylose and on sucrose.

TABLE VI. TOTAL YIELD OF SOLVENTS, IN TERMS OF DEXTROSE EQUIVALENT

Carbohydrate	Max. Solvent Yield	Hours to Max. Solvent Yield	Carbohydrate	Max. Solvent Yield	Hours to Max. Solvent Yield
Levulose	32.0	46	Xylose	30.0	131
Starch	31.7	48	Sucrose	29.5	168
Maltose	31.4	55			
Dextrose	29.4	81	Corn meal	29.6	46

Various investigators have shown that the yields of butanol, acetone, and ethanol from corn mash are approximately in the ratio 60 : 30 : 10. Table VII gives the percentages of the solvents produced by the fermentation of several sugars of different types. It is evident that this above ratio holds throughout the fermentation of all of the carbohydrates except xylose. As the fermentation of xylose proceeds, the proportion of *n*-butanol markedly increases, that of acetone remains practically constant, and the proportion of ethanol markedly decreases. The ratio varies from 29 : 25 : 46 at 40 hours to the normal ratio of 60 : 30 : 10 after 118 hours. Studies are in progress to determine whether this variation holds for other pentoses.

TABLE VII. SOLVENT RATIOS FOR SEVERAL CARBOHYDRATES

Time	% Butanol[a]				% Acetone				% Ethanol			
	D	L	Su	X	D	L	Su	X	D	L	Su	X
Hours												
24	71	63	..	..	22	24	..	..	7	13	..	..
31	64	62	..	..	26	25	..	..	10	13	..	..
40	66	60	..	29	22	27	..	25	12	13	..	46
46	63	55	73	31	23	26	26	24	14	19	1	45
55	63	59	67	40	25	24	30	28	12	17	3	32
65	60	61	65	54	25	23	28	29	14	16	7	17
81	65	61	67	55	25	24	29	30	10	15	3	15
100	..	..	62	54	..	..	30	34	..	..	8	15
118	..	..	58	59	..	..	31	29	..	..	11	12
131	62	58	65	60	26	25	31	28	9	17	4	12
168	..	..	64	60	..	..	32	30	..	..	4	10

[a] D = dextrose; L = levulose; Su = sucrose; X = xylose.

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HEAT INSULATION IN AIR-CONDITIONING

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Two important functions of heat insulation in air-conditioning systems are the prevention of condensation on pipes and ducts and the prevention of heat transmission to or from the surrounding atmosphere. This paper presents a rational method for the determination of the correct thickness of insulation to apply, in order to prevent sweating, and also gives useful tables and graphs for the calculation of heat transmission from objects at subzero temperatures, as well as for objects above room temperature.

HEAT is transmitted to or from pipes and ducts by radiation and convection. The radiant heat transfer per unit area is independent of the geometrical shape, whereas the convected heat depends to a considerable extent on the shape factor. In this paper only pipes and rectangular or square ducts are considered.

Heat Transmission by Free Convection

The heat transmission by free or natural convection can be determined from a formula published by the writer (*2*):

$$q_c = C\left(\frac{1}{D}\right)^{0.2}\left(\frac{1}{T_{\text{av.}}}\right)^{0.181} dt^{1.266} \text{ B. t. u./sq. ft./hr.} \quad (1)$$

where C = a constant depending upon the surface shape
D = diam. of pipe or circular duct or height of vertical wall, in. (effect of diam. or height becomes constant at 24 in.)
$T_{\text{av.}}$ = av. wall surface and surrounding air temp., ° F. abs.
dt = temp. excess between wall surface and surrounding air, ° F.

For horizontal cylinders the value of C = 1.016 has been well established by various investigators. C = 1.394 has been fairly well established for vertical plates. A value of C = 1.79 for horizontal plates warmer than the ambient air facing upward and 0.89 for horizontal plates warmer than air facing downward is indicated by the investigations of Griffith and Davis (*1*). More experimental work is needed on various sized plates in the three positions to determine accurately the effect of size and position.

Table I gives the heat transmission by free convection from vertical walls 24 inches or more in height as calculated from Equation 1 for an ambient air temperature of 80° F. The values in Table I will not be changed appreciably by a considerable change in air temperature for a given temperature excess. For instance, a change in air temperature from 80° to 40° F. will increase the heat transmission given in Table I by only 1.3 per cent.

Table I can also be used for calculating the free convection rate of transmission for various commercial shapes such as pipes and ducts. These calculations are simplified by the use of the factors in Tables II and III. Table II gives factors by which the values in Table I must be multiplied to obtain the convective transfer from various shapes whose characteristic dimensions are 24 inches or over, and Table III gives the factors to be used in conjunction with the factors in Table II for obtaining the free convection from Table I for pipes and ducts whose characteristic dimensions are less than 24 inches.

For example, the free convection transfer from a 3-inch o. d. horizontal cylinder for a temperature difference of 40° F. = 25.3 × 0.73 × 1.52 or 28.1 B. t. u. per square foot per hour. Similarly the free convection from the vertical side of a long horizontal duct 12 inches in height for the same temperature excess = 25.3 × 1.00 × 1.15 = 29.1 B. t. u. per square foot per hour.

Heat Transmission by Radiation

The heat transmission by radiation from a surface to the surrounding surfaces can be calculated from the well-known Stefan-Boltzmann formula:

$$q_r = 17.4 \times 10^{-10} \times p(T_1^4 - T_2^4) \text{ B. t. u./hr./sq. ft.} \quad (2)$$

TABLE I. HEAT TRANSMISSION BY FREE CONVECTION FOR LARGE VERTICAL SURFACES, IN B. T. U. PER SQUARE FOOT PER HOUR

	Temperature Difference between Body and Surrounding Air, ° F.												
	0	10	20	30	40	50	60	70	80	90	100	110	120
0° F.	0	4.4	11.1	18.3	25.3	33.3	41.4	49.5	57.6	67.7	78.8	89.9	101
1°	0.4	5.1	11.8	19.0	26.1	34.1	42.2	50.3	58.6	68.8	79.9	91.0	102
2°	0.9	5.7	12.5	19.7	26.9	34.9	43.0	51.2	59.6	69.9	81.0	92.1	103
3°	1.3	6.4	13.3	20.4	27.7	35.7	43.8	52.0	60.6	71.0	82.1	93.2	104
4°	1.8	7.1	14.0	21.1	28.5	36.5	44.6	52.8	61.6	72.1	83.2	94.3	105
5°	2.2	7.8	14.7	21.8	29.3	37.3	45.4	53.6	62.6	73.2	84.3	95.4	106
6°	2.6	8.4	15.4	22.5	30.1	38.2	46.3	54.5	63.7	74.4	85.5	96.6	107
7°	3.1	9.1	16.1	23.2	30.9	39.0	47.1	55.3	64.7	75.5	86.6	97.7	108
8°	3.5	9.8	16.9	23.9	31.7	39.8	47.9	56.1	65.7	76.6	87.7	98.8	109
9°	4.0	10.4	17.6	24.6	32.5	40.6	48.7	56.9	66.7	77.7	88.8	99.9	110

TABLE II. FREE CONVECTION FACTORS[a] FOR VARIOUS SHAPES

Horizontal cylinders 24 in. in diam. or over	0.73
Long vertical cylinders 24 in. in diam. or over	0.88
Vertical plates 24 in. in height or over	1.00
Horizontal plates warmer than air facing upward	1.28
Horizontal plates warmer than air facing downward	0.64
Horizontal plates cooler than air facing upward	0.64
Horizontal plates cooler than air facing downward	1.28

[a] These factors, multiplied by the values in Table I, give the convection transmission.

TABLE III. FREE CONVECTION FACTORS[a] FOR VARIOUS DIAMETER PIPES OR VARIOUS HEIGHT PLATES

Actual o. d., or height, in.	1	2	3	4	5	6	7	8
Factor	1.88	1.64	1.52	1.43	1.37	1.32	1.28	1.25
Actual o. d. or height, in.	9	10	12	14	16	18	20	22
Factor	1.22	1.19	1.15	1.11	1.09	1.06	1.04	1.02

[a] These factors, multiplied by the factors in Table II, multiplied by the values in Table I give the convection transmission.

TABLE IV. HEAT TRANSMISSION BY RADIATION[a] FOR BLACK-BODY CONDITIONS IN B. T. U. PER SQUARE FOOT PER HOUR

Temperature, ° F.						Temperature, ° F.												
−40	−30	−20	−10	0		0	10	20	30	40	50	60	70	80	90	100	110	120
54.2	59.3	65.2	71.4	78.0	0° F.	78.0	85.0	92.4	100	109	118	127	137	148	159	170	183	196
53.7	58.7	64.7	70.8	77.4	−1°+	78.7	85.7	93.3	101	110	119	128	138	149	160	171	184	197
53.2	58.2	64.1	70.1	76.7	−2°+	79.4	86.5	94.0	102	111	120	129	139	150	161	173	185	199
52.7	57.7	63.5	69.5	76.0	−3°+	80.1	87.2	94.8	103	112	121	130	140	151	162	174	187	200
52.2	57.2	62.9	68.9	75.4	−4°+	80.8	88.0	95.6	104	112	122	131	142	152	163	175	188	201
51.7	56.7	62.3	68.3	74.7	−5°+	81.5	88.7	96.4	105	113	123	132	143	153	164	176	189	203
51.2	56.2	61.7	67.7	74.0	−6°+	82.2	89.4	97.2	105	114	123	133	144	154	166	178	191	204
50.7	55.7	61.1	67.1	73.4	−7°+	82.9	90.2	98.0	106	115	124	134	145	155	167	179	192	206
50.2	55.2	60.5	66.4	72.7	−8°+	83.6	90.9	98.8	107	116	125	135	146	156	168	180	193	207
49.7	54.7	59.9	65.8	72.1	−9°+	84.3	91.7	99.6	108	117	126	136	147	157	169	182	195	209

[a] Example: Radiation from walls of room at 32° F. to surface at −25° F. for effective emissivity of 0.95 = (102 − 62.3) 0.95 = 37.7 B. t. u. per sq. ft. per hr.

where p = "effective" emissivity of surface and surroundings
T_1 = temp. of hotter surface, ° F. abs.
T_2 = temp. of cooler surface, ° F. abs.

The radiation under black-body conditions, or for an emissivity of 1.0, is given in Table IV for cold surfaces as low as −40° F. to warmer surfaces as high as 120° F.

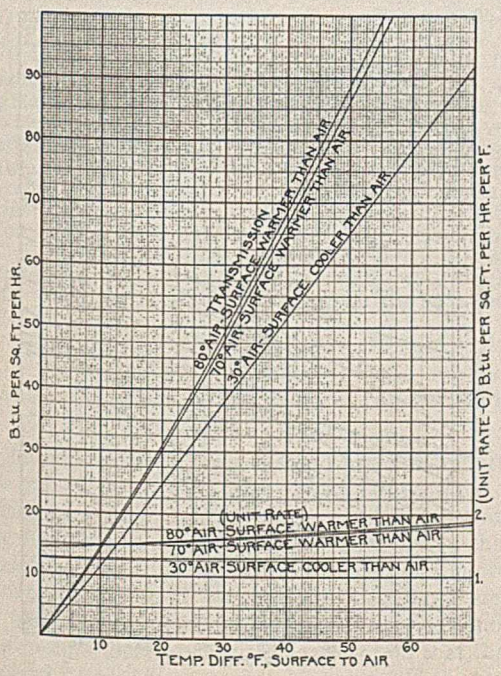

FIGURE 1. SURFACE HEAT TRANSMISSION FOR VERTICAL WALLS

The emissivities of a number of surfaces ordinarily encountered in engineering practice were determined by the writer and are shown in Table V. The effective emissivity as used in the Stefan-Boltzmann formula is a function of the individual emissivities, p_1 and p_2, of the radiating and receiving surfaces and also depends upon the extent and position of the surfaces. Hottel (*3*) has published formulas for a number of cases.

There are a great many instances in engineering practice where the individual emissivity of the radiating surface is the same as the effective emissivity in Equation 2. For instance, the heat transmitted by radiation from a small pipe in a large room is dependent only on the emissivity of the pipe, and the emissivity of the walls of the room have no practical effect on the actual rate of heat transmission. However, where large rectangular ducts almost completely fill a room or tunnel, the effective emissivity of the duct surface and surrounding walls is approximately that for infinite parallel planes or $p = \dfrac{1}{\dfrac{1}{p_1} + \dfrac{1}{p_2} - 1}$. The emissivities given in Table V should, therefore, be used with discretion when applying them to Table IV or the Stefan-Boltzmann equation.

Combined Heat Transmission by Radiation and Convection

To assist in the calculation of heat losses and surface temperature drops, the heat transfer by convection and radiation for an effective emissivity of 0.9 was calculated for temperature differences up to 70° F. for air temperatures of 30°, 70°, and 80° F. The curves are shown in Figure 1. The heat transmission curve for the 30° F. air temperature was calculated for the purpose of obtaining heat transmission from vertical surfaces cooler than the surrounding air. The 70° and

80° F. air temperature curves were calculated for vertical surfaces warmer than the surrounding air.

The appreciable difference between the heat transmission curves or the unit rate curves for the 30° and 70° F. air temperatures indicates the necessity of recognizing the considerably lower unit rate of heat transfer for subzero temperatures. This difference in heat transmission for the same temperature difference is due mainly to the dependence of radiation upon the fourth power of the absolute temperature. It is believed that most engineers either use a constant value for the unit rate of heat transmission or a heat transmission curve, such as the 70° F. air temperature curve, for practically all conditions in the air-conditioning and low-temperature heating fields. The curves given in Figure 1 cannot be used in determining the temperature drops or heat transmission for surfaces exposed to the direct rays of the sun. The surfaces of air ducts on roofs will often attain temperatures much higher than the surrounding air temperature. Surface temperatures of 165° F. have been obtained on roof decks at the Mellon Institute when exposed to the sun on summer days when the air temperature was approximately 100° F. The top of ducts exposed to the sun should, therefore, be more heavily insulated than the other surfaces in order to take care of the increased rate of heat transmission. Also a greater thickness of insulation should be applied to all surfaces of ducts exposed to the wind. The increased rate of heat transfer due to forced convection can be calculated from the formula:

$$q_{fc} = 1 + 0.225\,V$$

where q_{fc} = heat transfer by forced convection, B. t. u./sq. ft./hr./° F. temp. difference
V = velocity of wind, ft./sec.

This formula is approximately correct for large surfaces exposed to air currents at temperatures of approximately 70° to 80° F.

Table V. Emissivity Values for Various Surfaces

Surface	Temperature, ° F. 100	200	300	400
Bright galvanized iron	0.14	0.15	0.16	0.17
Badly tarnished galvanized iron	0.53	0.53	0.53	0.53
Very bright copper	0.07	0.07	0.07	0.11
Tarnished copper	0.43	0.44	0.46	0.48
Aluminum foil	0.06	0.06	0.07	..
Aluminum paint	0.28	0.28	0.28	..
Asbestos lumber (smooth side)	0.79	0.79	0.79	0.79
Hard wood (sanded)	0.90	0.90	..	..
Black Micarta	0.77	0.79	..	..
Black Feltex paper	0.87	0.89	..	..
Mica-surfaced asphalt roofing	0.76	0.76	..	..
Window glass	0.88	0.89	0.90	0.90
White canvas	0.88	0.88	0.89	..

Table VI. Thickness of Careycel to Prevent Sweating on Rectangular Ducts with Air inside Ducts at 50° F.

Per Cent Relative Humidity	Temp. Difference between Room and Air inside Duct, ° F. 20	25	30	35	40	45	50
60	0.11	0.18	0.24	0.30	0.37	0.43	0.49
70	0.24	0.33	0.42	0.51	0.60	0.69	0.77
80	0.53	0.66	0.79	0.92	1.05	1.18	1.31
90	1.29	1.54	1.79	2.03	2.28	2.52	2.76

Determination of Thickness of Insulation Required to Prevent Sweating

The thickness of insulation required to prevent sweating is that thickness which will raise the temperature of the outer surface of the insulation to a point slightly higher than the dew point for the corresponding air temperature and relative humidity. The difference in temperature between the air and the dew point for various humidities can be readily taken from a psychrometric chart. Figure 2 gives temperature differences between the air and dew point for air temperatures of 30° to 100° F. and for relative humidities of 50 to 90 per cent.

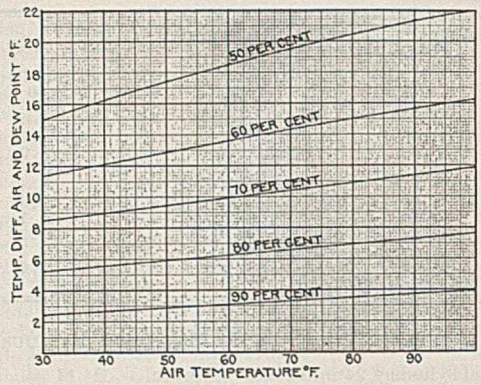

Figure 2. Temperature Difference between Air and Dew Points at Different Relative Humidities

Let T_1 = temp. of air in room
T_2 = temp. of surface of insulation
T_3 = temp. of cooler medium in duct or pipe
q = heat loss per sq. ft. of outer surface of insulation
C = unit rate of heat loss from surface of insulation,

$$= \frac{\text{total loss by radiation and convection}}{\text{temp. difference from surface of insulation to air in room}}$$

k = conductivity of insulation
L = thickness of insulation for flat surfaces

$r_2 \log_e \frac{r_2}{r_1} = L$ = equivalent thickness of insulation for cylindrical surfaces

where r_1 = radius of inner surface of insulation
r_2 = radius of outer surface of insulation

Then

$$q = \frac{T_1 - T_3}{\frac{L}{k} + \frac{1}{C}}$$

In any practical case T_1 and T_3 will be known, and, for any assumed value of relative humidity $(T_1 - T_2)$ can be obtained from Figure 2. C and q can be obtained from surface transmission or unit heat-loss curves, such as are shown in Figure 1 or from the radiation and convection tables for values of T_1 and T_2. Conductivity k can be obtained from curves such as are given in Figure 3 at a mean of temperatures T_2 and

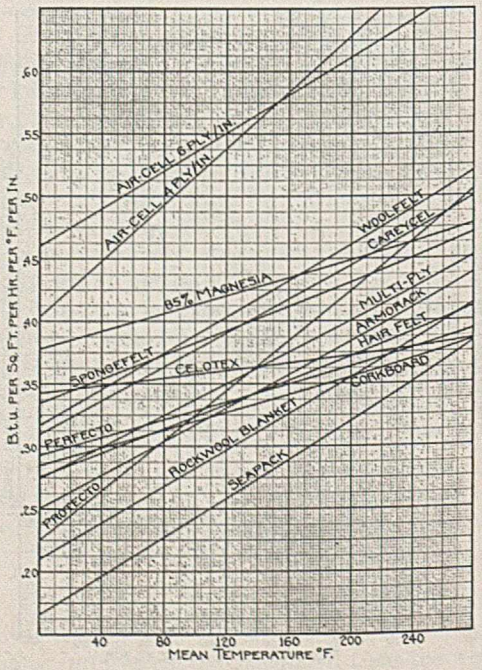

Figure 3. Thermal Conductivity of Insulating Materials

TABLE VII. THERMAL CONDUCTIVITY OF VARIOUS INSULATING MATERIALS

Material	Density	Conductivity at Mean Temp. of: 20° F.	100° F.	200° F.
	Lb./cu. ft.	*B. t. u./hr./sq. ft./° F./in.*		
Air-Cell, 4 ply per in. (corrugated asbestos)	13.0	0.425	0.516	0.630
Air-Cell, 6 ply per in. (corrugated asbestos)	17.7	0.475	0.536	0.612
Armorack (hair felt)	26.3	0.263	0.317	0.385
Aurora felt (rock wool)	22.9	0.263	0.300	0.344
Careycel (cellular asbestos paper)	17.8	0.324	0.379	0.446
Celotex (sugar cane fiber)	16.9	0.347	0.358	0.373
Cork covering	14.6	0.347	0.389	0.444
Corkboard	10.1	0.291	0.320	0.355
Flaxlinum (flax fiber)	14.3	0.262	0.329	0.413
Glass wool (loose)	1.5	0.260	0.375	0.522
	4.0	0.215	0.287	0.380
	6.0	0.196	0.262	0.346
Hair felt	8.2	0.284	0.323	0.372
	11.4	0.257	0.305	0.359
	12.8	0.280	0.314	0.354
Insulate board (wood pulp)	15.2	0.282	0.317	0.360
Kork-O-Board (peat moss)	14.9	0.315	0.351	0.398
Magnesia, 85%	16.9	0.385	0.413	0.447
Multi-ply (laminated asbestos paper)	25.5	0.286	0.337	0.400
Sponge felt (laminated asbestos paper)	31.1	0.345	0.385	0.432
Perfecto covering (wool felt)	23.8	0.298	0.327	0.363
Protecto covering (hair felt and wool felt)	16.7	0.244	0.323	0.424
Rocktex wool (loose rock wool)	4.0	0.180	0.269	0.380
	6.0	0.190	0.274	0.380
	8.0	0.205	0.273	0.358
	10.0	0.190	0.255	0.342
	12.0	0.220	0.271	0.337
Rocktex blanket (rock wool felted between wire mesh)	16.6	0.226	0.283	0.356
Rubber board (expanded)	5.7	0.230	0.256	0.289
Seapack board (ceiba pod fiber)	5.9	0.180	0.244	0.321
Weatherwood board (felted wood fiber)	18.1	0.320	0.360	0.409
Weatherwood tile (felted wood fiber)	16.2	0.285	0.337	0.403
Wool felt covering (smooth felt)	23.0	0.330	0.390	0.462

T_3. The thickness of insulation required to prevent sweating will then be slightly greater than the value obtained by the equation:

$$L = k\left(\frac{T_1 - T_3}{q} - \frac{1}{C}\right)$$

The process involved is illustrated by the following example:

Determine the thickness of Careycel insulation required to prevent sweating on a large rectangular air duct, with the air inside the duct at 50° F. and the temperature of the room at 70° F. dry bulb, with a relative humidity of 80 per cent, the effective emissivity of the surfaces being 0.9. From Figure 2, $T_1 - T_2 = 6.6°$ or $T_2 = 70 - 6.6 = 63.4°$ F.

Table II shows that the heat transfer by convection from a vertical surface is roughly midway between that from a horizontal surface facing upward and a horizontal surface facing downward; so for this example we will assume that the heat transfer by convection takes place at a rate equal to that of a large vertical surface, or from Table I the convected loss for a temperature difference of 6.6° F. = 2.9 B. t. u. per square foot per hour. From Table IV the radiant heat transfer = 0.9 (137.0 − 130.4) = 6.0 B. t. u., or $q = 2.90 + 6.0 = 8.90$ B. t. u. per square foot per hour. $C = (8.9/6.6) = 1.35$. The conductivity of Careycel at a mean temperature of (70 + 63.4)/2 or 66.7° F. from Figure 3 is 0.355. Substituting the above values in the equation:

$$L = 0.355\left(\frac{20}{8.9} - \frac{1}{1.35}\right) = 0.536 \text{ in.}$$

The thickness required is, therefore, slightly greater than 0.536 inch.

For cylindrical surfaces, this method gives the equivalent thickness of insulation, or $r_2 \log_e (r_2/r_1)$. The required thickness of insulation can readily be determined by the method given for flat surfaces and the use of Figure 4. In this case it is necessary to assume a thickness of insulation in order to determine the surface heat transfer rate which is different for pipes of various diameters. Assuming the same conditions as for the example illustrated, with the exception that the duct is a standard 3-inch pipe carrying brine at 30° F., we have the following:

Assuming first that the thickness of insulation required is 2 inches, then from Tables I to IV, the total rate of transfer by radiation and convection is 8.6 B. t. u., $C = (8.6/6.6) = 1.30$, and

$$L = 0.341\left(\frac{70 - 30}{8.6} - \frac{1}{1.30}\right) = 1.32$$

From Figure 4 for a 3-inch pipe and $r_2 \log_e (r_2/r_1)$ equal to 1.32, the thickness required is 1.05 inches.

This value will be found to be very close to the actual thickness required, since the free convection rate is not changed much for a variation in diameter of 7.5 to 5.5. Recalculating for a 1-inch thickness, we have from Tables I to IV a total rate of heat transfer by radiation and convection of 8.8 B. t. u., and

$$C = \frac{8.8}{6.6} = 1.33;\ L = 0.341\left(\frac{70 - 30}{8.8} - \frac{1}{1.33}\right) = 1.29$$

From Figure 4 the thickness corresponding to an $r_2 \log_e (r_2/r_1)$ value of 1.29 = 1.04 inches. The thickness of insulation required will, therefore, be slightly greater than 1.04 inches. This value is only 0.01 inch less than the value obtained by the first calculation.

In view of the increasing importance of air-conditioning in industry and the heating and ventilating field, Table VI gives the thickness of Careycel insulation required to prevent sweating for air ducts carrying air at 50° F. with room temperatures of 70° to 100° F. and relative humidities of 60 to 90 per cent. An emissivity of 0.9 was used in these calculations.

Conductivity of Commercial Insulations

Table VII gives the thermal conductivity of a number of commercial insulations. These values were obtained at

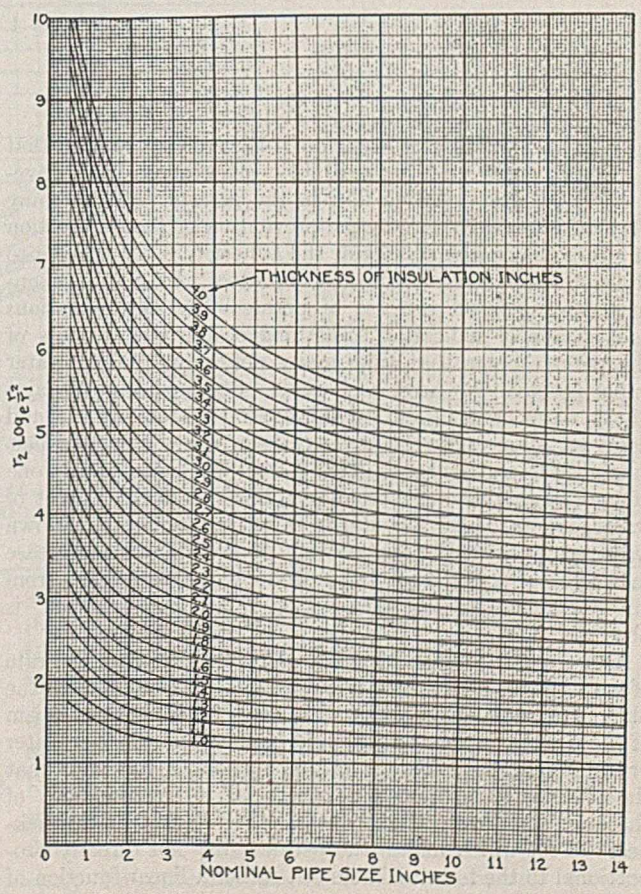

FIGURE 4. EQUIVALENT THICKNESS OF INSULATION

Mellon Institute and are the average results of a number of tests on each type of material. For convenience in calculating heat losses for various mean temperature conditions, the conductivity of a few of these insulations is given in Figure 3. The thickness of insulation required to prevent sweating on the above air duct for any of the insulations whose conductivities are included will be found to be directly proportional to conductivities of the insulations chosen and the insulation used in calculating the table.

In conclusion, the author wishes to express his thanks to R. W. Ortmiller who determined the conductivities of the various insulations.

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Water Impedance of Nitrocellulose Films

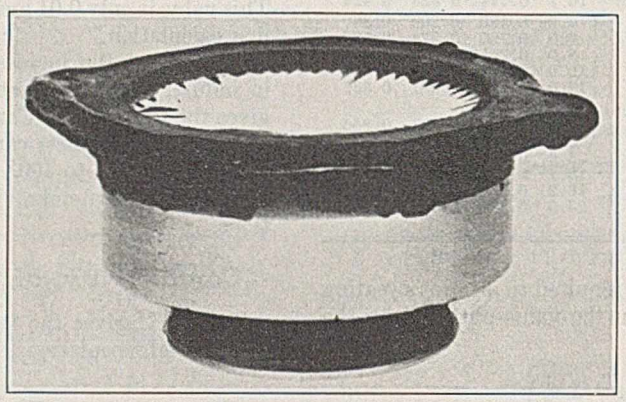

FIGURE 1. PREPARED CUP

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FOR a long time it has been recognized that the permeability of a given protective-coating film to the passage of water may play an important part in the prevention of the destruction of either the coated surface or the adhesion of the coating to the material which it is expected to protect. In 1913 Muckenfuss (*6*) suggested the use of permeability determinations as a means of indicating something of the effectiveness of the paint. Since that time many determinations of water vapor permeability have been made. Stripped films of paint (*3*, *8*), paint on thin and on thick wood sections (*1*, *8*), and paint on other supports (*3*) have been tested for their permeability to water vapor. This testing has been done by one of two ways. In one method the decrease in the weight of water, separated by the film from an atmosphere of known water vapor content, is measured. In the other, the increase in weight of a desiccant, separated by the paint film from an atmosphere of constant water vapor concentration, is observed (*3*, *6*, *8*).

There seems to have been no attempt to measure the rate of water penetration when liquid water is in contact with the film. However, Muckenfuss (*6*) states that the mechanism of the passage of the water should be the same whether water or water vapor is in contact. Other authors (*2*) have said that the impedance is directly proportional to the thickness of the film. However, it may be that there is an "extra thickness" effect which makes the permeability not directly proportional to the film thickness but rather a linear function of it (*7*).

Determination of Water Impedance

A series of experiments was carried out in which the impedance to water was determined for several different clear nitrocellulose lacquer films.

The material was a mixture of 77 per cent of $^1/_2$ second nitrocellulose and 23 per cent of 15–20 second nitrocellulose. The proper amount of resin and plasticizer, together with the required quantity of commercial lacquer thinner, was mixed with the nitrocellulose to give a lacquer of spraying consistency. Different plasticizers, resins, and plasticizer-resin combinations were used in the clear lacquers (Table I).

In order to use thin films, the lacquers were supported on plain Cellophane. A coating of the required thickness was sprayed on the Cellophane, which was in turn supported on a metal panel. This method did not give absolutely uniform films, but it had the advantages of convenience of formation and strength for handling. The thickness of the film was measured after the impedance determination. A thickness gage which read directly in 0.0001 inch (0.00025 cm.) was used. The average thickness, 0.0008 inch (0.0020 cm.), of the Cellophane was subtracted from the observed total thickness in order to obtain the thickness of the lacquer film.

In order to have a known area of water in contact with the lacquer film, a rubber ring (fruit-jar ring) was sealed to the lacquer side of the piece of the coated Cellophane. This combination was then inverted, and a 6-cm. filter paper was placed on the uncoated side. On this were piled about 8 grams of anhydrous calcium chloride. A small aluminum cup, 6.5 cm. in diameter and 2.5 cm. deep, was then inverted over the calcium chloride and sealed to the Cellophane. The film was trimmed slightly larger than the ring, and the whole edge was coated with the wax used for sealing so that no leakage could take place through the film edge. The wax used was made up of two parts of beeswax

and one part of rosin. It was applied at about 110° C. Figure 1 shows a prepared cup.

The prepared cups, after standing in a desiccator for about 2 hours and being weighed, were supported in a can which had a tight-fitting cover. Water was placed in the bottom of the can, and each ring was filled with distilled water. The whole was kept covered in a constant-temperature oven at 40° ± 1° C. for about 24 hours. At the end of this time the cups were removed. The water was poured off, and the surfaces of the cups and films were carefully dried with a filter paper and a soft cloth. The cups were allowed to stand overnight in a desiccator and were then weighed to determine the amount of water which passed through the film.

The area of the surface under water was computed from the average of six observations of the diameter of the ring as it lay in position on the film. This figure with the increase in weight was used in determining the impedance for a given film thickness.

Impedance to water may be thought of as the resistance offered by a film to the passage of water through it. It may be expressed as follows:

$$I = At/w$$

where I = impedance
A = area of film surface, sq. cm.
t = time of experiment, hours
w = gain in weight, mg.

That is, as used here the water impedance of a paint film is the number of hours required for the passage of 1 mg. of water through a film area of 1 sq. cm.

A number of different film combinations were tried as shown in Table I, which also gives the impedances obtained and the film thicknesses used.

In every case the result given is the average of at least two determinations. The largest differences from the average were not over ±5 per cent, and in general the differences were much less. The results were quite reproducible. Figure 2 shows the results graphically. Films 38 and 59 were made at different times and from different lacquers, but the results fall practically on the same line. The curves show the relationship between impedance and thickness, and are in every case practically straight lines. Probably the variations are due to the unavoidable inequalities in thickness of the films produced by spraying. These curves do not pass through the origin since not only the lacquer film but also the Cellophane was present. However, they all seem to have a common source as would be expected, since Cellophane of the same thickness and films of the same general type were used in each case. The extra thickness effect which has been reported (*7*) may be partly responsible for the fact that the curves do not pass through the origin. The determination of the impermeability of the Cellophane itself could not be made under these conditions, for, when wet with water, it gave an abnormal value for the impedance; in other words, the impedance of Cellophane when coated is different from what it is uncoated.

Table I. Impedance of Various Nitrocellulose Films to Liquid Water at 40° C.

Film No.	Thickness Inch	Thickness Cm.	Impedance Hours	Film Solids Compn.	Parts
4	0.0018	0.0045	1.6	Nitrocellulose	10.0
	0.0028	0.0070	2.4	Dammar	2.5
	0.0039	0.0098	3.2		
20	0.0015	0.0038	0.7		
	0.0023	0.0058	1.0	Nitrocellulose	10.0
	0.0028	0.0070	1.2	Dibutyl phthalate	5.5
	0.0032	0.0080	1.4		
21	0.0015	0.0038	1.0	Nitrocellulose	10.0
	0.0022	0.0055	1.5	Dammar	2.5
	0.0031	0.0078	2.0	Dibutyl phthalate	5.5
	0.0041	0.0082	2.3		
37	0.0021	0.0052	1.0	Nitrocellulose	10.0
	0.0027	0.0068	1.2	Alkyd resin	5.0
	0.0029	0.0072	1.3	Dibutyl phthalate	3.3
	0.0035	0.0088	1.6	Castor oil	2.2
38	0.0018	0.0045	1.5	Nitrocellulose	10.0
	0.0026	0.0065	2.0	Dammar	2.5
	0.0028	0.0070	2.2	Dibutyl phthalate	3.3
	0.0034	0.0085	2.7	Castor oil	2.2
47	0.0016	0.0040	1.0		
	0.0027	0.0068	1.6	Nitrocellulose	10.0
	0.0033	0.0082	1.8	Alkyd resin	2.5
	0.0037	0.0092	2.0		
50	0.0011	0.0028	0.7	Nitrocellulose	10.0
	0.0024	0.0060	1.3	Alkyd resin	2.5
	0.0031	0.0078	1.6	Dibutyl phthalate	5.5
	0.0036	0.0090	1.9		
59	0.0011	0.0028	1.0	Nitrocellulose	10.0
	0.0021	0.0052	1.7	Dammar	2.5
	0.0029	0.0072	2.3	Dibutyl phthalate	3.3
				Castor oil	2.2

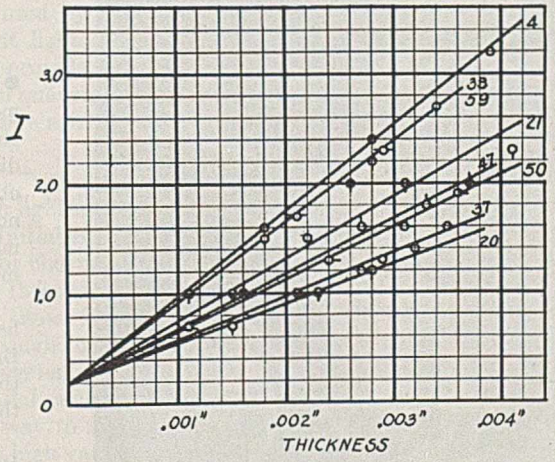

Figure 2. Relation between Impedance and Thickness

Interpretation of Results

These results indicate that the impedance of lacquer films to liquid water is a linear function of, and may be directly proportional to, the thickness. If, as has been reported (*6*), the mechanism of the passage of moisture is probably the same whether liquid water or water vapor is used, this behavior may be taken as indicat-

This study shows that, when liquid water is in actual contact with a paint or enamel film, the impedance to water is a linear function of the film thickness. Since it has been reported that the mechanism of the passage of water through a film is probably independent of whether the water is in contact with the film as vapor or liquid, probably the impedance to water vapor is also a linear function of the film thickness. If either a stripped film or a supported film is used, the determination of the impedance at two different thicknesses enables the impedance at any other thickness to be calculated. Or if the residual impedance is determined from a number of experiments, the impedance at any thickness may be calculated if the impedance at one thickness is determined.

ing that the impedance to water vapor has also a similar relation to the thickness of the film.

No comparison between the impedance of the films on the Cellophane and stripped films of the same material and thickness has been made. However, it is probable that the impedance would be slightly different in the two cases, since in the case of paint films a slight difference has been noted (*4*). This difference may be connected with the so-called valve effect. That is, it has been noted (*5*) that the impedance to water vapor of certain paint and nitrocellulose films shows a slight difference, depending on whether the top of the film or the side originally on the casting plate is exposed to the region of high humidity.

If the stripped film or the film supported on some uniform material, such as Cellophane, is used, then the determination of the impedance at two different film thicknesses would enable its calculation to be made for any other thickness. In this case the relation between impedance and thickness may be expressed:

$$I - I_1 = \frac{I_2 - I_1}{t_2 - t_1}(t - t_1)$$

where I_1 and I_2 are the impedances as determined at the respective thicknesses, t_1 and t_2.

If a number of determinations at several thicknesses are made so that the residual impedance can be determined, as in the present experiments, then the impedance for any film at any thickness may be calculated from one impedance determination. In this case the relationship may be expressed as follows:

$$I = a + \frac{I_1 - a}{t_1}$$

where I_1 and t_1 are the impedance and thickness of the film, as determined experimentally, and a is the residual impedance as determined from the other experiments.

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BRAND AND THE DISCOVERY OF PHOSPHORUS

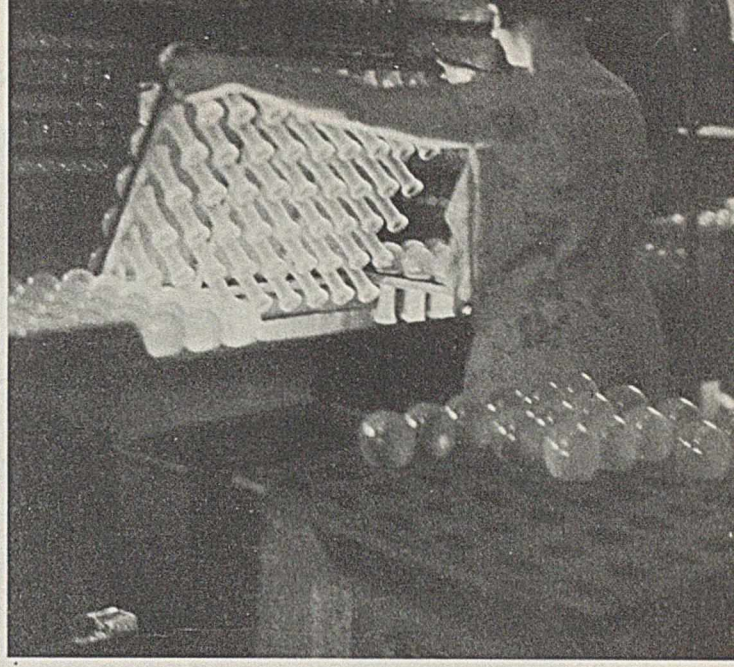
● In 1669, Brand, a Hamburg merchant, experimenting in chemistry, undertook the dry distillation of evaporated urine, obtaining phosphorus, which had not been known previously. For many years this was the sole method of preparing phosphorus.

A modern advertising artist has extended his conception of Brand's discovery as signifying the basis of the manufacture of the modern match.

Through the courtesy of E. Regensburg & Sons we are able to present here as No. 67 in the Berolzheimer series of Alchemical and Historical Reproductions a photograph made directly from the artist's original pen-and-ink drawing.

A detailed list of the first sixty reproductions, together with full particulars for obtaining photographic copies of the originals, appeared in our issue for January, 1936, page 129, where also will be found Reproduction No. 61. Reproduction No. 62 appears on page 241 of our February issue, No. 63 on page 280 of March, No. 64 on page 413 of April, No. 65 on page 572 of May, and No. 66 on page 677 of June.

AUTOMATIC GLASS BLOWING



Courtesy, Corning Glass Works
FROSTED BULBS IN A HAMPER RECEIVING PRELIMINARY INSPECTION

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GLASS blowing is one of the most ancient arts and, until recent years, has depended solely upon trained human lungs to supply the power for forming and shaping molten glass into useful articles. Lately the enormous demand for large numbers of thin glass bulbs for incandescent electric lamps and radio vacuum tubes has required the development of swifter production methods to meet mounting requirements of the electrical industry. It is only fitting that the organization which supplied the glass bulbs used by Edison in his earliest experiments with incandescent lights—the Corning Glass Works—should be the one to provide the means for making them accurately and cheaply in quantities beyond the most sanguine expectations of a few years ago.

History

The history of incandescent electric lighting is one of the most romantic of modern industry. Initial experiments with platinum filaments led to the search for cheaper materials to make the lamp practicable. Carbon threads made by carbonizing organic matter improved those first lights by cheapening them and were just good enough to encourage the long search for better filaments. Tungsten, finally selected as the nearest to an ideal filament material, could not be drawn to wires—and hence the search for a way to make tungsten ductile which led to final success. The high vacuum essential to the carbon filament lights required that expensive platinum wires be sealed in the glass to carry through the current. The high cost of platinum caused the development of composite wires of nickel-iron alloy and copper to serve this purpose. The blackening of bulbs from the volatilization of tungsten in the high vacuum was prevented by the subsequent adoption of inert gases—argon and nitrogen. The demand for artificial lighting grew as its cost was reduced, cheapened by a series of developments step by step. Continuing search for better methods of construction of the lamps themselves improved their service life and opened new fields of utility. Finally, machines have been perfected to perform the endlessly repetitive operations required to supply lamps by the millions from parts made with utter uniformity by automatic machines.

In this chain of development no one step can be considered more important than another in producing the ultimate result since without all of them the present high development of artificial lighting would never have been reached. The final fabrication of the huge numbers of lamps daily required would be impossible without the use of automatic machines, among which is the automatic bulb-blowing machine. Not only does this machine, intricate and accurate in operation almost beyond belief, supply the lamp makers with the veritable flood of bulbs they require, but it also makes them with a uniformity vital to the usefulness of other machines which assemble the completed lamps in the glass bulbs.

Fifty-eight years ago the first glass bulb for the first incandescent electric light was blown for Edison by the Corning Glass Works, in contrast to the bulbs previously made by hand over the blast lamp. The growth of the industry reached the point twenty years ago of requiring some 150 million lamps annually, and at that time automatic blowing of the glass bulbs was first undertaken. Subsequently, the improvement of machines for this purpose and the development of others for fabricating lamps has so cheapened the product that the demand for incandescent lamps has reached the enormous total of some 600 million per year. The cost of lamps during the two decades has dropped in almost precise inverse ratio with the number made and sold. The cost of light produced by them has been similarly reduced as efficiency has been raised.

To understand the value of the automatic blowing of bulbs, it is necessary to review older methods as a basis of comparison. Glass in the modern industry is by no means the single simple substance we are accustomed to consider. In a modern glass plant as many as three hundred and fifty-seven varieties of this useful material are employed for an even greater number of applications. Each of these varieties possesses qualities slightly different from others, and each must be handled in a manner which allows for its peculiarities. The most common are lime-soda glasses consumed in large daily tonnages in contrast to some of the special glasses used in quantities reaching, at most, a few hundred pounds a year. The amorphous nature of glass permits of an almost infinite variation of composition by small increments, and hence required properties in finished articles can be produced with great exactness. We must clearly differentiate between the blowing of a bottle, which is rather definitely a casting operation with air pressure used to create a hollow, and the blowing of a thin bulb whose shape and size are formed primarily by the air blast. The glasses used for the two

purposes are different and the handling of them must take this, as well as the differences in product, into account. Bottles have long been blown on machines, but they have not been required to operate with the precision of bulb blowing, a problem so different in degree as to be practically different in kind.

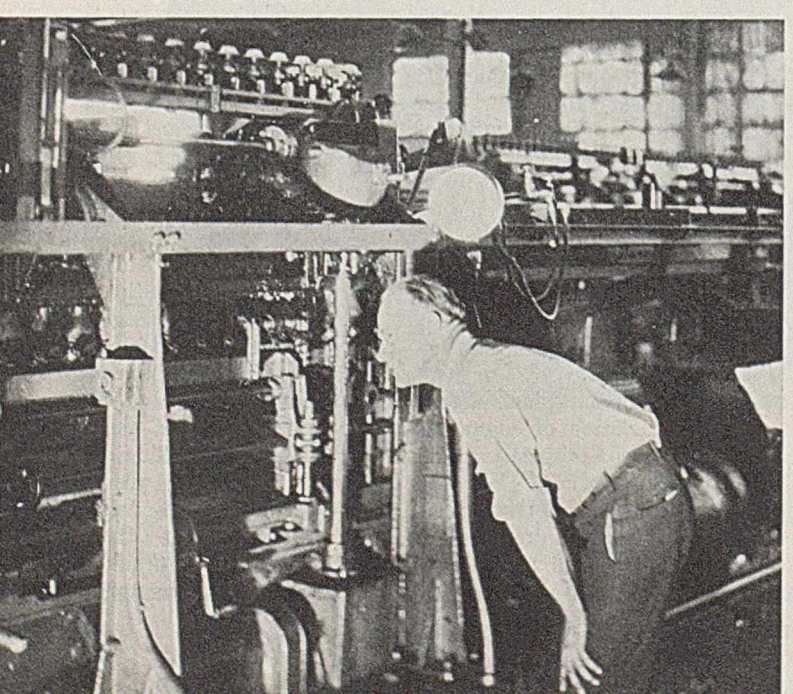
Manual Glass Blowing

Manual methods of blowing bulbs are still employed to make special shapes in great variety and innumerable products needed in quantities too small to justify the use of automatic machines. This will probably always be true since the setting up and adjustment of machines is both too tedious and too expensive to be justified by production of articles required in quantities less than millions.

The manual method may be outlined somewhat as follows: Glass is melted in a tank to which are added the necessary constituents in proper proportions together with a relatively large amount of scrap glass of the same composition, called "cullet." The proportion of cullet to new mix is variable, but it is usual to add as much as two parts of cullet to one part of new material. The tank heated by gas flames from the top through a regenerative reverberatory system is divided into two principal parts, the melting zone and the refining zone. In the first zone the mixture is melted, and the melt flows under a bridge wall, which skims off unmelted material, into the refining zone. Here the process of glass making is completed while the molten mixture is held at high temperature for a long enough period to reach complete equilibrium.

In blowing glass, teams of two workmen usually operate together. A helper gathers a mass of glass of appropriate size, from an opening in the tank, on the end of an iron blowing tube about 6 feet long and 0.5 inch in diameter, and hands it to the glass blower. That individual, by a series of dexterous whirling motions interspersed with puffs of air blown into the open end of the tube, gives the viscous glass an initial shape and at the proper instant places the partly formed mass into a two-part iron mold to whose shape it is accurately formed by further judicious puffings and whirlings. By the time this operation has been completed, the glass is hard enough to be broken from the tube, the waste is removed to the cullet pile to go back for remelting, and the tube is reloaded with new glass for a repetition of the operation.

Checking the Elongation of Glass Blanks
Courtesy, Corning Glass Works



In this way a team of two men is able to make an average of eleven hundred glass bulbs for electric lights per working day.

Obviously, the possibility of human error looms large in such an operation in spite of its continuing repetition. An error in judgment, however slight, on the part of either the blower or the helper will be evident at once in articles which must be made with the extreme accuracy of dimension required in such products as electric light bulbs and the vacuum tubes of radio. This, more even than the need for cheaper production, was the ruling factor in developing automatic machines to do this type of work. Some of the errors of manual production can be offset during the subsequent annealing and finishing operations, but dimensions once established in the blowing cannot be economically changed later.

Mechanical Glass Blowing

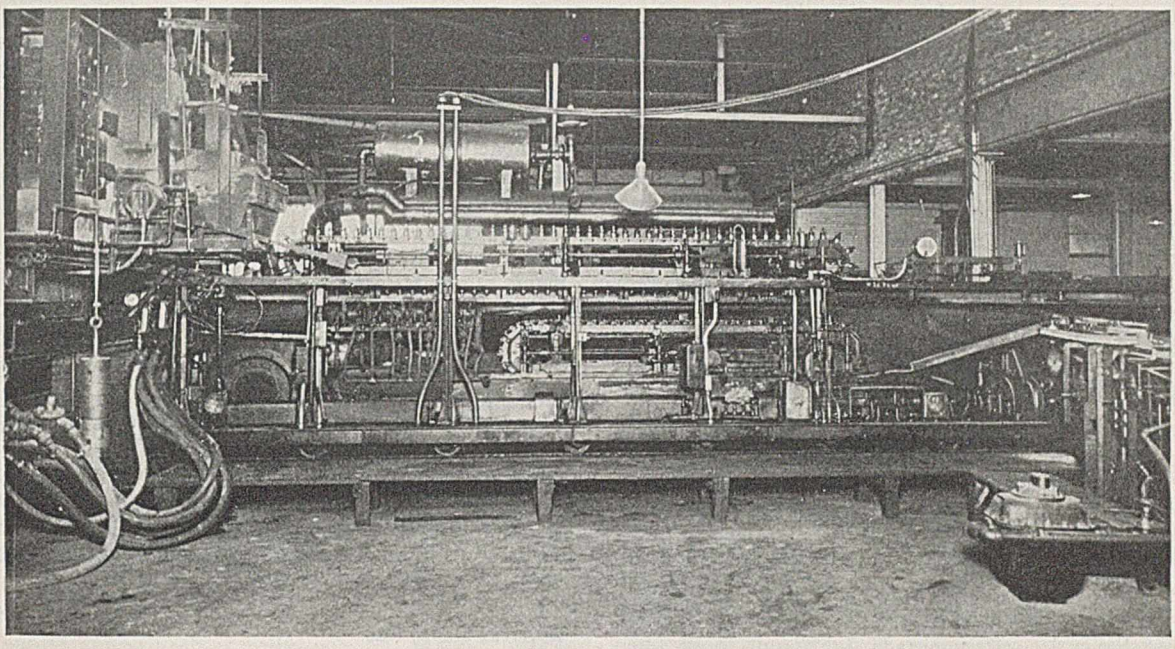
In a very remarkable way, the mechanical blowing of bulbs follows closely the older manual art. We are astonished in watching the machine in operation to note the closeness of the parallel despite the swiftness of each operation. We are impressed, too, with the exactness of control of the various parts of the machine which must operate in absolute unison and of the properties of the glass fed to it upon which depend the ability of the machine to function. The earliest automatic machine was able to produce fifty bulbs per minute, but subsequent development of both the type of machine and the glass have increased this speed nearly tenfold. Now one automatic machine produces in 3 minutes more bulbs of better finish than two men can turn out in a full day of labor.

The machine itself is intricate in the extreme. Each step of the hand operator is duplicated with the greatest precision as each mass of molten glass progresses through the cycle of operations. Exact repetition of the cycle occurs for each bulb blown so that the output will meet continuously the most demanding specifications as to dimension set up by the lamp industry to ensure optimum operation on its lamp making machines which consume glass bulbs by the millions.

The first essential of the operation is that the machine be continuously supplied with glass of uniform characteristics both as to composition and temperature. The immense glass melting tank in which this is produced looms large in the plant. To it are fed continuously and automatically some 125 tons of raw material each day. About 2 tons of cullet are fed with each ton of raw mix, and the whole is melted and refined to a uniform semi-fluid mass by the continuous play of flames of natural gas on top of the charge in the tank. The heating of the tank is regenerative. Fresh air is heated over a brick checkerwork before it is mixed with gas and burned over the glass in the tank. The hot flue gas is passed out over a second brick checkerwork which is thus heated. At 20-minute intervals the direction of flow is reversed so that at all times the incoming air is fed to the flame at a high temperature. Necessarily the fire is closely controlled to ensure uniform temperature.

The glass melted in the first zone of the tank passes under a bridge wall into the refining zone where time is allowed for diffusion and stabilization to make the mass completely uniform. From this refining zone the glass flows again under a skimming wall into a forehearth from which it pours in a continuous stream through a round opening onto the gathering rolls. The essential point here is the maintenance of a uniform stream of glass of uniform properties in every respect, since even slight variations of temperature, composition, or viscosity seriously affect the subsequent operations.

Molten glass streams from the forehearth between the gather rolls. One of the latter is a flat-faced cylindrical



Courtesy, Corning Glass Works

MACHINE FOR CONTINUOUS BLOWING OF ELECTRIC LIGHT BULBS

roll, and the other has indentations at intervals on its cylindrical face. These two rolls rotate toward each other and press the glass streaming down between them into a continuous ribbon with masses of the correct size for the machine formed at close intervals along its length. The ribbon of soft glass drops onto a horizontally moving series of steel orifice plates so adjusted as to speed and spacing that each mass of glass falls directly over an orifice. The orifices in these plates are accurately sized to the piece that is to be blown, and the continuous procession of plates moves swiftly through the machine.

The weight of the glass itself begins the shaping operation, and, as the plate carrying it proceeds, a nozzle through which the air blast passes is dropped on each mass. The nozzles form a reasonably good seal with the soft glass on one end, and on the other they are shaped to fit a slot in a blower box through which air is admitted to them. As the nozzle progresses along this box, air is blown at intervals under very slight pressure (not more that 2 inches water pressure) into its open end. These blasts of air are separately regulated, and the openings through which they are blown are so spaced along the machine that exactly the proper effect is obtained. Indeed the blowing is scheduled to follow almost exactly the blasts given the glass by a human glass blower.

The first puff of air is delivered to the molten glass while it hangs free from the orifice plate and this tends to stretch it into an elongated sack. At this instant the two parts of the mold which will form the outside of the bulb are brought together around the sack of glass, and the complete mold is set in rapid rotation around its vertical axis as more and more air is blown into the inside of the developing bulb. The two parts of the mold are cast iron with suitable vent holes through their surfaces to permit the escape of steam formed by contact between the hot glass and the water with which the molds are cooled. The molds are lined with a paste of cork dust and linseed oil which is burned in place in a furnace and finally dusted with soapstone to smooth the surface. As a final step in the preparation of the molds, bulbs are blown in them manually under conditions practically identical with those in the machine to ensure the proper surface for the job they are to do. The blowing and molding of the piece continue throughout the 25-foot length of the machine and at the end of that distance, traversed in 10 or 12 seconds by each unit in the continuous chain, the glass has been formed and cooled to the point of allowing it to be removed from the mold.

The breaking up of the chain of operations begins with the lifting of the nozzle from the glass and the opening and separation of the two parts of the mold. Immediately after these two events occur, a hammer strikes the bulb a smart blow at a point below the orifice plate, breaking the bulb off and applying enough force to throw it into a hand-shaped, asbestos-lined member ready to receive it. The ribbon of glass, with the excess unused in forming the bulb, is still slightly plastic and is lifted continuously from the procession of orifice plates by a bevel-edged rotating disk which wedges itself between the plates and the ribbon. The ribbon continues straight ahead while molds, orifice plates, and nozzles are returned on their respective tracks to start the operation over again. As these parts return to the point of beginning, they are cooled by sprays of water to bring their temperature to the proper point. The remainder of the ribbon, continuing straight ahead from the machine, is drenched with water which cracks it into small pieces, and these pieces are dropped into the cullet bins to be dried for inclusion in a subsequent batch of raw material for the tank.

The receiving members are on the circumference of a horizontally rotating wheel. As this wheel revolves (at a speed regulated to catch each bulb as it is broken off), the bulbs on it cool partially and finally are dropped off nine at a time onto a moving belt which carries them through the annealing lehr. The object of gathering the bulbs into groups of nine in this way is to spread the output of the blowing machine evenly across the width of the wide conveyor and thus to increase the efficiency of annealing as well as the capacity of the annealing oven. From the annealing oven the completed bulbs are carried on a continuous conveyor past inspectors, who remove any containing flaws, and then either to the frosting machines or to the packers.

The total time consumed in the operation from the moment the molten glass flows from the forehearth until the bulbs reach the inspectors is less than 8 minutes; only a few seconds are necessary for the actual blowing operation. The average

time consumed in the glass tank is considerably greater, about 48 hours being required for freshly introduced raw material to find its way to the forehearth outlet.

Inspection

Inspection is provided to remove any out-of-shape or offsize bulbs, as well as those containing bubbles, stones (unmelted mix), or strains as revealed by examination under polarized light. The character of the rejects is the governing factor in controlling the melting operation and the speed of the machine, since the cycle moves too swiftly to be followed in any other way.

The inside frosting of the completed bulbs is accomplished by spraying them in racks of one hundred with hydrofluoric acid solutions in three doses—the concentration of the acid used in each cycle being successively weaker—and finally washing them clean with water. By using several successive acid washes, the weaknesses set up in the thin glass by a single treatment are eliminated and the pleasing effect of diffusing the light from the filament is secured.

After final inspection the glass bulbs are ready for the lamp industry, whose automatic machines assemble the essential parts of lamps, vacuum tubes, or photoelectric cells into the bulbs.

Because numerous sizes and styles of bulbs are required in quantities large enough to justify manufacture on an automatic blowing machine, its working parts are assembled on what is virtually a railroad car running on light rails. Several such assemblies are at all times ready to be pushed up to the forehearth of the glass tank and set in motion. The assembly of the machine or its reassembly to make bulbs of different sizes or styles is a tedious operation requiring several men over a period of some hours to put in place the required molds and orifice plates and to adjust the air blasts to fit the requirements of a particular product. However, this assembling job is done on a spare machine, and, when it is ready for use, the shift from one machine in operation to another producing a different bulb is accomplished with barely half an hour's interruption of production. Ordinarily two machines taking glass from two different forehearths of the same tank are kept running. Each of them turns out half a million completed bulbs in a 24-hour day. The glass tank must be kept hot continuously since the congealing of the mass of glass in it is a major disaster, but operation of the blowing machines is adjusted to production and is continued from 5 to 7 days per week.

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GASOLINES AND GASOLINE FRACTIONS

SUSCEPTIBILITY TO TETRAETHYLLEAD AND ANILINE

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IN A PREVIOUS paper (*9*) the high octane number and high tetraethyllead susceptibility of certain fractions obtained in the efficient fractionation of straight-run gasolines were mentioned. Studies on the lead susceptibility of various types of gasolines were made by several investigators (*1, 3, 4, 5*); Campbell and co-workers (*2*) studied the lead susceptibility of pure compounds. Natural and straight-run gasolines are more responsive to tetraethyllead than other types of gasolines. However, the higher the octane number of the gasoline the smaller the increase in octane number per cubic centimeter of tetraethyllead added. This behavior, together with the comparatively poor lead susceptibility of cracked and polymer gasolines renders the preparation of stable fuels with an octane number of 90 or higher a difficult matter.

Campbell showed that there are hydrocarbons with not only a high octane number but also a high lead susceptibility. Some of these compounds are known to be in petroleum (*6, 8*). In view of the latter results and the work done in this laboratory on the chemical composition of the gasolines reported here, the high values obtained for octane number and lead susceptibility of certain fractions of these gasolines are not entirely unexpected.

Experimental Procedure

The gasolines were all fractionated in a column of seventy-five theoretical plates at a reflux ratio of 40 to 1. That is, the entire gasoline was fractionated by batch operation to obtain approximately two hundred consecutive fractions. This careful and efficient fractionation was done as part of a program on the composition of gasolines. The charge was 45 gallons. The properties of the original gasolines are given in Table I. Blends of the fractions obtained from each distillation were made by combining successive fractions. Only those fractions of high octane number and suspected high responsiveness to tetraethyllead were blended.

The octane numbers were obtained by a series 30B Ethyl knock testing engine operating at 345° F. jacket temperature and at a motor speed of 900 r. p. m. (procedure 345) (*9*). The knock ratings of secondary reference fuels C-9 and A-4 were obtained on this engine by comparing with the primary standards. These values and certain others given

in Table II indicate the relationship between the engine used and the C. F. R. engine operating under the motor method.

TABLE I. PROPERTIES OF ORIGINAL GASOLINES

Gasoline	A. P. I. Gravity	A. S. T. M. Engler Distn. Initial b. p. ° F.	50% ° F.	Final b. p. ° F.	Octane No. by Procedure 345 Original gasoline	Gasoline + 1 cc. T. E. L. [a]/gal.
W. Va. natural	74.0	95	173	310	57	69
Bradford straight-run	62.3	104	258	410	41	53
Mich. naphtha	71.4	111	185	274	41	60
Yates straight-run	54.9	108	294	410	59	66
A	57.7	112	246	432	52	64

[a] Tetraethyllead.

TABLE II. COMPARISON OF OCTANE NUMBERS BY C. F. R. MOTOR AND SERIES 30B METHODS

Fuel	Octane Number: C. F. R. motor	Procedure 345: Ethyl Gas Corp.	Pa. State
Secondary reference fuels:			
A-2	48	46	48
A-3	44	41	41
A-4	41	..	40
C-7	75	76	76
C-8	77	79	78
C-9	74	..	74
Pa. straight-run gasoline	44	..	41
Yates straight-run gasoline	59	..	59
Yates straight-run gasoline + 1 cc. T. E. L./gal.	67.5	..	66
Straight-run gasoline A	51	..	52
Straight-run gasoline A + 1 cc. T. E. L./gal.	62.5	..	64
W. Va. natural	56	..	57
W. Va. natural + 1 cc. T. E. L./gal.	69	..	69

Octane numbers above 78 were obtained by blending fuel C-9 with isoöctane or benzene to obtain secondary reference fuels which were checked against the primary standards of *n*-heptane and isoöctane. In a few instances the primary standard was used directly to rate the unknown fuel. Octane numbers below 40 were obtained by blending a base gasoline of low octane number with reference fuel A-4 obtained from the Standard Oil Company of New Jersey and checking the blends with the primary standards. Therefore all octane numbers obtained were actual octane numbers and not so-called blending octane numbers.

Results

The results obtained on the addition of tetraethyllead or aniline to various blends of the gasoline fractions are given in Table III. The results show that blends from certain gasolines are very responsive to tetraethyllead and that even high-boiling fractions may behave similarly. The blend 109–144° F. from the West Virginia natural gasoline gave the greatest increase in octane number for 1 cc. of tetraethyllead and also comprised the greatest percentage of the charge. Since this material is known to contain largely 2-methylpentane, the lead susceptibility of the latter was obtained and its octane number was found to increase 18 upon the addition of 1 cc. of tetraethyllead.

The addition of 2 cc. of tetraethyllead to the 109–144° F. blend from the West Virginia gasoline gave an octane number of approximately 98. In order to make the sample knock, it was necessary to open the throttle to maximum knock and then advance the spark to 17°. The gasoline was rated directly against the primary standards. The effect of the second cubic centimeter of tetraethyllead is much smaller in comparison to the first.

The data in Table III show clearly that octane number and lead susceptibility are not dependent alone on the boiling range of the fraction. Fractions of the same boiling range prepared from different gasolines have considerable differences in octane number and lead susceptibility. This is, at least in part, due to the fact that different hydrocarbons as well as perhaps different sulfur compounds are present and boil in the same ranges. These observations on knock are entirely in agreement with more complete physical and chemical studies being made on these fractions. The work on the constitution of these gasolines in this laboratory has shown that the Yates gasoline contains a high proportion of naphthenic hydrocarbons—i. e., cyclohexane and cyclopentane derivatives—and fewer paraffinic hydrocarbons. This work further shows that there are considerable differences in the compounds present even in the paraffinic gasolines.

It should be remembered in the high octane number region that not only is it difficult to obtain reliable octane numbers with the knock-testing engines now in use, but also that as far as ultimate engine performance is concerned, octane numbers, as well as changes in high-octane values, are much more important than in the lower portion of the octane scale. This is because considerably greater changes in compression ratio are possible for a given change in octane number in the high part of the octane scale than in the low part. For these reasons this work was intended to point out briefly the general and more important characteristics of these fuels rather than to place emphasis upon any particular fraction or any particular octane number. There still remains a large amount of work to be done before all the facts and observations relating to these materials can be adequately formulated and explained.

The previous treatment of the gasoline, and particularly the presence of sulfur compounds, markedly influences the responsiveness of gasoline to tetraethyllead (*5*, *7*). Because of this the sulfur content of certain fractions were obtained. These values are as follows: Yates (97–145° F.) 0.05 per cent; Bradford (97–142° F.) 0.05; Yates (162–192° F.) 0.03; Bradford (165–189° F.) 0.15; Yates (211–237° F.) 0.08; Yates (274–283° F.) 0.10; Yates (319–338° F.) 0.20 per cent. In view of these results and the work of Schulze

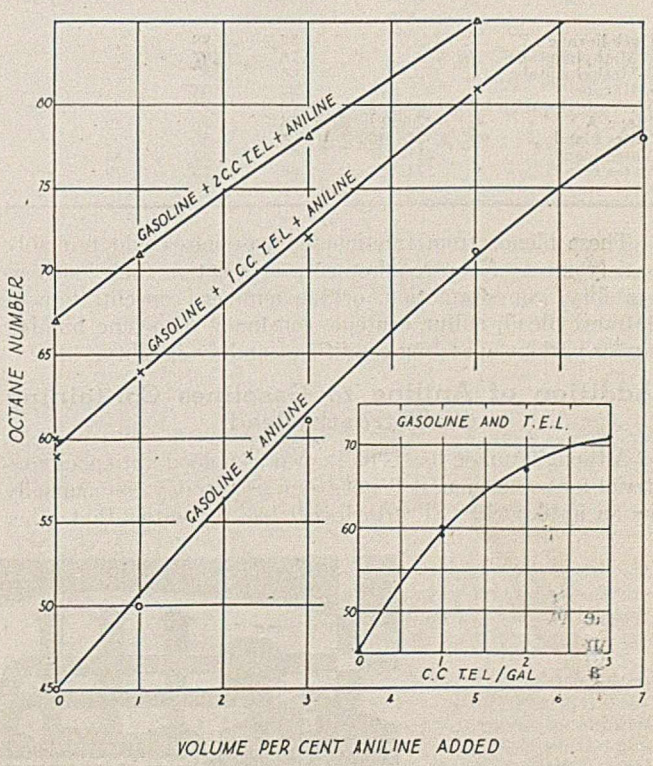

FIGURE 1. EFFECTIVENESS OF TETRAETHYLLEAD AND ANILINE IN PENNSYLVANIA STRAIGHT-RUN GASOLINE

TABLE III. SUSCEPTIBILITY OF GASOLINE FRACTIONS TO TETRAETHYLLEAD AND ANILINE

Gasoline Fractionated	Boiling Range of Blend ° F.	Vol. % of Charge	Octane No. Original blend	Octane No. Blend + 1 cc. T. E. L./gal.	Octane No. Blend + 1% aniline	Octane No. Increase Lead blend	Octane No. Increase Aniline blend	Compounds Probably Present
W. Va. natural	109–144	10.0	73	91	79	18	6	Cyclopentane and isomeric hexanes
Bradford straight-run	97–142	3.7	72	82	76	10	4	
Mich. naphtha[a]	115–145	3.5	78	92	80	14	2	
Yates straight-run	97–145	3.1	78	85	79	7	1	
W. Va. natural	160–189	5.5	81	90	84	9	3	Cyclohexane, benzene, and isomeric heptanes
Bradford straight-run	165–189	2.0	79	86	82	7	3	
Mich. naphtha[a]	160–181	4.4	79	90	83	11	4	
Yates straight-run	162–192	3.8	79	88	82	9	3	
W. Va. natural	213–233	5.2	72	82	76	10	4	Methylcyclohexane, toluene, and isomeric octanes
Bradford straight-run	213–236	5.3	72	82	76	10	4	
Mich. naphtha[a]	212–235	6.2	75	86	80	11	5	
Yates straight-run	211–237	5.6	74	82	77	8	3	
Bradford straight-run	270–283	4.1	72	83	77	11	5	Ethylbenzene, xylenes, and isomeric nonanes
A	273–284	6.0	76	86	79	10	3	
Yates straight-run	274–283	4.8	66	73	70	7	4	
Bradford straight-run	312–333	6.3	52	60	56	8	4	9 carbon aromatics and naphthenes, and isomeric decanes
A	318–333	3.9	56	61	56	5	0	
Yates straight-run	319–338	8.2	53	59	58	6	5	

[a] 111° to 274° F.

and Buell (7), it is possible that some, but not all, of the variations in lead susceptibility are due to sulfur compounds. The effect of differences in hydrocarbon structure in these fractions should not be overlooked.

For comparative purposes the octane numbers of certain compounds and blends are given in Table IV. The responsiveness of *n*-hexane to tetraethyllead is of interest and is in agreement with the high lead susceptibility of the Michigan naphtha. The fact that a gasoline or naphtha has a low octane number does not necessarily preclude its use as a motor fuel if its responsiveness to tetraethyllead is good.

TABLE IV. OCTANE NUMBERS OF COMPOUNDS AND BLENDS

Fuel	Boiling Range of Blend ° F.	Octane No. Procedure 345 Original blend	Octane No. Procedure 345 Blend + 1 cc. T. E. L./gal.	Octane No. Procedure 345 Blend + 2 cc. T. E. L./gal.
Cyclohexane	.....	83	88	..
2-Methylpentane	.....	70	87	..
3-Methylpentane	.....	66	83	..
n-Hexane	.....	22	54	..
W. Va. natural blend	109–144	73	91	98 (approx.)
Blend A	273–284	76	86	89
Yates blend	97–145	78	85	92
Yates blend	211–237	74	82	84
Yates blend	274–283	66	73	79

These blends from fractionated gasolines could probably satisfy most of the requirements of aviation fuels, such as stability, gum formation, octane number, concentration of tetraethyllead, sulfur content, constancy of octane number under various operating conditions, and availability.

Addition of Aniline to Gasolines Containing Tetraethyllead

Although aniline has been known as a good antiknock material for some time, it is not being used today commercially as an antiknock. Nevertheless it has properties that other antiknocks do not have. The addition of aniline up to 7 volume per cent gives practically a linear increase in octane number for straight-run gasolines, whereas tetraethyllead, for example, gives only small increases in octane number when over 2–3 cc. are used. In cracked gasoline aniline gives a greater increase in octane number for the first 2 per cent than it does for the second 2 per cent, but from 2 to 7 per cent the increase is again practically linear. This property of aniline points to the possibility that it might supplement the action of tetraethyllead by acting independently of it. In Figure 1 the effect of adding aniline to a straight-run gasoline and to the same gasoline containing 1 cc. of tetraethyllead per gallon is shown. The slopes of the aniline-gasoline and aniline-tetraethyllead-gasoline curves are about the same. In other words, the tetraethyllead and the aniline are acting independently of one another.

Certain cracked gasolines behave similarly and can be easily brought up to 80 octane number or higher by the use of aniline and tetraethyllead together, whereas the use of tetraethyllead alone would fail to accomplish this result.

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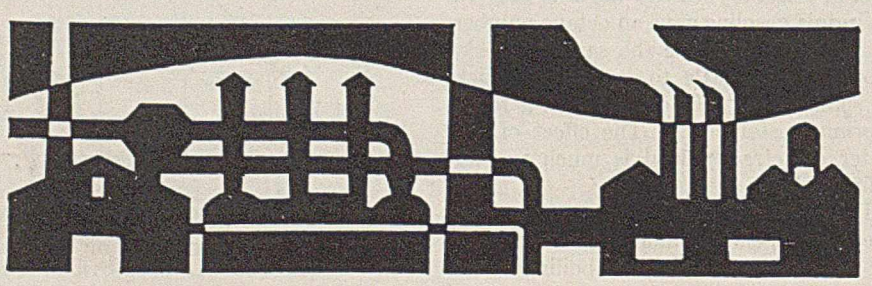

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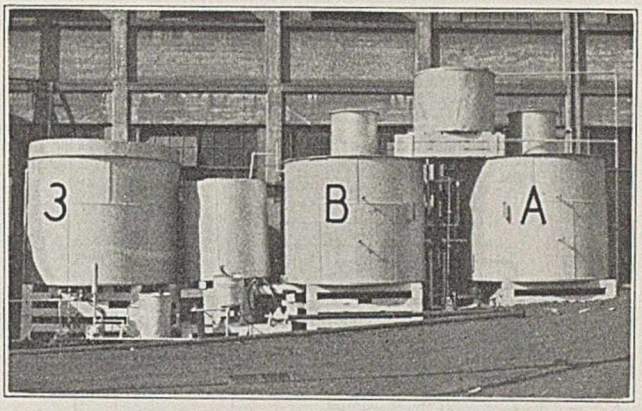

FIGURE 1. UNITS OF THE DEMONSTRATION PLANT

Complete Treatment of Distillery Wastes

ANAËROBIC fermentation under especially controlled conditions has been recommended for the treatment of heavy wastes such as distillery slop (*3, 5–8, 10*), milk and whey (*1, 11, 14*), packing-house wastes, etc. (*2, 4*).

This process has two limitations, as previous authors have pointed out. Anaërobic fermentation cannot be economically used with wastes containing less than about 1 per cent dry weight of digestible organic matter. When the wastes contain 2 per cent or more, the methane recovered will carry most or all of the cost of treatment. In some cases this limitation of the process can be overcome by suitable changes in plant operation to avoid diluting the wastes with clean water (e. g., cooling water).

The second limitation of the process is that, although anaërobic treatment is capable of removing 80 to 90 per cent of the organic matter in the wastes, the remaining liquor is still about ten times as strong as domestic sewage. In many cases this degree of purification is sufficient—for example, where the effluent can be discharged into a sewer or large stream or where five or six volumes of cooling or condenser water are available for dilution. Where complete purification (i. e., to less than 100 parts per million B. O. D.) is required, some other method of treatment must be applied.

Early in the summer of 1935 the authors were asked to set up and operate a pilot plant to determine whether anaërobic digestion plus some subsequent treatment could be used for complete treatment of distillery wastes. Numerous earlier experiments with various chemical coagulants (not reported) had failed to produce any substantial improvement in the liquid remaining after anaërobic digestion. Since Naylor (*15*) had shown that similar wastes after septic action could be treated on aërobic bacterial filters and Hoover (*9*) had successfully treated diluted wastes on trickling filters, this form of secondary treatment was chosen.

Digestion Tanks

The major units of the demonstration plant, as shown on Figure 1, consisted of two steel digestion tanks, *A* and *B*, and one tank, 3, in which was located a trickling filter. Each of the digestion tanks, *A* and *B*, was 9 feet in diameter and 7.5 feet deep, with a capacity of 3600 gallons, making a total capacity of 7200 gallons or 960 cubic feet. These tanks were already available and required considerable adaptation in order to serve their purpose. Steam coils were placed in the center of the tanks at the bottom, and covers, with gas domes 3 feet in diameter and 3 feet high, were welded in place over the tanks.

The process consisted essentially of passing the slop through two digestion tanks in series and applying the digested effluent, diluted with a part of the finally purified waste, to a trickling filter.

The flow through the digestion tanks was as follows (Figure 2):

The raw thin slop was pumped to the cooling and feed tank, 1. Although provision was made in this tank for cooling the slop to the proper temperature (130° F.), the cooling facilities were seldom used. The heat of the slop could ordinarily be utilized in heating the first tank, *A*. After a dose had been measured and sampled, it was allowed to flow into the primary digestion tank, *A*.

This tank was heavily loaded, accomplishing the greater part of the digestion and yielding most of the gas generated. From tank *A* the partially digested slop was forced by succeeding doses to secondary digestion tank *B* where a further digestion at a decreasing rate was accomplished.

A back-circulation pump, 5, made it possible to return liquid from secondary tank *B* to primary tank *A* for seeding and dilution. This is an important control measure, which, in conjunction with other control tests, made it possible to place on the primary tank, loadings of the order of ten times those used in common sewage-sludge digestion practices.

Pilot plant results confirm laboratory data on the purification of distillery waste by anaërobic fermentation. The effluent from anaërobic fermentation when diluted 1 to 5 with trickling filter effluent can be successfully stabilized on a trickling filter at the rate of 250,000 gallons of the undiluted digestion liquor per acre per day. The high nitrate content in the recirculated filter effluent prevents odor nuisance. The sludge is small in amount and contains the phosphate of the grain as magnesium and calcium ammonium phosphate.

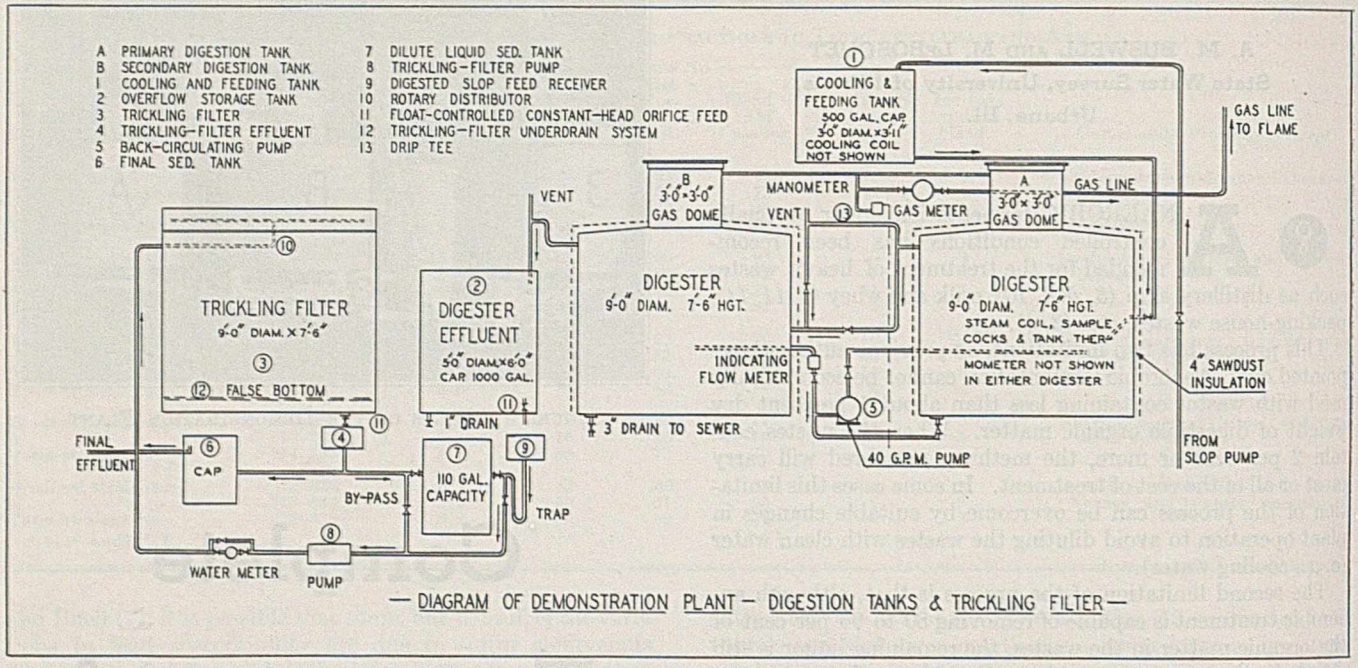

FIGURE 2

A 1000-gallon, digested liquid overflow tank, 2, made it possible to place the full 24-hour load on the filter in 8 hours, or during one shift. The trickling filter, 3, which required little or no attendance, was operated at a constant rate over the 24 hours; the necessary equalizing storage was furnished by overflow tank 2.

Trickling Filter

Dilution of some sort had to be provided in the design of trickling filter 3 in order to reduce the oxygen demand of the liquid supplied to the filter. If, at the same time, this dilution could result in a reduction of the odors, the filter could be operated without causing a serious nuisance.

Trickling filter 3 was constructed in a circular steel tank. The stone bed was 9 feet in diameter and 7 feet deep. Although the filter was of an experimental nature, its size would be sufficient for a small dairy and could almost be considered a plant-scale demonstration.

The effluent from trickling filter 3 was used to dilute the digester effluent fed to filter 11. This idea was used elsewhere in treating a concentrated industrial waste (*15*). In order to accomplish the desired result, the effluent from the trickling filter was discharged into a small box, 4, with two outlets. One outlet led to a final sedimentation tank, 6, the overflow from which was the final effluent. The other outlet led to a diluting liquid sedimentation tank, 7. The discharge line from this tank was conducted to the suction of trickling filter pump 8. Also connected to this suction was the digested distillery slop feed line, 9. By this arrangement pump 8 dosed filter 3 at a rate equal to a rate of raw feed, plus a quantity of trickling filter effluent. For example, when pump 8 was operated at a rate of 2 gallons per minute and digested distillery slop (2 and 11) was fed at a rate of 0.5 gallon per minute, the pump automatically made up the difference (1.5 gallons per minute) from diluting liquid sedimentation tank 7. With the arrangement used, feed 11 could be turned off entirely, in which case the pump would take its entire pumpage from diluting liquid sedimentation tank 7. A closed system would then result, the trickling filter effluent being pumped in its entirety back onto filter 3 again and again.

Sedimentation tank 7 was installed for the purpose of removing settleable solids from that portion of the trickling filter effluent which was used for deodorizing and diluting the feed of digested distillery slop. This was important in reducing the amount of suspended matter put on the trickling filter. As a consequence no troubles due to filter clogging were encountered.

Other details of the design included a distributor of the rotary type, 10, and an orifice, 11, to accomplish a constant rate of feed of digested liquid. A wooden false bottom, 12, was constructed in trickling filter tank 3 as an underdrain system. Adequate vents were supplied. The filter material used was 1.5–3 inch blast furnace slag.

The 9-foot trickling filter had an area of 63.6 square feet or 0.001462 acre. A rate of 1,000,000 gallons per acre daily, therefore, would be 1462 gallons daily, or slightly over 1 gallon per minute.

Digestion Tank Loadings

Difficulties were encountered during the early stages of the demonstration in obtaining high rates of feed on the digestion tanks. Since the digestion tanks were placed in operation less than 2 weeks after the decision to proceed, there was insufficient opportunity of preparing adequate seeding material. As a consequence it was necessary to use digesting sludge from a sewage treatment works for this purpose, where the digestion takes place at ordinary sewage temperatures, whereas the slop was digested within the thermophilic range or at 130° F. The first four weeks of operation elapsed before the sludge was conditioned sufficiently for appreciable amounts of slop to be fed. After this time (September 10) the feed had been increased to 100 gallons per day. This greater feed was continued until September 20 when it was possible to increase the feed until, by September 29, feed had been increased to 250 gallons per day.

At this point both of the tanks were covered with a proper insulating material to reduce the heat loss and, therefore, greatly reduce the number of times steam had to be applied. A 4-inch layer of sawdust was used. It was then possible to increase the feed further until, on October 5, 350 gallons per day were being fed. This dose was maintained until October 17, at which time the volatile acids had risen so high that it was necessary to curtail the feed until, on October 24, only 100 gallons per day could be fed.

In previous experiments the sludge occasionally compacted during the earlier stages and required agitation until the fermentation was well established. Accordingly, arrangements were made to increase the circulation and agitate the sludge from time to time.

Following the agitation, it was possible to increase the feed from 100 to 550 gallons per day in the course of 6 days. This rapid rate of increase is significant as indicating the rate at which it is possible to start the tanks when the right type of installation is available.

Gas Production

The gas production confirmed results of previous laboratory-scale work and the work on a larger scale at the sewage treatment works of Peoria Sanitary District (*11*). A uniform rate of 11 cubic feet of gas was obtained per pound of volatile solids fed to the tank.

Analytical Data

It was not possible, with the personnel and equipment available, to make complete daily analyses. A large number of samples were analyzed at the plant, and several samples were brought to Urbana for check analyses. The raw screened slop ran from 3 to 4 per cent solids (80 per cent volatile) with a B. O. D. of 15,000 to 16,000 p. p. m. and an organic nitrogen content of 1900. The effluent from the digestion showed a B. O. D. of 1500 to 2000 p. p. m. The effluent from the trickling filter, while operating at a rate of 250,000 gallons per acre per day (based on the undiluted digester effluent fed), had a B. O. D. of 138 p. p. m. (average of sixteen field samples). The four samples of trickling-filter effluent brought to Urbana for analysis showed B. O. D. values of 39, 98, 80, and 104 p. p. m., respectively. These samples showed nitrate nitrogen values ranging from 60 to 820 p. p. m. and nitrite nitrogen from 25 to 150 p. p. m. Tightly stoppered samples showed no putrefaction after several weeks. Kiby (*10*) reported 200 p. p. m. nitrate nitrogen and 70 p. p. m. nitrite nitrogen in the effluent from a trickling filter treating similar wastes.

Odors

Anaërobic fermentation always results in production of hydrogen sulfide and other odorous compounds. In this installation the escape of odors is avoided by completely sealing the fermentation tanks. The gas which carries the odors is burned for heat or power. Odors from the digester effluent as it discharged to the trickling filter were anticipated. However, as soon as nitrification had become established, the high nitrates in the recirculated filter effluent stabilized the digestion effluent so that no odor was produced when the usual 4 or 5 to 1 mixture of the two liquids was sprayed onto the trickling filter. This stabilizing effect of nitrates has been known for many years and was once suggested as a means for treating raw sewage (*12*). An analytical method for determining oxygen demand by means of nitrates was once in use

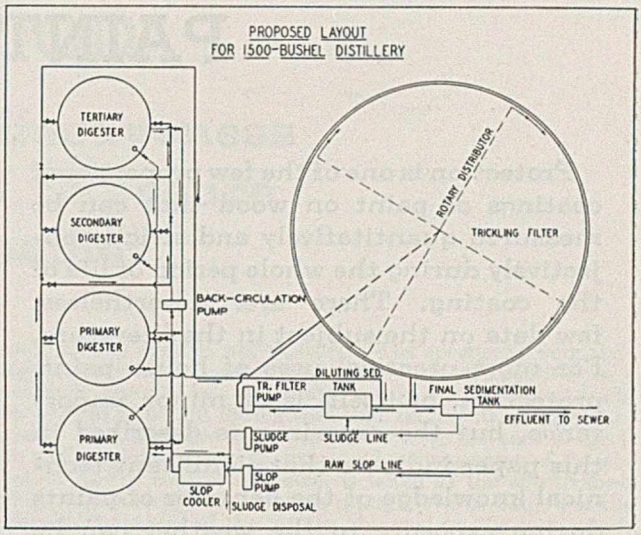

FIGURE 3

(*13*) This early work, together with the results of the present experiment, amply justify the conclusion that this process can be operated without odor nuisance.

Sludge

Since the fermentation resulted in 90 per cent gasification, the amount of sludge produced was relatively small. Some sludge was carried over with the effluent so that actual accumulation of sludge was relatively negligible when compared with the sludge from other types of material. No accurate measure could be made within the period of this experiment. Practically all of the phosphorus of the grain was recovered as magnesium and calcium ammonium phosphate. One sample of sludge showed 3.3 per cent phosphorus and another 4.2 per cent on a dry basis.

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PAINTS AS PROTECTIVE

Protection is one of the few properties of coatings of paint on wood that can be measured quantitatively and strictly objectively during the whole period of life of the coating. There are, nevertheless, few data on the subject in the literature. For most practical uses of house paint, protection, of itself, is of minor importance, but the experiments described in this paper indicate that significant technical knowledge of the behavior of paints during exposure to the weather can be gained by measuring the changes taking place in their protective power.

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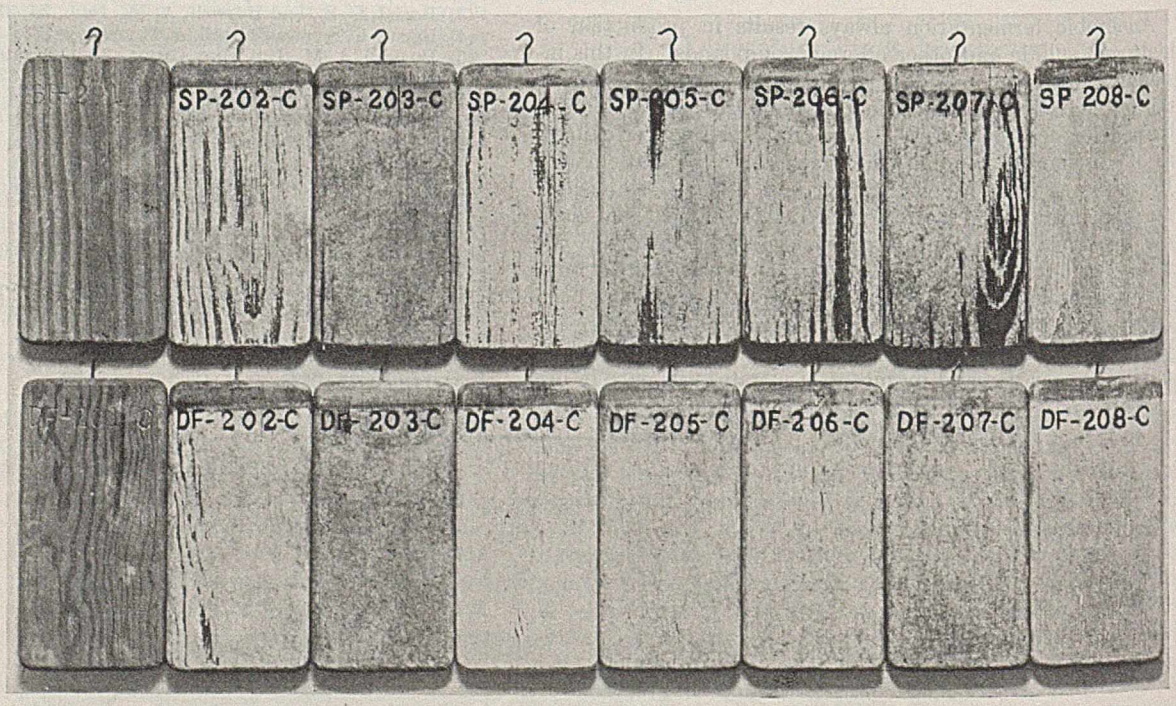
THE customary methods of testing exterior house paints for durability on wood consider only the changes in appearance and integrity of the coatings that are apparent to the eye during the period of exposure. No account is taken of changes in the degree of protection afforded the wood against wood weathering. Such preoccupation with appearance and integrity is fully justified because protection, as a rule, is of minor importance. For the most part appearance and integrity must be judged by personal inspections that suffer from the difficulties inherent in subjective methods of measurement. Protection, on the other hand, can be measured quantitatively by objective methods (*3*, *7*, *11*) since it depends upon the effectiveness of the coatings in retarding the exchange of moisture between wood and its environment. If there should prove to be a relation between protection and maintenance of integrity by coatings, measurement of the effectiveness against moisture movement would greatly aid the paint technologist in evaluating the durability of house paints. In certain uses of paints—for example in mill-priming and back-priming—protection itself is of dominant interest. Possible future developments in the use of wood, such as plywood for exterior exposure, may increase the number of places in which protection by coatings is of real importance.

The first part of this study has already been published (*4*, *5*). The previous papers reported the effectiveness of ninety-three priming paints (tests of group A), of the ninety-three priming paints followed by two coats of white lead in linseed oil (tests of group B), and of three-coat paint jobs in which the second and third coats were similar to the primers in composition (tests of group C). All tests were repeated on southern yellow pine, Douglas fir, northern white pine, and redwood. The initial effectiveness and the effectiveness after exposure to the weather for 6 months at 45° facing south at Madison, Wis., were reported. Exposure of the 896 specimens of groups B and C was continued, and tests for effectiveness were made at intervals of 6 months. This paper reports the results with groups B and C up to a total exposure of 3 years, by which time many of the coatings had lost nearly all protective value.



SERIES 200, GROUP C, SPECIMENS 201 TO 216 (IN ORDER, LEFT TO RIGHT); 209 TO 212 EXPOSED TO THE WEATHER
DOUGLAS FIR. SPECIMENS 201 AT LEFT, UNPAINTED

COATINGS FOR WOOD

Variation in Effectiveness with Length of Exposure to the Weather

For details of the experimental procedure, the layout of the tests, the composition of the paints, and the spreading rates with which the paints were applied, reference should be made to the earlier publication (*4*).

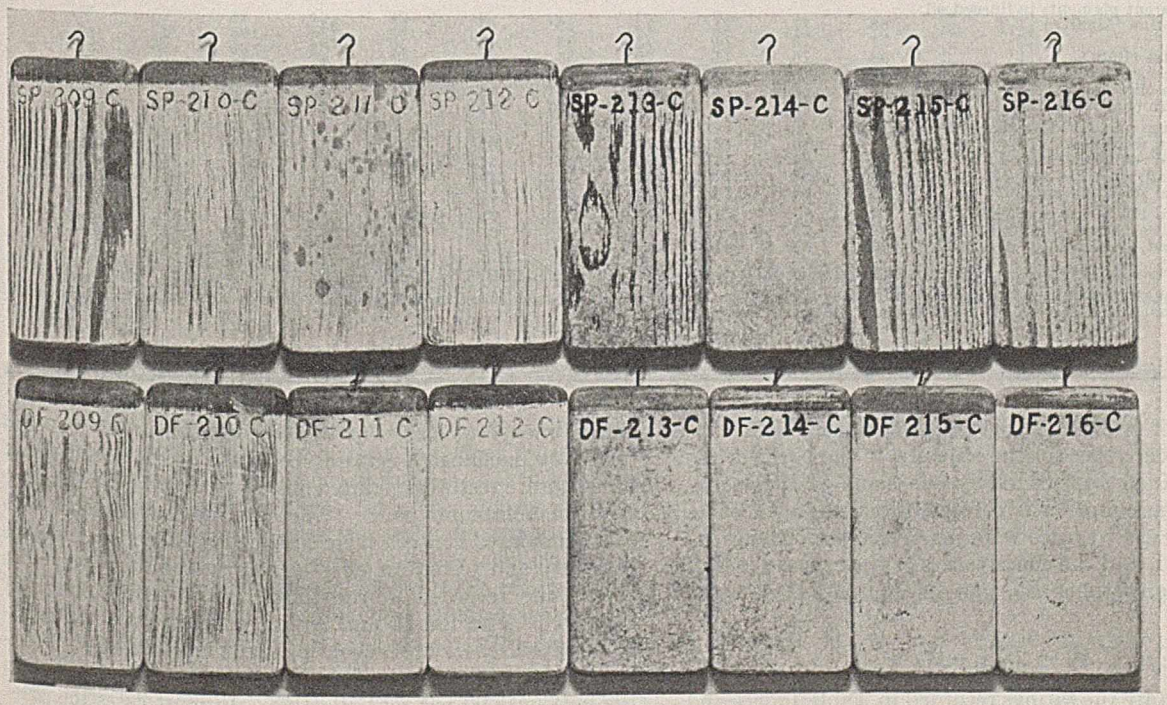
Reviewing briefly, each group of tests is further subdivided into seven series known, respectively, as the 100 series, 200 series, etc. For each series four sets of wood specimens were provided, one set of each kind of wood. Each set consisted of sixteen specimens carefully matched for reasonable uniformity in weight, grain, and rate of absorption of moisture. One specimen of each set was left unpainted, one painted with white lead in linseed oil, and one painted with white lead in a Bakelite resin paint oil, leaving thirteen specimens for experimental paints related in such a way that particularly close comparisons between them were possible. Repetition of the two control paints in each series made it possible to gage the precision of the testing procedure and to make more reliable comparisons between paints in different series. The unpainted control specimens were used to determine for each series the moisture absorbed from damp air by the wood when uncoated, which is the basis for calculation of the moisture excluded by the coating and from it the effectiveness rating. Unpainted control specimens were never exposed to the weather but remained in a room kept at 65 per cent relative humidity while the painted specimens were being exposed.

The effectiveness of the coatings against moisture movement was determined before exposure to the weather and after each interval of 6 months during exposure by hanging the specimens in a room kept at 65 per cent relative humidity and 80° F. (27° C.) until equilibrium moisture content was approximated. As a rule the specimens were approximately in equilibrium when taken from the exposure racks unless they were removed immediately after a spell of wet weather. The specimens were then weighed and placed, together with their unpainted controls, in a room at 97 per cent relative humidity and 80° F. for one week. The increase in weight during that time represents moisture absorbed. The difference in absorption between the control specimen and a painted specimen, expressed as percentage of the absorption by the control specimen, is taken as the effectiveness rating. The average effectiveness rating given in Table I is the arithmetical average of the ratings obtained on the four woods separately.

Correction for Unexposed Backs of Specimens

Only one side of the painted specimens was fully exposed to the weather when they were in position on the exposure racks, but both sides were subject to absorption of moisture while they were hanging in the 97 per cent room to determine the effectiveness. On the freshly painted specimens the effectiveness was the same for both sides, but after exposure to the weather the two sides differed materially. The effectiveness measured is the average of the exposed and unexposed sides. For that reason the changes in effectiveness caused by weathering were materially greater than the data of Table I show.

Visual inspection of the painted specimens at the end of 36 months showed that the coatings on the backs of nearly all specimens were still glossy, free from fissures, intact, and similar in appearance to young coatings except that many of the white paints were distinctly yellow as would be expected from repeated exposure to 97 per cent humidity without subsequent



FOR 24 MONTHS, OTHER SPECIMENS EXPOSED 36 MONTHS. TOP ROW, SOUTHERN YELLOW PINE; BOTTOM ROW, CONTROL SPECIMENS NOT EXPOSED TO THE WEATHER

TABLE I. AVERAGE EFFECTIVENESS OF COATINGS AGAINST MOISTURE MOVEMENT AT INTERVALS DURING EXPOSURE

Reference No.	Description of Primer for Group B and of All Three Coats for Group C	Group B, Primer Plus Two Coats of White Lead Paint: Av. effectiveness rating[a]								Integrity[b]			
		E_0	E_6	E_{12}	E_{18}	E_{24}	E_{30}	E_{36}	E^F_{end}	SP	DF	WP	RD
	Series 100												
102	White lead in linseed oil	72	80	73	71	62	43	52	32	28	26	F−	F
103	White lead in Bakelite oil	84	87	84	82	83	70	70	56	34	34	F	F
	Aluminum paints:												
104	Paste Al in varnish A	85	88	84	84	82	74	76	67	36	F	F	F
105	Paste Al, Bakelite varnish	90	91	88	87	80	70	76	62	30	36	F	F
106	2 lb. powder, varnish A	88	89	86	86	80	73	77	66	P+	F−	F	F
107	1 lb. powder, varnish A	80	84	76	76	70	55	59	38	36	P+	F	F
108	2 lb. powder, Bakelite varnish	91	91	88	89	84	73	76	61	35	P+	F	F
109	1 lb. powder, Bakelite varnish	84	86	82	82	73	56	63	42	32	34	F	F
	2 lb. powder in:												
110	75-gal. ester gum varnish	86	88	83	80	74	63	67	48	36	36	F	F
111	33-gal. ester gum varnish	91	92	87	84	77	62	70	49	24	27	F	F
112	Glyceryl-phthalate varnish	86	86	86	86	78	67	69	52	P+	30	F	F
113	Shellac–castor oil	87	86	55	..	..	..	..	23	12	12	12	..
114	Raw linseed oil	82	86	81	80	76	65	66	50	P+	F−	F	F
115	Kettle-bodied linseed oil	84	87	82	82	80	70	72	60	P+	F−	F	F
116	Nitrocellulose lacquer	86	88	53	..	..	..	..	20	12	12	12	..
	Series 200												
203	White lead in Bakelite oil	79	86	79	82	81	66	64	49	32	32	F	F
	White pigments in linseed oil:												
202	Basic-carbonate white lead	68	78	71	68	59	38	46	8	28	24	F−	F
204	Basic-sulfate white lead	69	79	68	58	54	38	..	7	30	24	F	F
205	35% leaded zinc oxide	72	81	71	66	61	43	..	14	24	24	24	24
206	Mixt. of 204 and 207	72	81	74	68	59	43	..	14	24	24	24	24
207	Zinc oxide, lead-free	73	83	74	69	61	45	..	17	21	24	24	24
208	Antimony oxide	68	81	69	72	66	52	52	36	F−	36	F	F
209	Titanium dioxide	68	78	71	69	57	43	50	18	36	36	F	F
210	Titanium-barium pigment	68	76	66	62	55	39	48	10	36	36	F	F
211	Zinc sulfide	68	76	70	70	61	45	51	22	36	P+	F	F
212	Lithopone	67	77	67	65	59	42	51	17	30	36	F	F
213	Mixt. of 202, 207, 404	72	82	69	60	56	38	..	4	21	21	24	24
214	Mixt. of 210, 207, 404	69	81	67	57	55	38	..	7	21	21	24	24
215	Mixt. of 212, 205, 404, 405	70	79	69	55	52	35	..	0	21	21	24	24
216	Mixt. of 202, 207, 404, much 407	70	79	69	58	52	36	..	2	21	21	24	24
	Series 300												
302	White lead in linseed oil	71	77	71	68	60	39	41	11	28	30	F	F
303	White lead in Bakelite oil	80	85	81	82	79	66	65	50	30	F	F	F
	Colored pigments in linseed oil:												
304	Iron oxide red, 99% Fe_2O_3	70	77	71	70	69	61	44	18	F	F	F	F
305	Spanish oxide, 85% Fe_2O_3	69	76	72	71	70	62	60	51	F	F	F	F
306	Venetian red, 40% Fe_2O_3	69	76	71	70	67	55	54	39	F	F	F	F
307	Venetian red, 9% Fe_2O_3	72	77	75	70	66	53	51	30	F	F	F	F
308	Iron oxide yellow, 92% $Fe_2O_3 \cdot H_2O$	68	75	70	68	67	58	56	44	F	F	F	F
309	Yellow ocher, 18–24% Fe_2O_3	70	76	73	72	71	61	58	46	F	F	F	F
310	Chrome yellow, lemon	69	75	73	72	71	62	61	53	F	F	F	F
311	Chrome yellow, orange	69	79	73	72	71	61	61	53	30	30	30	30
312	Prussian blue	69	76	72	73	71	59	55	41	F−	F	F−	F
313	Lampblack	71	77	71	73	73	63	60	49	30	30	30	30
314	Graphite	75	80	76	75	75	65	61	47	F−	F−	P+	F−
315	Red lead	72	82	76	71	62	37	39	6	20	27	P+	P+
316	Litharge	83	89	82	73	66	43	42	1	28	30	F	F
	Series 400												
402	White lead in linseed oil	68	76	71	73	59	41	38	8	27	36	F	F−
403	White lead in Bakelite oil	80	85	80	79	80	64	60	40	27	P+	F	F
	Transparent pigments in linseed oil:												
404	Asbestine ($MgSiO_3$)	68	77	71	73	69	51	..	34	..	..	..	..
405	Silica	71	79	74	73	65	45	..	19	..	..	..	..
406	Barytes ($BaSO_4$)	68	76	71	70	55	38	..	8	24	..	..	..
407	Blanc fixe ($BaSO_4$)	60	78	70	69	57	38	..	16	27	..	..	..
408	China clay	68	77	72	75	66	46	..	24	..	..	..	..
409	English chalk ($CaCO_3$)	68	76	72	73	60	41	..	14	..	..	..	..
	Aluminum and granular pigments:												
410	Al and white lead, 114 and 202	73	80	76	76	73	61	53	33	F	F	F	F
411	Al and red lead, 114 and 315	75	83	79	75	65	51	48	21	27	P+	F	F
412	Al, lead, zinc, 114 and 213	75	83	72	65	57	42	..	9	24	24	24	24
413	Al and ZnO, 114 and 207	75	83	76	73	66	51	..	27	24	24	24	24
414	Al and Fe_2O_3, 114 and 304	74	80	76	77	77	71	63	52	F	F	30	F
415	Al and asbestine, 114 and 404	72	79	75	75	72	63	54	36	F	F	F−	F
416	Al, lead, Bakelite, 108 and 203	80	85	81	83	80	70	60	40	P+	F	F	F

[a] E_0, E_6, etc. = average effectiveness rating on four woods determined at the age in months indicated by the subscript.

E^F_{end} = average effectiveness rating calculated for the exposed faces at the last time of test (in series 200, group B, at age 30 months); effectiveness of unexposed backs taken from Table II if recorded there, otherwise assumed equal to E_0.

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exposure to direct sunlight. It is therefore reasonable to suppose that the effectiveness of the coatings on the backs of the specimens remained approximately the same as it was initially. If that assumption is correct, the changes in effectiveness of the exposed faces were just twice the changes recorded in Table I, and the effectiveness of the exposed face of a specimen at any time, E^F_T, can be computed from the formula:

$$E^F_T = 2\,E_T - E_0$$

where E_T and E_0 are the ratings recorded in Table I for T and 0 months, respectively.

To test the validity of the assumption that the effectiveness of the unexposed backs of the painted specimens remained relatively unchanged, certain specimens at the conclusion of the exposure test were painted on the exposed faces with three coats of aluminum paint. These specimens, together with their unpainted controls were seasoned in 65 per cent relative humidity and tested for effectiveness in the usual way with the results recorded in the third and seventh columns of Table II. The fourth and eighth columns give the calculated effectiveness of the coatings on the backs of the specimens, assuming that the freshly applied aluminum paint on the faces was 90 per cent effective. In most cases the effectiveness of the old coating on the backs of the specimens agrees satisfactorily with the effectiveness of the entire coating ini-

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TO WEATHER AT 45° FACING SOUTH, AND SUMMARY OF VISUAL OBSERVATIONS OF DETERIORATION OF COATINGS

Group C, Three Coats of Paint of Kind Described															
Av. effectiveness rating[a]								Chalking[c]	Checking[c]	Cracking[c]	Integrity[b]				Reference No.
E_0	E_6	E_{12}	E_{18}	E_{24}	E_{30}	E_{36}	E^F_{end}				SP	DF	WP	RD	
Series 100															
73	85	75	72	67	41	49	25	6	12	..	28	32	F−	F	102
92	95	92	93	94	90	88	84	12	..	..	P+	G	G	G	103
92	94	88	89	89	87	86	80	..	..	..	G	G	G	G	104
94	95	85	91	91	90	90	86	..	..	..	F−	G	G	G	105
94	95	91	92	92	89	88	82	..	..	..	G	G	G	G	106
89	91	82	82	82	75	74	59	..	..	..	G	G	G	G	107
95	96	91	91	92	90	90	85	..	..	..	G	G	G	G	108
90	93	85	85	85	80	79	68	..	..	..	F−	G	G	G	109
90	93	87	87	87	83	83	76	..	..	..	G	G	G	G	110
98	97	93	93	91	88	90	82	..	..	..	34	G	G	G	111
93	95	89	89	91	87	86	79	..	..	..	G	G	G	G	112
92	90	70	..	..	..	..	48	..	..	..	12	12	..	..	113
77	85	75	75	77	70	69	61	..	..	..	F	G	G	G	114
89	92	85	85	86	83	79	69	..	..	..	G	G	G	G	115
43	55	38	..	..	..	..	23	..	..	..	12	6	12	..	116
Series 200															
89	93	92	92	91	87	88	87	12	..	..	36	G−	G	G	203
73	79	75	75	65	47	49	25	6	12	..	28	28	F	F	202
69	78	75	68	59	44	45	21	6	..	12	28	36	F	F	204
72	80	78	75	66	50	47	22	6	..	24	28	P+	F	F	205
75	81	80	74	62	47	45	15	6	..	24	26	36	P+	F	206
75	82	80	73	63	49	47	19	12	..	24	26	P+	P+	F	207
68	74	65	68	62	55	54	40	6	..	..	G−	G−	G	G	208
63	66	48	45	40	..	..	17	6	..	..	18	18	24	22	209
64	68	55	53	46	..	..	28	6	..	..	18	18	24	18	210
65	69	56	48	44	..	..	23	6	12	..	20	24	..	24	211
55	55	47	39	38	..	..	21	6	18	..	20	24	..	24	212
74	82	80	78	70	54	51	28	12	24	..	26	F	36	F	213
70	79	77	77	81	70	62	54	6	..	30	F+	F+	F+	F+	214
75	82	78	66	56	35	41	7	6	12	..	25	36	F−	F−	215
73	80	77	69	58	42	44	15	6	18	..	26	36	P+	F−	216
Series 300															
69	76	76	71	62	38	37	4	6	12	..	34	30	F	F	302
86	90	90	89	88	84	81	76	12	..	..	P+	F	G	G	303
56	63	58	61	60	50	45	34	18	..	..	G	G	G	G	304
53	55	51	52	55	39	37	21	18	..	..	G	G	G	G	305
45	55	54	56	56	42	36	27	18	..	..	G−	G−	G−	G−	306
62	65	62	63	60	51	48	34	12	..	..	F+	F+	F+	F+	307
63	66	60	65	56	46	41	19	30	..	..	P+	P+	F+	F+	308
52	58	54	55	54	42	42	32	18	..	..	F	F	F	F	309
56	71	60	64	61	57	55	54	36+	..	..	G	G	G	G	310
62	73	71	74	72	68	65	68	24	..	..	F	F	F	F	311
58	65	62	65	61	54	47	36	6	..	..	P+	F+	F+	F+	312
58	60	56	61	56	50	47	36	18	..	..	G	G	G	G	313
64	67	64	66	62	56	50	36	18	..	..	G	G	G	G	314
67	78	78	81	67	53	47	22	18	30	..	21	36	F	F	315
60	70	58	54	50	28	19	12	18	30	..	F	F	F	F	316
Series 400															
67	76	70	67	54	41	49	31	6	12	..	28	30	P+	F	402
88	91	88	93	89	74	84	80	12	..	..	P+	G−	G−	G−	403
55	59	49	43	30	..	..	5	6	..	..	24	24	..	..	404
69	70	59	55	40	..	..	11	6	..	..	24	24	..	..	405
60	64	43	34	32	..	..	4	6	..	..	18	24	..	..	406
60	63	46	41	32	..	..	4	6	..	..	18	24	..	..	407
55	59	41	47	35	..	..	15	6	..	..	24	24	..	..	408
59	64	37	31	27	..	..	−5	6	18	..	18	24	..	..	409
72	74	72	76	69	64	64	56	..	..	..	F	F	F	F	410
75	83	79	86	79	70	69	63	..	..	..	30	F	F	F	411
78	81	79	84	79	76	73	48	..	..	..	F	F	F	F	412
77	81	81	84	80	80	75	73	..	..	..	F	F	F	F	413
73	76	72	77	70	72	64	55	..	..	..	G	G	G	G	414
67	67	61	66	57	55	59	51	..	..	..	G	G	G	G	415
90	89	93	95	91	92	90	90	..	..	..	F	F	F	F	416

[b] Integrity recorded as durability in months or rating at 36 months. G, good; F, fair; P, poor; B, bad. SP, southern pine; DF, Douglas fir; WP, white pine; RD, redwood. Blank spaces mean specimen rated better than poor when removed from test prior to age 36 months.
[c] Under chalking, checking, and cracking are recorded the ages when the defects were first observed without a magnifying glass; cracking refers to sigmoid cracking only.

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tially, columns 2 and 6 of Table II. Specimens 316C, however, are notable exceptions in that the effectiveness of the coating over the unexposed backs fell from 60 to 26 during the 36 months of testing. This paint was litharge stirred in linseed oil without grinding in a paint mill and was imperfectly dispersed. Unlike most of the other paints, the unexposed backs of the specimens at the end of the test were lacking in gloss. It seems probable that reaction between the litharge and linseed oil continued long after the paint dried and left a distinctly porous coating. The measured effectiveness of the coating after 36 months was 19; if that of the back was 26, the effectiveness of the face was 12. The data of Table II, however, justify the assumption that the coatings of the practical exterior paints retained about the same effectiveness against moisture movement on the unexposed backs of the specimens throughout the test and that the changes in effectiveness of the coatings on the exposed faces were, in general, twice the changes recorded in Table I.

Visual Inspections of Exposed Paints

At each interval of 6 months during the exposure tests the coatings were inspected for chalking, checking, cracking, and integrity by the methods of the Forest Products Laboratory (*6*) for ordinary exposure tests. The results are summarized in abbreviated form in Table I. The term "chalking" has

TABLE I. AVERAGE EFFECTIVENESS OF COATINGS AGAINST MOISTURE MOVEMENT AT INTERVALS DURING EXPOSURE TO

Reference No.	Description of Primer for Group B and of All Three Coats for Group C	Group B, Primer Plus Two Coats of White Lead Paint: Av. effectiveness rating[a]							Integrity[b]			
		E_0	E_6	E_{12}	E_{18}	E_{24}	E_{30}	E_{36}	E^F_{end}	SP	DF	WP	RD
					Series 500								
	Vehicles without pigments:												
516	Linseed oil	63	72	67	55	53	48	..	33	..	24	..	..
514	75-gal. ester gum varnish	62	72	65	54	50	41	..	20	24	24	..	..
515	33-gal. ester gum varnish	64	73	68	59	52	44	..	24	24	24	..	..
512	Bakelite paint oil	62	70	64	55	49	43	..	24	27	29	..	..
513	Bakelite varnish	62	71	67	58	52	44	..	26	30	29	..	..
	Basic carbonate white lead in:												
502	Linseed oil	70	77	73	68	59	48	45	20	28	32	F	F
504	75-gal. ester gum varnish	67	75	69	61	56	42	..	17	26	30	..	.
505	33-gal. ester gum varnish	70	77	72	64	52	42	..	14	24	28	..	..
503	Bakelite paint oil	81	84	83	83	84	72	72	63	30	F	F	F
	Iron oxide red in:												
507	75-gal. ester gum varnish	70	77	73	73	73	62	61	52	F−	F−	F	F
508	33-gal. ester gum varnish	69	76	73	71	66	59	58	47	36	P+	F	F
506	Bakelite paint oil	63	71	65	61	58	48	47	31	F−	F−	F	F
	Asbestine in:												
510	75-gal. ester gum varnish	66	74	69	64	49	40	..	14	27	..	..	..
511	33-gal. ester gum varnish	67	75	71	66	52	42	..	17	26	30	..	..
509	Bakelite paint oil	74	80	78	76	79	68	63	52	P+	P+	F	F
					Series 600[d]								
	White lead in linseed oil:												
602	Pigment vol., 24.6%	68	77	72	72	63	42	47	26	24	P+	F	F
604	Pigment vol., 29.0%	68	77	72	72	63	40	42	16	27	F−	F−	F−
605	Pigment vol., 33.0%	68	77	73	72	61	41	44	20	27	36	F−	P+
606	Pigment vol., 38.7%	79	77	72	71	57	37	44	19	24	36	F−	P+
607	Pigment vol., 43.0%	71	78	73	71	59	38	47	23	24	36	F−	P+
608	Pigment vol., 47.7%	71	79	75	72	58	37	44	17	24	26	P+	F
	Titanium-barium pigment, ZnO, asbestine in linseed oil:												
609	Pigment vol., 29.0%	69	78	77	82	86	74	71	73	36	F	F	F+
610	Pigment vol., 33.0%	68	78	77	80	85	74	76	84	P+	F	F	F+
611	Pigment vol., 38.7%	69	78	78	80	85	72	69	69	P+	P+	F	F
612	Pigment vol., 43.0%	68	78	78	81	84	67	61	54	34	35	F	F
613	Pigment vol., 47.7%	70	79	78	80	85	68	59	48	36	35	36	P+
	White lead in Bakelite oil:												
603	Pigment vol., 24.6%	89	93	91	90	97	85	93	97	P+	G	G	G
614	Pigment vol., 29.0%	88	92	92	90	97	84	88	88	P+	G	G	G
615	Pigment vol., 38.7%	88	93	91	90	97	82	86	84	30	G	G	G
616	Pigment vol., 47.7%	89	93	87	79	81	78	69	49	18	F	G	G
					Series 700								
702	White lead in linseed oil	73	75	71	63	58	42	48	23	34	36	F−	F
703	White lead in Bakelite oil	83	84	84	90	86	73	81	79	36	F	F	F
	Paints applied by spray gun:												
704	202 sprayed	75	75	71	61	55	38	52	29	36	36	F	F
705	213 sprayed	78	81	74	75	61	44	58	38	24	24	24	24
706	214 sprayed	76	80	69	76	55	40	46	16	24	24	24	24
707	104 sprayed	84	85	80	82	82	71	77	70	F−	F−	F−	F−
708	108 sprayed	88	89	87	82	89	78	73	58	F−	F−	F−	F−
709	108 thinned and sprayed	87	88	84	84	84	71	69	51	F−	F−	F−	F−
710	709 force-dried	85	85	82	80	78	62	60	35	36	F−	F−	F−
711	110 sprayed	85	87	80	79	75	64	67	49	F−	F−	P+	F−
712	110 thinned and sprayed	85	83	75	65	66	57	58	31	F−	F−	F−	F
713	712 force-dried	84	84	74	58	66	54	60	36	F−	F−	F−	F
714	112 sprayed	85	86	83	80	82	72	69	53	F−	F−	F−	F
715	112 thinned and sprayed	86	86	84	70	81	70	69	52	F−	F−	F	F
716	715 force-dried	85	87	83	61	78	68	71	57	F−	F−	F−	F

[a] On group B the second- and third-coat paints have the same pigments as the primer and pigment volumes of 38.8 and 28.0%, respectively; on group C the second- and third-coat paints have the same pigments and the same pigment volumes as the primer.

its usual significance. "Checking" refers to readily visible checking; the earlier stages in which a magnifying glass was necessary to see checking clearly are not recorded in Table I. "Cracking" refers only to sigmoid cracking, which is not followed immediately by curling or flaking. Cracking followed immediately by curling and flaking is reflected promptly in the rating for integrity. The integrity of coatings is rated on a scale of good, good−, fair+, fair, fair−, poor+, poor, poor−, bad+, bad, and bad−. When the rating reaches poor, the coating is considered in need of repainting and durability is therefore defined as the age at which integrity is first rated "poor." If between inspections the rating falls from one better than poor to one worse than poor, the age at which poor was attained is calculated by linear interpolation. In Table I the data for integrity are summarized by recording either the durability or, if the integrity remained better than poor at the end of 36 months, the rating for integrity at age 36 months. Specimens removed from test before the last cycle, though still rated better than poor in integrity, are left blank under the integrity heading.

Chalking, checking, and sigmoid cracking depend on the nature of the coating, not on the nature of the wood, and therefore occurred simultaneously on the four woods. Crumbling, curling, and flaking, however, usually develop much more rapidly on southern yellow pine and Douglas fir than on northern white pine and redwood. For that reason it is necessary to record the durabilities, or final ratings in integrity, separately for the four woods.

Changes in Effectiveness of Paints with Age

In general the effectiveness of paints against moisture movement increases during the first few months of exposure to the weather. Nearly all of the coatings tested were more effective at age 6 months than they were before exposure. Previous tests likewise reveal that tendency (*3*). Some paints remain near their maximum effectiveness for many months while others soon pass through the maximum and decrease steadily in effectiveness thereafter. The two control paints, white lead in linseed oil (X02) and white lead in Bakelite paint oil (X03), illustrate the two types. White lead in linseed oil declined steadily in effectiveness after its maximum at 6 months, while white lead in Bakelite paint oil was almost as effective after 36 months as it was at the beginning. Chalking, checking, and cracking of paint coatings clearly determine which of these two types of behavior shall prevail, but the significant feature of chalking and checking in this connection is not the age at which they first appear but the rate at which they penetrate through the coating.

WEATHER AT 45° FACING SOUTH, AND SUMMARY OF VISUAL OBSERVATIONS OF DETERIORATION OF COATINGS (*Concluded*)

Group C, Three Coats of Paint of Kind Described															Reference No.
Av. effectiveness rating[a]								Chalking[c]	Checking[c]	Cracking[c]	Integrity[b]				
E_0	E_6	E_{12}	E_{18}	E_{24}	E_{30}	E_{35}	E^F_{end}				SP	DF	WP	RD	
Series 500															
21	21	10	..	..	..	..	−1	..	..	..	12	12	12	12	516
35	32	17	..	..	..	..	−1	..	..	..	6	6	6	6	514
65	55	31	..	..	..	..	−3	..	6	..	6	6	6	6	515
66	63	50	46	..	..	..	26	..	..	..	15	18	..	..	512
73	69	59	57	..	..	..	41	..	..	..	15	18	..	..	513
75	77	73	69	62	42	47	19	6	12	..	27	28	F	F	502
83	84	66	53	46	..	..	9	6	12	..	18	21	..	..	504
91	91	70	65	52	..	..	13	6	..	..	12	18	..	..	505
91	91	91	93	92	77	82	73	12	..	..	24	F	G	G	503
82	79	76	78	82	73	78	74	6	..	..	F	F	G	G	507
88	84	79	83	82	68	75	62	6	..	..	30	P+	G	G	508
81	79	75	80	84	73	77	73	6	..	..	G	G	G	G	506
70	65	52	43	..	..	..	16	6	..	12	15	18	..	..	510
83	76	54	48	..	..	..	13	6	..	12	15	..	..	..	511
78	75	71	73	67	44	44	10	6	..	12	21	33	36	36	509
Series 600[d]															
66	76	70	68	64	41	45	22	6	12	.	33	35	F	F	602
62	73	67	61	55	35	39	26	6	12	..	32	30	P+	F	604
63	73	68	62	55	36	38	20	6	12	..	30	30	P+	F	605
63	75	68	57	43	32	39	20	6	..	..	28	30	P+	F	606
64	75	66	53	46	31	38	22	6	..	..	26	28	P+	F	607
67	76	68	60	36	29	36	20	6	..	..	26	26	P+	F	608
53	75	72	74	80	68	63	73	6	..	30	36	F−	F−	F	609
63	73	71	72	79	66	63	63	6	..	30	P+	F−	F−	F	610
67	76	75	73	73	59	48	34	6	..	30	36	P+	F−	F	611
66	76	74	70	61	38	40	26	6	..	30	24	36	P+	F	612
66	76	72	58	48	26	28	12	6	..	30	24	30	24	F	613
87	90	88	79	95	81	89	91	12	..	..	P+	G	G	G	603
87	91	89	88	96	82	88	88	12	..	..	30	G	F	G	614
87	91	87	84	87	56	55	40	12	..	..	24	F	P+	G	615
85	90	86	80	64	28	29	22	12	..	..	18	36	36	G	616
Series 700															
72	73	69	63	53	35	37	2	6	12	..	27	30	F−	F	702
88	90	89	80	91	85	88	88	12	..	..	34	F	G	G	703
68	71	66	64	52	30	41	14	6	12	..	30	36	F	F	704
73	79	75	64	73	60	50	27	6	24	..	24	P+	F	P+	705
72	74	79	58	78	69	68	64	6	..	30	24	F−	F−	F−	706
84	86	81	80	83	78	84	84	..	..	..	F	F	G	G	707
85	87	82	84	84	77	87	89	..	..	..	F	F	G	G	708
86	89	86	80	86	80	87	88	..	..	..	F	F	G	G	709
84	86	80	78	80	74	80	76	..	..	..	F	F	G	G	710
83	84	83	74	82	79	82	81	..	..	..	F	F	G	G	711
67	68	63	65	66	59	65	63	..	..	..	F	F	G	G	712
63	63	58	66	59	51	54	45	..	..	..	F	F	G	G	713
85	86	83	79	84	80	88	91	..	..	..	F	F	G	G	714
77	77	71	78	72	60	73	69	..	..	..	F	F	G	G	715
65	69	63	77	64	57	61	57	..	..	..	F	F	G	G	716

Series 100, Aluminum Paints

As priming coats under white lead paint in place of conventional priming (group B), all of the aluminum paints improved both the initial and the maximum effectiveness during subsequent exposure that is characteristic of white lead paint when used for all three coats. From the point of view of protection this long maintenance of effectiveness is more important than increased initial effectiveness (*9*).

Aluminum in the paste form proved as effective as dry aluminum powder of standard varnish grade when substituted pound for pound in the same vehicles (compare 104 with 106 and 105 with 108). The paste aluminum, however, contained 40 per cent mineral spirits and made paint equivalent in composition to a mixture of 1.07 pounds (0.485 kg.) of dry aluminum per gallon (3.79 liters) of varnish of slightly lower nonvolatile content. Such mixtures made with dry aluminum (107 and 109) proved less effective than the paints made with 2 pounds of dry powder or 2 pounds of paste aluminum per gallon.

For equal effectiveness, therefore, less aluminum is required in the form of aluminum paste than in the form of dry powder of standard varnish grade. Subsequent tests not reported here indicate that dry powder of standard lining grade is likewise effective with lower proportions of aluminum than the coarser standard varnish grade.

Two vehicles, shellac plasticized with castor oil and a nitrocellulose lacquer, proved lacking in durability either as

TABLE II. AVERAGE EFFECTIVENESS[a] OF UNEXPOSED BACKS OF CERTAIN SPECIMENS DETERMINED AT CONCLUSION OF WEATHERING TESTS

Reference No.	E_0	$(E^B_{36} + E^F_{Al})/2$ (Detd.)	E^B_{36} (Calcd.)	Reference No.	E_0	$(E^B_{36} + E^F_{Al})/2$ (Detd.)	E^B_{36} (Calcd.)
202B	68	77	64	302C	69	80	70
203B	79	85	80	315C	67	81	72
204B	69	78	66	316C	60	58	26
205B	72	80	70	602C	66	74	58
206B	72	80	70	604C	62	71	52
207B	73	80	70	605C	63	73	56
208B	68	79	68	606C	63	74	58
209B	68	78	66	607C	64	72	54
210B	68	77	64	608C	67	71	52
211B	68	77	64	611C	67	76	62
212B	67	78	66	612C	66	72	54
213B	72	78	66	613C	66	67	44
214B	69	79	68	614C	87	89	88
215B	70	79	68	615C	87	80	70
216B	70	79	68	616C	85	63	36

[a] E_0 = initial effectiveness rating, the same for face and back; E^F_{Al} = effectiveness of aluminum paint applied to face at conclusion of exposure test, assumed to be 90; E^B_{36} = effectiveness of back of specimens at age 36 months.

primers for white lead paint (group B) or as complete paints (group C). All the other vehicles tested made aluminum primers that greatly improved the maintenance of effectiveness throughout the life of white lead paint. From this point of view there was little basis for preference among the satisfactory vehicles; all left coatings that were more effective after 36 months than were many good paints initially (series 300, group C, for example). Among the satisfactory aluminum primers, however, some proved more successful than others in prolonging the life of the coating on southern yellow pine and Douglas fir. Primer 111B, for example, made with ester gum varnish of 33-gallon length, was not entirely satisfactory in improving durability on southern yellow pine and Douglas fir although it was satisfactory in maintaining effectiveness. Primers 114 and 115, made with linseed oil without resin, were very satisfactory from the point of view of durability but were not correspondingly superior to the other satisfactory aluminum primers in effectiveness against moisture movement. Raw linseed oil does not make an aluminum primer of proper consistency for good working properties, but kettle-bodied linseed oil makes a very satisfactory one.

As complete paint coatings (group C), all of the satisfactory aluminum paints proved outstandingly durable both in maintenance of integrity of the coatings on all woods and in maintenance of effectiveness against moisture movement.

Series 200, White Pigments in Linseed Oil

Except where otherwise indicated, all paints made with granular pigments only throughout this study were mixed in such proportions that the priming-coat paint contained 19 per cent total pigment, 58 per cent nonvolatile vehicle, and 23 per cent volatile thinner by volume; second-coat paint, 29 per cent total pigment, 45 per cent nonvolatile vehicle, and 26 per cent volatile thinner; and third-coat paint, 27 per cent total pigment, 69 per cent nonvolatile vehicle, and 4 per cent volatile thinner. Second-coat white lead paint for group B was mixed with 29 per cent pigment, 41 per cent linseed oil, and 30 per cent volatile thinner.

As priming coats under white lead paint, the white paints of series 200 did not alter significantly the initial or maximum effectiveness against moisture movement or the changes in effectiveness with age. All primers that contained zinc oxide —205 to 207, and 213 to 216—gave rise to conspicuous alligatoring of the top coats of white lead paint in place of the usual finely reticulated and inconspicuous checking normal for white lead paint. Similar alligatoring occurred throughout the tests wherever there was zinc oxide in a primer under white lead—for example, 412B, 413B, 705B, and 706B—and was severe enough to reduce the durability of the coatings to 24 months or less even on white pine and redwood. Over primers made with antimony oxide, titanium dioxide, titanium-barium pigment, zinc sulfide, and lithopone (208 to 212, inclusive), white lead paint checked in the normal inconspicuous manner and the coatings proved fully as durable as the control specimens with white lead paint for primer and top coats. Specimens 204 on which the primer was basic-sulfate white lead developed alligatoring of the white lead top coats on group B and sigmoid cracking of the basic-sulfate white lead paint on group C. It was therefore inferred that the pigment manufacturer, through an error, had supplied a basic-sulfate white lead containing some zinc oxide. Analysis of a sample of the original supply of dry pigment revealed 6.8 per cent zinc oxide by weight.

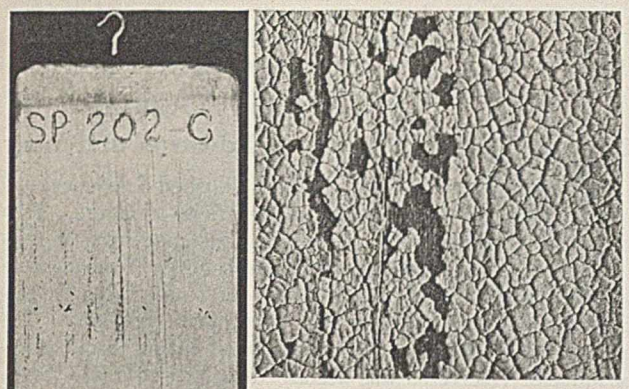
The effectiveness at 36 months was slightly higher than that at 30 months for most of the specimens of group B that survived until the 36-month period. This is an experimental error resulting from the fact that the 36-month period ended when the exposed specimens were at an unusually high moisture content because of a thaw following a heavy fall of snow. Two weeks in 65 per cent relative humidity failed to establish equilibrium moisture content closely enough and reduced the subsequent absorption in 97 per cent relative humidity. The uncoated control panels were not subject to that error, which therefore operated to make the effectiveness seem higher than it actually was. All of the values for the 36-month period throughout the study are probably slightly too high, but the error is greater for coatings of low effectiveness than for those of high effectiveness.

In group C of the 200 series where the same pigments were used in all three coats of paint, the paints represent three different types of disintegration with age: (*a*) rapid chalking leading to early failure by erosion, (*b*) moderately rapid chalking followed by checking and eventually by crumbling, (*c*) slow chalking, sometimes followed by checking, but always followed eventually by cracking, curling, and flaking (*2*), though the type of cracking is not always sigmoid. The distinction between rapid and slow chalking refers to the rate at which chalking penetrates through the coating, not to the age at which it is first observable; with most of the white paints, this occurred at about 6 months. To the first type belong paints 209 to 212, made, respectively, with titanium dioxide, titanium-barium pigment, zinc sulfide, and lithopone. These paints showed very material loss of effectiveness as early as 12 months, and within 2 years the coatings became too thin to hide the surface of the wood, failure taking place about as rapidly on white pine and redwood as on southern pine and Douglas fir. To the second type belongs paint 202, made with basic-carbonate white lead. The effectiveness declined from the maximum at 6 months at first slowly, then more rapidly, and crumbling developed more rapidly on southern pine and Douglas fir than on white pine and redwood. Pure basic-sulfate white lead probably belongs in this class, but the presence of zinc oxide in the sample for paint 204 caused it to develop sigmoid cracking instead of checking. To the third type belong paints 205, 207, and 213 to 216, which contain zinc oxide alone or in admixture with other pigments. The effectiveness of these paints varied with age between the course exhibited by basic-carbonate white lead and the course exhibited by paint 214, which changed little if at all in effectiveness between 6 and 24 months and was still high in effectiveness and intact on all woods after 36 months. The facts that chalking, though clearly evident at 6 months, penetrated the coating very slowly, checking remained entirely absent, and sigmoid cracking was delayed to the thirtieth month account for the long retention of effectiveness by this paint. Paint 208, made with antimony oxide, did not proceed far enough in deterioration during the 36 months for definite classification. It probably resembles white lead paint, but chalking and checking proceed less rapidly. Microscopic checking appeared at 30 months and was not yet visible without magnification at 36 months.

In initial and maximum effectiveness all of the paints that contained either white lead or zinc oxide were superior to any of the paints that contained neither white lead nor zinc oxide. The difference is too small to be significant as far as protection of wood is concerned but is of interest in connection with the theory of the action of pigments in paints.

Series 300, Colored Pigments in Linseed Oil

As primers under white lead paint, the colored pigment paints except red lead and litharge proved slightly superior to any of the white priming paints of series 200 but inferior to the satisfactory aluminum primers of series 100 in their effect on maintenance of effectiveness against moisture movement. The iron oxide pigments, lemon chrome yellow, Prussian blue, and graphite likewise improved the integrity of the



SPECIMEN 202C, PAINTED WITH THREE COATS OF WHITE LEAD IN LINSEED OIL, AFTER 24-MONTH EXPOSURE

The specimen is 4 inches (10.1 cm.) wide; magnified area is 3/8 inch (1 cm.) square. Typical of failure by checking and crumbling; effectiveness, 57.

coating on southern yellow pine and Douglas fir. However, they were not quite so satisfactory in that respect as the summarized data of Table I indicate, because in most cases the checking pattern of the coating was coarser and more conspicuous by reason of the color showing through, although it was not coarse enough to be classified as alligatoring.

As complete paint coatings, the colored pigment paints except red lead proved lower in initial and maximum effectiveness than the paints of series 200 that contained white lead or zinc oxide and approximately equal to the white paints containing neither white lead nor zinc oxide. Red lead increased in effectiveness up to the eighteenth month, after which its effectiveness decreased rapidly. The litharge paint rapidly lost effectiveness after 6 months; as already pointed out, the unexposed backs as well as the faces became ineffective by the end of the test. The two chrome yellow paints remained as effective after 36 months as they were initially. The other colored pigment paints followed a course of change in effectiveness similar to that of white lead paint but at somewhat slower rates so that, while less effective than white lead paint at the beginning, they were as effective or a little more effective at the end of 36 months. In maintenance of the integrity of the coatings all of the colored pigment paints except red lead paint were more durable than any of the white paints of series 200 except 208 and 214, neither of which had yet reached the end of its life. On the whole the colored pigment paints took longer to develop chalking than did the white paints. The colored pigment paints, except red lead and litharge paints, developed neither checking nor sigmoid cracking during the test.

Series 400, Transparent Pigments in Linseed Oil

As primers under white lead paint the transparent pigment paints, 404 to 409, group B, proved very similar to each other and to the white paints of series 200 that contained no zinc oxide, such as 208 to 212. Checking of the white lead paint over the transparent pigment primers followed the normal inconspicuous pattern. Up to 30 months, when these specimens were removed from test, the coatings maintained their integrity about as well as the coatings based on white primers free from zinc oxide.

The complete paint coatings with transparent pigments, group C, looked more like varnishes than paints when freshly applied, but chalking set in within 6 months and penetrated rapidly, after which the coatings turned white and had fairly good hiding power. Paint 409, made with English chalk, developed checking within 18 months. None of the others developed checking and none sigmoid cracking. The course of the changes in effectiveness and the durability were very similar to those of the rapidly chalking white paints, 209 to 212, group C.

Series 400, Aluminum and Granular Pigments in Linseed Oil

As primers under white lead paint, paint 411, which contained red lead, and 412 and 413, which contained zinc oxide, led to early failure both in integrity and in effectiveness. The other primers of this group, in which aluminum powder was mixed with white lead, iron oxide, or asbestine, proved very satisfactory in maintenance of both effectiveness and integrity of the coatings. In each case the addition of aluminum powder made the primer more satisfactory than the corresponding primers made with the granular pigments without the aluminum. In group C where the paints were used for all three coats, the admixture of aluminum improved the effectiveness, the maintenance of effectiveness, and the durability.

Series 500, Vehicles

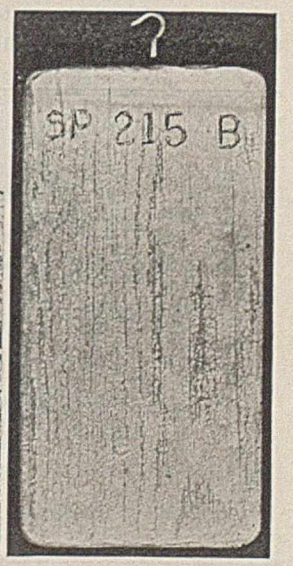
As primers under white lead paint none of the clear vehicles (512 to 516) exhibited any advantage either in effectiveness or in durability. As complete coatings they were all much less durable than good paints. Linseed oil and 75-gallon ester gum varnish were low in effectiveness from the beginning. The 33-gallon ester gum varnish, Bakelite resin paint oil, and Bakelite resin varnish were fairly effective initially, increasingly so in the order named, but they all lost effectiveness much more rapidly than good paints.

As a vehicle for white lead pigment either for the priming coat only or for all three coats, neither of the ester gum varnishes proved as satisfactory as linseed oil. The Bakelite resin paint oil with white lead, however, made a priming paint that compared favorably with good aluminum priming paints (series 100B) and a three-coat paint of high initial effectiveness, excellent maintenance of effectiveness, and good durability. Both chalking and checking were retarded by substituting the Bakelite paint oil for linseed oil but the paint finally failed by cracking and flaking rather than by crumbling.

The Bakelite paint oil was a poorer vehicle than the ester

SPECIMEN 215B, PAINTED WITH A PRIMER CONTAINING ZINC OXIDE AND LITHOPONE FOLLOWED BY TWO COATS OF WHITE LEAD PAINT, AFTER 24-MONTH EXPOSURE

The specimen is 4 inches (10.1 cm.) wide; the magnified area is 3/8 inch (1 cm.) square. Typical of failure by alligatoring; effectiveness, 34.



gum varnishes for iron oxide primers to be used under white lead paint, at least from the point of view of maintaining effectiveness. With iron oxide for pigment the ester gum varnishes made distinctly better primers than they did with either white lead or asbestine for pigment, but with Bakelite paint oil iron oxide made a less satisfactory primer than was obtained with either white lead or asbestine.

As a vehicle for all three coats of paint the Bakelite paint oil was superior on the whole to either of the ester gum varnishes when pigmented with white lead, iron oxide, or asbestine. The 75-gallon ester gum varnish was more satisfactory than the 33-gallon varnish when pigmented with white lead or iron oxide but not when pigmented with asbestine. Although all three paints made with asbestine were comparatively short-lived (and were transparent), in each case they were more effective and more durable than the corresponding clear vehicles without pigmentation.

Series 600, Varying Pigment Volume

In the 600 series the paints in both groups B and C have the same kind of pigment in all three coats, but in group B the second and third coats have pigment volumes of 38.8 and 28.0 per cent, respectively; in group C they have the same pigment volumes as the priming coats. Pigment volume is defined as the proportion of pigment by volume in the nonvolatile part of the paint. The experiments cover the range from moderate to high pigment volumes for gloss paints. Commercial paints often have lower pigment volumes than any of the paints tested.

The experiments on pigment volume are not extensive enough to justify too detailed discussion. It appears, however, that there is a fairly wide range of pigment volume within which the effectiveness and maintenance of effectiveness do not vary greatly but that the extremely high pigment volumes lead to earlier loss of effectiveness and reduced durability. Even the unexposed backs of the coatings of pigment volume 38.7 per cent and higher lost effectiveness seriously by the end of 36 months, as shown in Table II.

Series 700, Spray Application

Comparison of the results of application by spray gun with the results of brush application of similar paints in other series reveals no significant differences attributable to the method of application. Addition of extra volatile thinner to aluminum primer or paints before spraying seems to be detrimental to the maintenance of effectiveness. Such thinning has been common practice in spray application of aluminum primers, but there seems to be no good reason for it inasmuch as aluminum paint without such thinning is particularly easy to apply with good spraying equipment. Forced drying is likewise frequently practiced in mill priming. In these tests the results with forced drying are not consistent enough to justify conclusions on the subject.

Comparison with Data of Edwards and Wray

Edwards and Wray (*10*) recently published data on changes with age in the permeability of paints to moisture. They used a different technic for measuring the movement of moisture (*12*) and expressed their results in terms of the moisture impedance of the coatings, which is the reciprocal of the permeability in mg. of moisture per sq. cm. per hour. The method of calculating the effectiveness rating from the impedance or vice versa was described by Edwards (*8*). Seven paints tested by Edwards and Wray at New Kensington, Pa., resemble paints reported in this paper closely enough to permit comparisons.

In Table III the data reported by Edwards and Wray for three coats of paint on white pine are recalculated and expressed in terms of the effectiveness ratings. Below each paint selected, the writer's results with a similar paint are given, expressed in terms of the effectiveness of the exposed face only, assuming that the unexposed backs retained their initial effectiveness. For five of the seven kinds of paint the results agree excellently. Paints usually deteriorate somewhat more rapidly at Madison, Wis., than at New Kensington, Pa. For two coatings, lithopone in linseed oil and unpigmented 50-gallon Bakelite varnish, the writer's results are lower than those of Edwards and Wray. Apparently the Bakelite varnish was much more durable at New Kensington than at Madison.

Maintenance of Effectiveness on Different Woods

The effectiveness recorded in Table I is the average of separate determinations on four woods. In general, paints behave in the same way on all woods during the early life of the coatings, but, once crumbling or flaking sets in, the disintegration proceeds more rapidly on southern pine and Douglas fir than on white pine and redwood. Paints that fail rapidly by chalking, however, do so at nearly the same rate on all four woods.

In Table IV the initial effectiveness and the calculated effectiveness of the exposed face of the specimens when last examined are given for each wood separately in the cases of sixteen coatings selected for illustration. Eight of the coatings exhibited little or no difference in behavior on the four woods as judged by visual inspection, while eight failed in integrity much more rapidly on some woods than on others. Of the first group of eight coatings, six were exceedingly durable and remained fair or good in integrity on all woods after 36 months while two failed rapidly on all woods—209C by rapid chalking and 213B by conspicuous alligatoring. The second group of eight coatings includes six of average durability, one (203C) of great durability but failing on southern pine within 36 months, and one (513C) a durable varnish but low in durability as compared with paints.

The variations in initial effectiveness of coatings on the different woods are due principally to differences in the rate of absorption of moisture by the uncoated control specimens and to practical difficulties in applying the coatings in exactly the same thickness on all woods. All coatings except 203C were less effective at the end of the exposure test than they were initially, and 203C had less than its initial effectiveness on

Table III. Comparison of Paints with Results Reported by Edwards and Wray

No. in Table I	Description of Paint (Edwards and Wray)	Effectiveness Ratings[a] E_0	E_6^F	E_{12}^F	E_{18}^F	E_{24}^F	E_{36}^F
	Aluminum powder in 80-gal. ester gum varnish	95	97	96	96	..	..
110		90	96	84	84	84	76
	Aluminum powder in glyceryl-phthalate varnish	97	98	97	97	98	97
112		93	97	85	85	89	79
	Aluminum powder in 50-gal. Bakelite varnish	97	98	97	97	98	98
108		95	97	87	87	89	85
	White lead and zinc oxide in linseed oil	86	87	90	83	83	48
213		74	90	86	82	66	28
	Lithopone in linseed oil	83	89	82	65	..	..
212		55	55	39	23	21	..
	Gray Bakelite enamel	88	93	89	87	..	..
203		89	97	95	95	93	86
	Clear 50-gal. Bakelite varnish	91	90	87	87	87	85
513		73	65	45	41	..	..

[a] E_0, E_6^F, etc. = effectiveness rating for exposed face of the coatings at age indicated by subscript.

TABLE IV. EFFECTIVENESS[a] OF COATINGS ON DIFFERENT WOODS BEFORE AND AFTER EXPOSURE, AND INTEGRITY RATINGS AFTER EXPOSURE

Reference No.	E_0 SP	E_0 DF	E_0 WP	E_0 RD	E^F_{end} SP	E^F_{end} DF	E^F_{end} WP	E^F_{end} RD	Integrity at End of Test SP	Integrity at End of Test DF	Integrity at End of Test WP	Integrity at End of Test RD	Age at Last Inspection, Months
Coatings Remaining Approx. Equal in Integrity on All Woods at Last Inspection													
104C	94	92	93	88	86	72	81	86	G	G	G	G	36
105C	96	93	93	93	86	77	81	85	F	G	G	G	36
115C	93	87	89	81	79	65	85	57	G	G	G	G	36
208C	74	62	64	72	44	22	52	46	G	G	G	G	36
214C	73	64	66	74	59	58	40	64	F+	F+	F+	F+	36
304C	66	49	58	42	48	19	42	36	G	G	G	G	36
209C	66	57	56	68	18	17	−4	34	B	B	P	P−	24
213B	75	73	72	64	−3	3	6	22	B−	B	P	P	30
Av.	80	72	74	73	52	42	48	54					
Coatings Showing Marked Differences in Integrity on Four Woods at Last Inspection													
203C	91	86	89	90	75	90	91	90	P	G−	G	G	36
202C	76	65	71	76	20	9	31	46	B	B+	F	F	36
207C	79	68	73	76	3	26	9	40	B−	P+	P+	F	36
213C	77	69	71	78	13	29	27	48	B	F	P	F	36
111B	92	90	90	90	16	44	82	60	B	B	F	F	36
216C	74	69	70	76	−4	17	20	34	B	P	P+	F−	36
315C	76	58	69	56	24	20	20	24	B	P	F−	F−	36
513C	81	60	72	70	23	46	70	40	B	P	F	F	18
Av.	81	71	76	76	21	35	42	48					

[a] E_0 = initial effectiveness rating; E^F_{end} = effectiveness of exposed face at end of exposure test. SP = southern pine; DF = Douglas fir; WP = white pine; RD = redwood.

southern pine. Among the coatings showing little difference in integrity on the four woods at the end of the test, there is, as a rule, no striking contrast in final effectiveness on southern pine and Douglas fir as compared with white pine and redwood. For the group as a whole the average final effectiveness on southern pine and Douglas fir is 52 and 42, and on white pine and redwood 48 and 54, respectively. For coatings 209C and 213B, which failed early on all woods, the final effectiveness seems to be higher on redwood than on the other woods, but to all practical purposes it is as low on white pine as it is on southern pine or Douglas fir. Of coatings 304C and 104C, both of which retained good integrity at 36 months, 304C was relatively low in effectiveness and 104C relatively high in effectiveness throughout the life.

Among the coatings showing marked difference in integrity on the four woods at the end of the test, there is a fairly good parallel between final effectiveness ratings and final integrity on the four woods. Coating 203C failed in integrity and showed loss of effectiveness only on southern pine. Coating 202C failed in integrity on southern pine and Douglas fir and had less effectiveness on those woods than on the others. Coating 207C remained intact for 36 months on redwood only and retained moderate effectiveness on redwood only. For the group as a whole the average final effectiveness on southern pine and Douglas fir was 21 and 35, and on white pine and redwood 42 and 48, respectively. Coating 315C, however, was about equally ineffective on all woods at 36 months although it still rated fair− in integrity on white pine and redwood and was considered a failure in integrity on southern pine as early as 21 months. On the other hand, coating 203C was rated 75 in effectiveness at 36 months although rated poor in integrity on southern pine.

For closer comparison of the changes in effectiveness during the life of coatings with the changes in integrity judged by visual inspection, Table V records average results obtained with the two control paints in group C. These paints were white lead in linseed oil (X02) and white lead in Bakelite paint oil (X03), the former a paint of fairly high initial effectiveness steadily decreasing after passing its maximum and the latter a paint of very high and long-maintained effectiveness. Each paint was applied to seven specimens of each wood, one specimen in each of the seven series of tests. The values recorded in Table V are averages for these seven specimens in each case.

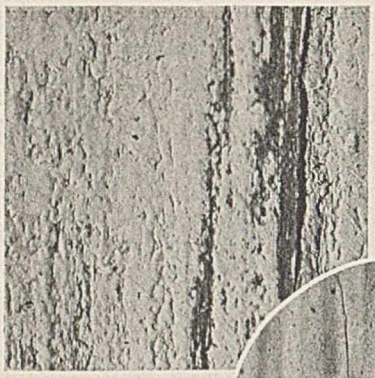
At age 12 months, coatings of X02 on all woods were approximately equal in effectiveness and as effective as they had been initially. They were chalking markedly and were checking enough to be seen without a magnifying glass. At 18 months they appeared much the same to visual inspection, but on southern pine and Douglas fir the effectiveness was slightly lower than its initial value. At 24 months, decrease in effectiveness on southern pine and Douglas fir was definitely more serious than on white pine and redwood, though to visual inspection the coatings remained intact on all four woods. At 30 months the effectiveness was very low on all four woods, though lowest on southern pine and Douglas fir, and failure in integrity was clearly visible on southern pine and Douglas fir though the coatings remained intact on white pine and redwood even at 36 months. It seems safe to conclude that paints of this type fail as protective coatings before they fail visibly in integrity. It is also clear that such paints on woods that hold paint well may remain intact to visual inspection for a long time after they have failed in protection, a conclusion drawn by the writer as early as 1926 from observations of wood checking and other signs of wood

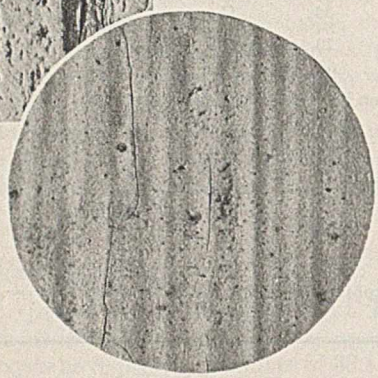
TABLE V. EFFECTIVENESS[a] AND INTEGRITY RATINGS FOR TWO PAINTS ON FOUR WOODS AT EACH INTERVAL OF 6 MONTHS DURING THE TESTS

Reference No.[b]	E_0	E^F_6	E^F_{12}	E^F_{18}	E^F_{24}	E^F_{30}	E^F_{36}
X02C:							
SP	76	86	76	66	42	−2	8
DF	63	85	71	61	47	9	17
WP	71	83	77	77	63	23	23
RD	65	83	75	65	59	21	35
X03C:							
SP	91	95	91	87	93	59	65
DF	87	93	89	93	93	85	87
WP	89	93	91	93	95	85	89
RD	87	93	91	91	93	85	87

	Integrity Detd. by Visual Inspection 0 mo.	6 mo.	12 mo.	18 mo.	24 mo.	30 mo.	36 mo.
X02C:							
SP	Glossy	Chalking	Checking	F	F−	P−	B
DF				F	F	P	B
WP				F	F	F	F
RD				F	F	F	F
X03C:							
SP	Glossy	Flat	Chalking	Microscopic checking	F	F−	P
DF					G	F+	F
WP					G	G	G
RD					G	G	G

[a] E_0 = initial effectiveness rating; E^F_6, E^F_{12}, etc. = effectiveness of exposed face at 6, 12, etc., months.
[b] X02C = average of specimens numbered 102C, 202C, etc., to 702C.





MAGNIFIED VIEWS OF TWO TYPES OF FAILURE AFTER 24-MONTH EXPOSURE; EACH AREA IS 3/8 INCH (1 CM.) WIDE

Left: Specimen 210C, titanium-barium pigment in linseed oil. Typical of failure by rapid chalking; effectiveness, 28.

Right: Specimen 214C, titanium-barium pigment, zinc oxide, and asbestine in linseed oil. Typical of very durable white paint chalking slowly and with sigmoid cracking in early, still microscopic stage; effectiveness, 92.

weathering in painted panels on which the coatings were still considered intact (*1*).

Paint X03 presents a different picture. Chalking was first observed at 12 months, microscopic checking at 18 months. The checking remained microscopic even after 36 months. On southern pine, slight cracking and flaking on most specimens at 24 months led to a rating of fair in integrity which was not yet paralleled by any loss in effectiveness but did appear as loss of effectiveness at 30 and 36 months, by the end of which time the integrity was rated poor on most specimens. On Douglas fir slight flaking was evident in the integrity ratings at 30 and 36 months, but the effectiveness remained practically as high as it was initially. On white pine and redwood the integrity remained good, and the effectiveness retained its initial value at 36 months. Coatings of this type, therefore, do not exhibit loss of effectiveness until break-up of the coating is clearly evident to visual inspection.

Effectiveness as a Technical Measure of Paint Durability

Measurement of the changes in effectiveness against moisture movement during the aging of paint coatings might prove useful as a basis for an arbitrary definition of paint durability for strictly technical purposes.

Durability might be defined, for example, as the age of the coating at which its effectiveness falls to 50 per cent of its initial value. Such a definition would give significance to a term that is now a meaningless catchword unless carefully defined in accordance with a standardized system of visual inspections and evaluation such as that in use by the Forest Products Laboratory (*3*). Even in the latter event, measurement of durability by visual inspection rests upon personal judgments and the uncertainties inherent in subjective methods. Measurement of durability in terms of effectiveness against moisture movement would eliminate personal judgments entirely, substituting readings of the balance instead.

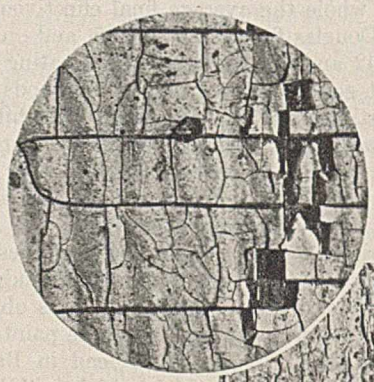
On the other hand, durability defined in terms of effectiveness is not identical with durability as the user of house paint understands it. Paints, like white lead in linseed oil, that the average user considers durable for at least 4 or 5 years on white pine and redwood would be rated as durable for less than 3 years; paints like white lead in Bakelite paint oil would have to reach a very advanced stage of disintegration at which successful repainting is impossible before reaching the end of the technical life. Present methods of evaluating durability, however, suffer more or less from the same disadvantage because the technologist is prone to set the point of failure much earlier than does the practical user of paint.

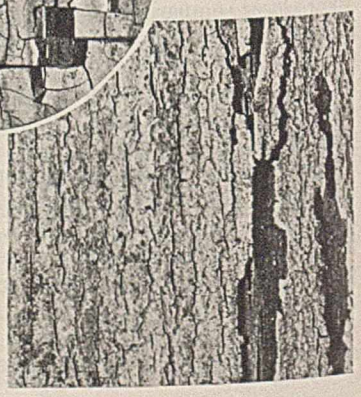
Most of the common white paints lie between the extremes represented by white lead in linseed oil and white lead in Bakelite paint oil; that is, they retain effectiveness somewhat longer than white lead in linseed oil but become practically ineffective long before the coatings disintegrate badly on woods like white pine and redwood. The assumption often made by paint technologists that protection is satisfactory as long as integrity is satisfactory is unsound. The fallacious assumption has survived so long because little or no effort was made to measure protection, and in the common uses of house paint protection is of minor consequence anyway.

For special uses where protection by paint is really necessary, paints should be chosen in accordance with their ability to retain effectiveness against moisture movement for a long time, as revealed by tests of the kind described in this paper. Paints exhibiting the effectiveness history of white lead in Bakelite paint oil possess the necessary quality but are subject to the disadvantage that the form of ultimate failure is very unsatisfactory from the point of view of repainting. Much the same effectiveness history is attained when the white paint is applied over a good aluminum primer but in that case the white paint, if wisely chosen, gradually wears thin enough to show the color of the aluminum beneath, revealing the need for repainting, at a time when the effectiveness of the coating is still fairly high.

Conclusions

1. The protection afforded wood by paint coatings, which can be measured in terms of effectiveness against moisture movement, usually increases slightly during the first few months of exposure to the weather after which it may remain nearly constant until the coating disintegrates or, as is more often the case, it may decrease steadily to a negligible value according to the nature of the paint.





MAGNIFIED VIEWS OF TWO TYPES OF FAILURE AFTER 24-MONTH EXPOSURE; EACH AREA IS 3/8 INCH (1 CM.) WIDE

Left: Specimen 205C, leaded zinc oxide in linseed oil. Typical of failure by conspicuous sigmoid cracking, curling, and flaking; effectiveness, 60.

Right: Specimen 213C, white lead, zinc oxide, and asbestine in linseed oil. Typical of failure by cracking, curling, and flaking; effectiveness, 66.

2. Practically negligible protection is reached with many paints long before the integrity of the coating is seriously impaired, especially on those woods, like white pine and redwood, that hold paints well.

3. Deep chalking, deep checking, and cracking of coatings lead to loss of protection in advance of failure in integrity. Coatings in which chalking and checking penetrate slowly, or in which checking and cracking are long delayed, retain approximately their initial protection until very serious flaking or scaling has developed. The initial protection by coatings, however, varies widely with different kinds of paint and cannot be determined by visual examination.

4. In the common uses of house paints on wood, protection is of minor importance. For special uses in which maintenance of protection may be important, good aluminum priming paints followed by ordinary paints are especially useful because disintegration of the top coats can be made to reveal the need for repainting at a time when the protection is still satisfactory and the surface is still in good condition for repainting.

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TOXICOLOGY OF ROTENONE

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NOTEWORTHY advances in knowledge of the chemistry of derris products have caused related toxicological studies to be devoted largely to rotenone and closely allied compounds. Such studies on warm-blooded animals have been summarized by Haag (*2*) and by Roark (*3*). Experimental administration of rotenone has been conducted either by mixing the solid compound with the food, by feeding it in capsules, by dusting it on the animal's coat, or by injecting it hypodermically in solution in an organic solvent. Haag reported marked differences in toxicity depending upon the species of animals used and the method of administration. For example, the fatal dose for guinea pigs was about 75 mg. per kg. when solid rotenone admixed with food was given, but the dose was only 2 mg. per kg. when rotenone dissolved in glycol was injected intraperitoneally. Similarly, for rabbits the oral fatal dose was 1.6 mg. per kg., while the intravenous dose was 0.35 mg. per kg. In connection with an investigation on the use of rotenone as a parasiticide, Crane (*1*) found that dogs could tolerate doses of solid rotenone up to 200 mg. per kg. without toxic effects.

Such marked differences in the toxicity of rotenone with the various methods of administration suggest that the high oral fatal dose may be due either to the rapid destruction of the drug or to slow absorption. The latter is more probable, for rotenone is practically insoluble in aqueous media. More rapid absorption might be expected if the drug were given in a finely divided state or, better still, in solution. As the common organic solvents for rotenone are not without effect on animals, they cannot be used without influencing the results. The most desirable solvent should be physiologically inactive and one that might be expected to be ingested as food. The liquid fats are suitable but are poor solvents for rotenone. However, it was found that the compound formed comparatively stable supersaturated solutions in olive oil, although the solubility at ordinary temperatures was only about 0.75 per cent. Therefore, olive oil has been used generally throughout this investigation as a solvent for rotenone.

When given orally, rotenone dissolved in oil is much more toxic than when given as the solid or in suspension. The oral minimum lethal dose for white rats is about 25 mg. per kg., and for guinea pigs 12 mg. per kg.

The toxicity of rotenone ingested orally depends upon the physical state of the compound. Finely divided rotenone is more toxic than coarse crystals. The toxicity of solid rotenone is increased by feeding fats, the increase being roughly parallel to the amount of fat ingested. When sublethal doses of rotenone are given daily in olive oil, the total dose received before death is larger than the acute toxic dose by an amount which varies in inverse order with the size of the daily dose. This is taken to indicate that there is a partial elimination or detoxification of the rotenone, and either that the compound accumulates in an active form in the tissues or that the injuries are additive.

Toxicity in Olive Oil

It was soon found that rotenone in olive oil solution fed to white rats had a toxicity comparable to that of strychnine—that is, at least twenty times that reported by Haag (*2*) who found that rats developed no symptoms of poisoning after ingesting up to 500 mg. of solid rotenone per kg. of body weight. Since rotenone in olive oil is in a highly dispersed condition, probably in true solution, it appeared that particle size also might be an important factor in determining toxicity. The problem then resolved itself into the following phases: (*a*) measuring the minimum lethal dose (M. L. D.)[1] of rotenone when fed in olive oil solution to one or more species of animals; (*b*) estimating the effect of the size of the rotenone particles on the rate of absorption of the poison as measured by the toxicity; (*c*) determining the action of fatty foods ingested with or following solid rotenone; and (*d*) determining whether or not there is an accumulation of the compound or whether additive injurious effects occur when sublethal doses are periodically ingested.

The results of the administration of rotenone in olive oil solution to white rats by stomach tube are given in Table I. Depending upon the size of the dose, the symptoms of poisoning appeared within a few minutes to several hours. Respiratory and cardiac rates were increased, and the animal frequently made slight convulsive movements. Later the respiration slowed and the animal lapsed into a coma which terminated in death. Post-mortem examination showed that the heart had stopped with the left ventricle in marked systole. This cardiac condition is characteristic of fatal poisoning in this species and, as far as has been observed, invariably accompanies death. The administration of 25 mg. of rotenone in olive oil per kg. body weight of rat caused death in 65 per cent of the animals within 36 hours. Under these conditions 25 mg. is considered to be the M. L. D.

Guinea pigs also were fed graduated doses of rotenone in olive oil, with the results given in Table I. The symptoms of poisoning were similar to those observed with rats. Post-mortem examination revealed that the heart stopped with the left ventricle in systole, but this condition was not as striking as with the rats. The M. L. D. was found to be about 12 mg. per kg. Since these results differ from those previously reported (*2*) when the solid was administered to this species, a series of cavies was fed with graduated doses of solid rotenone which had been suspended in a 3 per cent starch paste. Under these conditions the M. L. D. was about 50 mg. per kg., an amount which is comparable with that which Haag reported.

[1] As used here the M. L. D. is that dosage which will cause death of 50 per cent of the animals during the 14-day period of observation.

TABLE I. RESULTS OF FEEDING ROTENONE IN OLIVE OIL TO ANIMALS

Animal	Dosage	No. of Animals	No. of Deaths	Per Cent Deaths	Max. Hours of Survival
	Mg./kg.				
Rats	1000	1	1	100	0.5
	500	1	1	100	1
	300	2	2	100	0.75
	200	3	3	100	0.75
	100	3	3	100	1
	50	3	3	100	24
	35	5	5	100	36
	30	16	15	94	48
	25	17	11	65	36
	22.5	6	1	17	24
	20	6	0	0	...
	17.5	3	1	33	48
	15	3	0	0	...
	10	3	0	0	...
Guinea pigs	25	2	2	100	8
	20	6	5	83.3	48
	15	14	8	57	80
	12.5	12	9	75	48
	10	8	1	12.5	20
	7.5	4	0	0	...

Effect of Particle Size

In further experiments designed to estimate the effect of particle size when solid rotenone is fed, two separate fractions of crystals were used. These were separated from the bulk sample of rotenone by screening. The coarse crystals were those which passed through a 40-mesh screen but were retained by a 60-mesh screen. The finer material was composed of that fraction which passed through a 100-mesh screen. The two samples were separately suspended in a 60 per cent sucrose sirup and fed to rats (Table II). When the coarse crystals are fed, the M. L. D. is about 1000 mg. per kg.; but when the fine material is used, the absorption as measured by the toxicity is increased, the M. L. D. being only about 150 mg. per kg.

TABLE II. EFFECT OF PARTICLE SIZE OF ROTENONE

Rotenone[a] Crystal Size, Mesh	Dosage	No. of Rats	No. of Deaths	Per Cent Deaths	Max. Hours of Survival
	Mg./kg.				
40–60	80	4	1	25	190
	100	4	1	25	96
	120	4	1	25	196
	140	4	1	25	96
	160	4	0	0	...
	200	4	0	0	...
	300	4	0	0	...
	400	4	1	25	48
	500	4	0	0	...
	1000	10	4	40	120
<100	100	12	1	8	48
	150	12	7	58	120
	200	12	9	75	120
	250	8	6	75	48
	300	4	4	100	20
	400	4	4	100	48
	500	4	4	100	20

[a] 2000 mg. of rotenone suspended in 100 cc. of sirup.

TABLE III. EFFECT OF ROTENONE FOLLOWED BY OIL[a]

No. of Animals	Olive Oil	Butter Fat	Av. Rotenone Total	Range of Total Doses	Loss of Weight at Death	Av. Time of Survival
	Cc./kg.	*Cc./kg.*	*Mg./kg.*	*Mg./kg.*	*Per cent*	*Days*
15	0	0	527	100–1100[b]	22.2	6.1
13	10	0	253	100–500	11.1	2.7
5	5	0	340	200–400	26.6	4.3
10	0	10	290	100–400	13.6	2.9

[a] 1000 mg. rotenone in 100 cc. starch suspension, fed to rats by stomach tube at daily dose of 100 mg. per kg. and followed by oil as indicated.

[b] Of the group of fifteen controls, three received less than the average fatal doses of the groups fed rotenone followed by 10 cc. of olive oil or butter fat. Of the two groups fed 10 cc. of olive oil, or 10 cc. of butter fat following rotenone, none received as much rotenone as constituted the average fatal dose in the control group.

Effect of Fats on Rotenone Absorption

Conditions of practice make it unlikely that rotenone might be ingested by man or animals in a fat solution. Possibilities of consumption do, however, make it desirable to determine the effects which fats, ingested with or following the administration of solid rotenone, may have on the absorption of the compound. To ensure that all rats received rotenone of the same degree of fineness, sufficient suspension of solid rotenone in starch paste was prepared for a series of feedings. Four groups of rats were used, three receiving oil in addition to rotenone and one receiving rotenone alone (serving as a control group). All rats received 100 mg. per kg. of rotenone daily. The oil-fed groups received in addition 5 and 10 cc. per kg. of olive oil and 10 cc. per kg. of butter fat, respectively. The feedings were continued daily until death ensued. The results are given in Table III. The absorption of rotenone in the absence of oil is small as measured by the physiological response, the average amount fed before death being about 527 mg. per kg. The variation in the individual intakes was large. In this group the average time of survival was about 6 days. When the administration of rotenone was followed by oil, both the total intake and the time of survival decreased.

In the groups receiving 10 cc. of olive oil and butter fat, the total intakes fell to 255 and 290 mg. per kg., and the average times of survival were 2.7 and 2.9 days, respectively. When only 5 cc. of olive oil were given, the total rotenone fed was higher (340 mg. per kg.), and the survival longer (4.3 days). From these results it is evident that the presence of fats in the digestive tract increases the absorption of rotenone, the amount of increase being roughly proportional to the amount of fat present. Olive oil and butter fat are equally effective in increasing the toxicity of rotenone.

Effect of Method of Administering

In order to compare the oral and intravenous lethal dosages when rotenone is administered in the same physical state and yet in an inert carrier, a number of rats were given the compound in olive oil solution by injection into the tail vein. The symptoms of poisoning follow the same order as when the rotenone is given orally, but their onset is much more rapid. The M. L. D. was found to be about 6 mg. per kg. or about one-fourth of the oral M. L. D. This marked lowering may mean either partial absorption or partial detoxification. It is probable that considerable detoxification is effected even after absorption from the intestine. Haag found dogs and rabbits to possess considerable power of "destruction, fixation, or elimination" when sublethal doses were administered by vein, since more than the acute toxic vein dose can be tolerated if repeated small fractions of the M. L. D. are given at intervals.

Chronic Toxification

In studies of chronic intoxication carried out here, three groups of rats were subjected to prolonged daily feeding of rotenone in olive oil, at three sublethal levels. Time of survival was used as an index of injury. Since the changes in the body weights of the experimental animals might furnish some clue to the injurious effects, and since the weights may be influenced to some extent by the amount of fat which the animals received, all the groups were given the same daily dose of olive oil, 2.5 cc. per kg. A control group, which received olive oil alone, and three experimental groups were fed daily for 37 days, at which time the last experimental animal died. The experimental groups were fed rotenone dissolved in olive oil at the rates of 5, 10, and 15 mg. per kg. per day. The results are given in Table IV. The 15-mg. group received on an average about twice the oral acute M. L. D. and survived 3.4 days. In the groups receiving the lower doses the total intakes were larger and times of survival longer. The 10-mg. group received a total of 140 mg. per kg. and survived, on an average, 14 days. The 5-mg. group received 116 mg. per kg. and survived 24 days. The total intakes in the 10- and 5-mg. groups are not inversely proportional to the daily dose. Whether this represents a real difference or whether it might be expected to be adjusted if attacked on a statistical basis cannot be stated. However, it is evident that either there is an accumulation of the rotenone or the injuries are additive. The ability of rats to consume several times the lethal dose when sublethal doses are given periodically may be due to a partial destruction of the absorbed rotenone, or to decreased or retarded absorption. The losses in weight in the 5 and 10 mg. per kg. groups at death are about the same, but the rate of loss in the first group is only about half that in the second. During the 37 days of the experiment, the controls slowly gained in weight. The food intake of the rotenone-fed groups was markedly lower than that of the controls. The substance also showed a strong purgative action. Post-mortem examination revealed evidence of severe hyperemia of the entire digestive tract.

Table IV. Effect of Sublethal Doses of Rotenone in Olive Oil[a]

Daily Dose	No. of Animals	Av. Initial Weight	Av. Weight at Death	Change in Weight	Av. Total Intake	Range of Total Intake	Av. Time of Survival
Mg./kg.		*Grams*	*Grams*	*Per cent*	*Mg./kg.*	*Mg./kg.*	*Days*
15	9	160	...	..	42	15–60	3.4
10	10	188	159	−15.7	140	50–260	14
5	9	188	160	−14.9	116	50–180	24
0[b]	9	178	191[b]	+ 8.7	...	....	...

[a] Rats fed sublethal doses by stomach tube daily except Sundays, with solution of rotenone of such concentration that the daily olive oil intake in all groups was the same (2.5 cc. per kg.).
[b] Controls—all survived and gained weight averaging 8.7 per cent at end of 37 days.

An unsuccessful attempt was made to study the chronic toxicity of rotenone in olive oil using dogs as the experimental animals. It was found that the substance had a very strong emetic action. Three dogs were fed periodically with decreasing doses of rotenone in olive oil. One dog was able to retain a dose of 0.2 mg. per kg., but the other two vomited once after a dose of 0.1 mg. per kg. Other than emesis, there were no signs of toxicity, except that one dog had diarrhea after a dose of 0.6 mg. per kg. All three dogs tolerated large doses of olive oil without emesis or other observed effects.

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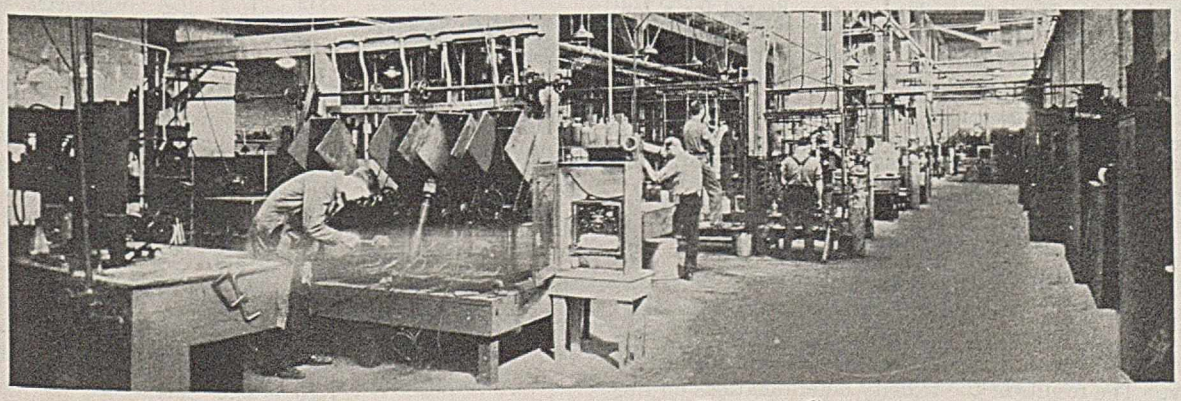

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TOXICITY OF DERRIS AND CUBE

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ECONOMIC considerations lead to the use of powdered derris or cube, or extracts made from them, as insecticides instead of the highly active principles, rotenone and its relatives, which have been isolated from these plants. Although in the earlier studies of the action of derris it was believed that rotenone was the essential constituent, recent work (*3*, *5*) has strengthened the view that the roots of derris and cube possess more insecticidal activity than can be accounted for by their rotenone content. Experiments reported in the preceding paper (*4*) indicate that rotenone may under certain circumstances be distinctly toxic to warm-blooded animals and must, therefore, be considered as potentially toxic to man.

The present report is a similar study of the toxicity of derris and certain extracts made from it for warm-blooded animals, with an attempt at correlation of the findings with the rotenone content as determined chemically, and with the toxicity for insects as determined on house flies.

Experimental Procedure

Three samples of powdered derris root and one of cube were obtained through the courtesy of the Bureau of Entomology and Plant Quarantine; that bureau also supplied information as to the rotenone content by determination, and the apparent rotenone or "rotenone based on toxicity." This figure represents the amount of rotenone that would be present were all the toxicity for house flies due to the rotenone. The materials were as follows: derris 2581, of which only that portion passing through a 100-mesh screen was used with an estimated rotenone content of 5.1 per cent (the original powder was rotenone 4.7 per cent, and rotenone based on toxicity not determined); derris 401, rotenone none, rotenone based on toxicity 5.5 per cent; derris 2217-M-1, rotenone 7.8 per cent, rotenone based on toxicity 15.0 per cent; cube 2218-M-1, rotenone 3.8 per cent, rotenone based on toxicity 8.5 per cent.

For the determination of toxicity, young adult white rats were used. Prior to use, food was withheld for 16 hours. The materials studied were given by stomach tube, and the animals were subsequently kept under observation for 7 days, although rarely did a fatality occur after the third day.

Since it was shown in the preceding paper (*4*) that solution of rotenone in liquid fats affords a means of controlling particle size, and since particle size seems to be a factor in the toxicity, all materials used in the present study, unless otherwise stated, were administered in solution in olive oil. When organic solvents were used, the solid extracts left on evaporation of the solvent were powdered, triturated with oil, and warmed in a steam bath for several hours with frequent stirring, or were heated for a few minutes over a free flame to slightly over 100° C. The mixtures were then cooled and made to volume with olive oil. Oil extracts of powdered roots were prepared in a similar manner, the residues being separated by centrifugation.

The determination of toxicity consisted in finding the dose in milligrams of material per kilogram of rat weight necessary to kill 50 per cent of a group of rats. Whenever the expression M. L. D. (minimum lethal dose) is used, it refers to this value.

Effect of Solvent

The symptoms of toxicity are essentially those described for rotenone in the preceding paper and need not be discussed here. Of the material obtained from the Bureau of Entomology and Plant Quarantine, derris 2581 was studied most extensively. The results of the toxicity determinations on this material are given in Table I. Table I shows that, whether given as a suspension in olive oil or as a solution in olive oil with the insoluble material removed by centrifugation, the amounts of powdered derris required to kill 50 per cent of a group of rats were approximately the same—that is, about 244 mg. per kg. Since the rotenone content of this sample of derris is 5.1 per cent, this amount of powdered derris would contain about 12.5 mg. of rotenone. In the previous paper it was reported that, given in solution in olive oil, about 25 mg. per kg. of rotenone were required to kill. The apparent rotenone value is, therefore, approximately twice the actual rotenone value or about 10 per cent. The equivalence in toxicity of the whole powder (the suspension) and the oil-soluble fraction would indicate that only those substances which are soluble in olive oil share in the lethal action, and that whatever remains in the marc is either innocuous or is in such a state that it does not contribute to the toxicity. That the latter supposition is correct, and that a considerable portion of the potentially toxic fraction of the whole root powder is not active as a poisonous agent when ingested orally or when extracted by oil, is indicated by the results of the administration of the acetone and ether extracts, respectively. Table I shows that the fatal doses from these fractions are, respec-

TABLE I. RESULTS OF TOXICITY DETERMINATIONS ON DERRIS 2581

Form	Dosage per Kg. Powder	Dosage per Kg. Rotenone	No. of Rats	No. of Deaths	Per Cent Deaths	Apparent Rotenone
	Mg.	*Mg.*				*Per cent*
Suspension in olive oil	195	10	4	0	0	10
	244	12.5	12	7	58	
	293	15	20	12	60	
	342	17.5	7	6	86	
	390	20	7	7	100	
Olive oil extract	195	10	4	1	25	10
	244	12.5	12	7	58	
	293	15	20	10	50	
	342	17.5	7	5	71	
	390	20	7	7	100	
Acetone extract in olive oil	78	4	8	2	25	25
	98	5	4	2	50	
	117	6	8	5	63	
	156	8	4	3	75	
	176	9	4	3	75	
	235	12	4	4	100	
	293	15	4	4	100	
	352	18	4	4	100	
Ether extract in olive oil	80	4.1	4	1	25	20
	90	4.6	4	1	25	
	100	5.1	08	3	38	
	120	6.1	12	6	50	
	150	7.8	6	5	83	
	200	10.2	4	4	100	
	300	15.4	4	3	75	
	400	20.5	4	4	100	
	500	25.6	4	4	100	
Carbon tetrachloride extract in olive oil	250	12.8	8	1	13	8.3
	300	15.3	12	6	50	
	350	17.9	8	6	75	
	400	20.4	4	3	75	
	500	25.6	4	4	100	

TABLE II. COMPARISON OF CHEMICAL AND TOXICITY DATA

Sample No.	Per Cent Rotenone by Analysis	Per Cent Toxicity to House Flies[a]	M. L. D. of Root Powder, Mg./Kg.					Per Cent Apparent Rotenone in Powder				
			Suspension in olive oil	Olive oil extract	Acetone extract	Ether extract	CCl_4 extract	Suspension in olive oil	Olive oil extract	Acetone extract	Ether extract	CCl_4 extract
Derris 2581	5.1	..	244	244	98	120	300	10	10	25	20	8.3
Derris 401	None	5.5	...	700	..	...	960	..	3.6	..	..	2.6
Derris 2217-M-1	7.8	15	...	100	80	...	200	..	25	30.1	..	12.5
Cube 2218-M-1	3.8	8.5	...	300	..	...	370	..	8.3	..	..	6.7

[a] Rotenone based on toxicity.

tively, 100 and 120 mg. per kg., equivalent to an apparent rotenone value of 25 and 20 per cent. If the toxicity of the acetone extract were ascribed only to the rotenone present, the fatal dose would be of the order of 5 or 6 mg. per kg., far from the actual value of 25 mg. reported in the preceding paper. The carbon tetrachloride extract, however, did not prove as effective; the apparent rotenone value was 8.3 per cent, corresponding to an amount of powdered root of 300 mg. per kg.

Comparison of Toxicities

As further check on the part played by oil in increasing availability as measured by lethal action, a solid acetone extract of derris 2581 was powdered and administered as a suspension in starch paste. Although, as previously stated, such an acetone extract in solution in olive oil has a fatal dose of about 100 mg. per kg., or an apparent rotenone value of 25 per cent, that fed in starch had about half this activity, the fatal dose being 195 mg. per kg., or an apparent rotenone value of 12.5 per cent. The increase in toxicity of the materials administered in olive oil as compared to that administered in starch suspension is less than would be expected from the results reported in the previous paper (*4*). There the toxicity of rotenone was increased as much as twenty times by administration in oil. If the toxicity of the starch suspension is largely due to nonrotenone materials, and this theory appears justifiable because of the low solubility of rotenone in water, then the enhancement of the rotenone fraction in the oil probably does not account for all of the fivefold increase shown by the figures.

In order to test the completeness of extraction, the marc from the acetone extraction was fed in amounts up to 10,000 mg. per kg. without any signs of toxicity. The carbon tetrachloride marc was reextracted with acetone, and the small amount of material was dissolved in oil and fed in amounts corresponding to 1000 mg. per kg. of the dried powder, without production of any symptoms. Either carbon tetrachloride changes the solubility, or the toxicity of the toxic material is reduced, since only approximately one-third as much activity can be obtained from the carbon tetrachloride as from the acetone extract.

Results similar to those described were obtained in experiments with derris 401 which contains no rotenone (Table II). The olive oil solution is here again more toxic than the carbon tetrachloride extract, the respective fatal doses being 700 and 960 mg. per kg., based on the original powder. The two extracts are as effective as though they contained 3.6 and 2.6 per cent rotenone—i. e., apparent rotenone.

Derris 2217-M-1, which contained 7.8 per cent rotenone, was fed in the form of three extracts—olive oil, acetone, and carbon tetrachloride—with the results given in Table II. Here again the same order holds in the relative toxicities, the acetone extract having a fatal dose of about 80, olive oil about 100, and carbon tetrachloride about 200 mg. per kg. Expressed as apparent rotenone, these values are 31, 25, and 12.5 per cent, or approximately four, three, and two times the actual rotenone content. These ratios are essentially the same as were found for derris 2581. Here again the total apparent rotenone does not appear in the olive oil extract, though the fraction is greater than that in sample 2581. After the separation is made, however, olive oil does serve to enhance the availability, at least as shown in the toxicity figures.

Cube 3218-M-1, which contains 3.8 per cent rotenone, was fed to rats as the carbon tetrachloride and olive oil extracts (Table II). Here again the olive oil extract is the more toxic of the two, and the relations between rotenone and apparent rotenone are similar to those found for derris root powder.

Table II as a whole shows that there is no fixed relation between the rotenone content of any of the four root samples and the toxicities of the several extracts. In general, the acetone extract is the most toxic and the carbon tetrachloride least toxic. The olive oil preparation falls between the two, but it may approach one or the other of the values. When the toxicities of the various extracts are used for the calculation of the apparent rotenone

When extracts from derris or cube root powders are fed to rats in olive oil solution, the toxicity is greater than would be expected on the basis of the rotenone content, indicating that there may be present substances, other than rotenone, which are physiologically active.

The relations between the toxicity of extracts and rotenone content vary with the solvent used and with the sample of derris from which they are prepared. Acetone and ether extracts are about equally toxic, and these solvents appear to remove completely the active substances. Carbon tetrachloride likewise appears to remove completely the toxic agents but with partial loss of physiological activity. Olive oil fails to remove completely the principle from the powders but does markedly accentuate the toxic properties if the reagents are extracted by acetone or ether and subsequently fed in oil solution.

Rotenone content is not a measure of toxicity of derris when administered orally to warm-blooded animals. The possible presence of still other substances that may be injurious is discussed.

in the root, it is seen that the chemical determination of rotenone will give no definite measure of how toxic the various preparations made from the root will be when fed.

Toxic Constituents of Derris Extractives

The toxic properties of the acetone extract of derris 2581, when attributed to rotenone, indicate a content of 25 per cent, five times that found by chemical examination. Since it is unlikely that a substance of toxic properties equal to rotenone could be present in such amounts and still remain unfound, it seems more reasonable to suppose that there is present one or more substances of much greater pharmacological activity than rotenone, or else that studies based on the crystalline rotenone as isolated do not portray the real danger involved in human ingestion.

In this connection Fink and Haller (*1*) believe that rotenone is probably to be regarded as the most important insecticidal constituent in derris extractives. The other well-characterized crystalline compounds present (deguelin, tephrosin, and toxicarol) do not in the isolated form possess sufficient toxicity to account for the effectiveness of derris extractives. They point out that, as isolated, only rotenone possesses optical activity. Haller and LaForge (*2*) have, however, shown indirectly that at least part of the deguelin present in the extractives is in optically active form, and Fink and Haller (*1*) have shown that the optically active derivative of deguelin, dihydrodeguelin, is more toxic to mosquito larvae than the corresponding inactive form. Whether or not the variations in apparent rotenone can be associated with changes in the optical rotation is not as yet apparent.

Acknowledgment

The writers are indebted to H. A. Jones, Division of Insecticide Investigation, and F. L. Campbell, Division of Control Investigations, both of the Bureau of Entomology and Plant Quarantine, for the selection of the samples of derris and cube and permission granted by that bureau to repeat in summary their data.

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Vinegar from Dates

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THE raw material is the fleshy part of the date fruit (*Phoeina sylvestria*). The ripe fruit is bright red, and the fleshy edible part is 60 per cent of the weight of the fruit. The average percentage composition of the fleshy part is as follows:

Moisture	20.20
Raw fiber	38.53
Sugars	35.80
Mineral substances	2.97
Not specified	2.50

To secure a rapid and uniform alcoholic fermentation, the fruit is worked into a juice by mixing it with an equal weight of water, boiling for an hour, and pressing. This procedure is repeated three times for maximum extraction. It is then filtered, made to known volume, and analyzed for sugars by standard methods. Although the amount of juice and its Balling degree vary considerably according to the ripeness of the fruit, its quality, extent of fermentation already developed in the fruit, and variety of the fruit, we may expect a yield of juice of about 15° Balling, equal to one and a half times the weight of the fruit.

Juice containing 15 to 17 per cent sugar (specific gravity, 13° Balling) is inverted by boiling with hydrochloric acid (1 to 3 cc. per liter) and is then inoculated with a culture by the addition of 0.25 ounce of fresh yeast per gallon of juice to which previously have been added 70 cc. of a solution of nutrient salts (2 grams potassium phosphate, 0.2 calcium phosphate, 0.2 magnesium phosphate, and 10.0 ammonium phosphate dissolved in 860 cc. of water). A good fermentation sets in within 24 hours; the optimum temperature varies from 80° to 90° F. for the reaction which reaches its climax on the seventh day. The absence of reducing sugars indicates the end of fermentation. After the seventh day the Balling measurement is 1° to 2°, and the acetic acid content is 0.25 gram per 100 cc.

The fermented juice is then subjected to acetous fermentation in an open vat by the inoculation of pure, young, and vigorous *mycoderma aceti*, preferably by the addition of 10 per cent unpasteurized "mother vinegar" and keeping the mixture still for 2 months. Light is excluded from the room as far as possible, since acetic fermentation is inhibited by the direct rays of the sun. By the use of special cultures, the loss of acid during acetification can be materially reduced, since it is intimately associated with the life of the microörganism.[1]

Vinegar, when formed, is pasteurized and stored for some months in air-tight containers for aging. During this long storage period the vinegar deposits albuminous matter, bacterial cells, etc., and undergoes partial clarification.

Clarification

Vinegar from inferior-quality dates often becomes cloudy or hazy on standing, which may be due to the presence of colloidal materials, pectin, protein, gums, and tannins. This objectionable property becomes apparent within 30 to 60 days or may be delayed for 12 to 15 months or more. This clouding may occur in both pasteurized and unpasteurized vinegar, in sealed bottles or in those exposed to the air through cotton plugs. This cloudiness is removed more easily by a process of sedimentation and filtration than by simple filtration; the method employed is chiefly mechanical. Hyflo Filter-Cel (1 to 2 per cent) is stirred with the vinegar; as it settles, it carries with it the albuminous particles causing the turbidity. By subsequent filtration under pressure, the sample filters brilliantly clear.

Sterilization

After clarification, vinegar still contains acetic bacteria; on exposure to air, the bacteria grow on the surface and make the liquid turbid. Since all acetic bacteria perish at a relatively low temperature, it is sufficient to heat the vinegar to 150° F. by dipping the container in a water bath heated by steam. The vinegar is subsequently cooled by a current of cold water nearly to normal temperature.

Sterilization also has the effect of maturing the vinegar and of giving it a softer taste and less acid aroma. This is probably due to its promoting the combination of the residual alcohol in the vinegar with acetic acid and thus accelerating the formation of the ester to which matured vinegar owes its flavor.

The final vinegar is clear blackish red in color and smells like wine vinegar. It has a specific gravity of 1.18, a total acid content (as acetic) of 4.98 per cent, traces of ethyl alcohol, 2.17 grams of solids, and 0.17 gram of ash per 100 cc. Twelve to fifteen gallons of standard vinegar are obtained per 100 pounds of fresh fruit. The yield of vinegar from dried or cured fruit is greater because of the greater concentration of sugar.

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[1] Mitchell, C. A., "Vinegar Manufacture and Examination," London, Charles Griffin & Co.

Toxicological Study of DERRIS[1]

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This paper presents the experimental results obtained in a study of the acute oral toxicity of several samples of derris containing varying percentages of rotenone, together with the determination of the toxicity of extracts of derris for mammals. The data show that the rotenone content of derris is no reliable index of its toxicity, since, as a stomach poison, derris is more toxic than rotenone.

Studies on the toxicity of derris by inhalation for various laboratory animals indicate that it is extremely more toxic than when administered orally, suggesting a possible health hazard to those engaged in milling, grinding, and diluting derris without the use of suitable protective measures.

Pharmacological studies are presented, showing that the probable site of action of derris and water extracts of derris is upon the respiratory center, regardless of the mode of administration.

DERRIS is a genus of tropical plants embracing about forty species. The roots of several species have been employed, probably for centuries, by the natives of Borneo and the Malay Peninsula as fish poisons and in the concocting of arrow poisons. In 1848 Oxley (*18*) reported upon the use of *Derris elliptica* as an insecticide. It had been only sporadically so employed until several years ago when, chiefly due to the coöperative efforts of several bureaus of the United States Department of Agriculture, extensive experimentation involving studies on the possibilities of derris was encouraged and begun; today derris occupies the spotlight of attention as a source of insecticides of great promise. Roark (*20*) has recently prepared an extensive bibliography on derris, and no attempt will be made here to mention references other than those that bear directly upon this problem.

Four definite constituents have thus far been isolated from derris: rotenone, deguelin, tephrosin, and toxicarol. Rotenone is the best known member of the group. It was first isolated by Geoffroy (*8*) in 1895 from a native plant of French Guiana called "Robinia nicou," now known as *Lonchocarpus nicou*. To this substance Geoffroy gave the name "nicouline," which later was found to be identical with rotenone (*6*). Of these four compounds, only rotenone is obtained by direct crystallization from an extract of derris with organic solvents. LaForge, Haller, and Smith (*15*) have prepared a comprehensive review dealing with the structure and reactions of rotenone. The remaining constituents, all chemically related to rotenone and present in the uncrystallizable residue (deguelin, tephrosin, and toxicarol), are removed only after previous treatment with alkali. Clark (*5*) determined the structure of deguelin and tephrosin, but the exact structure of toxicarol (*4*) has not yet been definitely established.[3]

There appears to be considerable difference of opinion in the literature concerning the toxicity of derris for man. Ridley (*19*) as well as Brooke (*1*) stated that a decoction of *Derris elliptica* can be toxic to humans only when taken in large quantities. Lewin (*16*) claimed that men drinking water treated with derris for the purpose of killing fish have become ill, collapsed, and died. Corbett (*7*) stated that derris is definitely toxic to both humans and animals. Campbell (*3*) cited a case of suicide with derris root in Singapore. Necropsy in this instance revealed nothing characteristic. Kelsall, Spitall, Gorham, and Walker (*13*), Kingzett (*14*), and Shutt (*21*) expressed the opinion that derris is practically nonpoisonous to man.

Symes (*22*) stated that derris is nontoxic to higher animals. Van Hasselt (*23*), however, when testing a substance obtained from derris by alcoholic extraction (derrid), found it to be toxic to cats, dogs, rabbits, mice, frogs, and cavies, acting chiefly upon the respiratory center. Campbell (*3*) showed that the sap from 2 grams of the root of *Derris elliptica* was fatal to a monkey (*Macacus nemestpinus*) upon oral administration. His observations upon fish (*Ophiocephalus gachua* Buch.-Ham.), toads (*Bufo melanostictus*), and monkeys led him to conclude that derris stimulates the respiratory center initially but finally causes death by paralysis of this center. No effect was noted upon the heart, but blood pressure tended to fall because of a vascular dilatation. Vomiting frequently occurred, probably as a result of stimulation of the emetic center. He further concluded that fish poisoned by derris can be eaten with impunity by man because fish are killed by such minute quantities of the poison. Buckingham (*2*) fed a derris extract in amounts of about 50 mg. per kg. orally to dogs without observing any untoward effects. Haag (*10*) noted that the inhalation of derris dust could be fatal to guinea pigs.

[1] This is the second of a series of papers on the toxicology of *Derris elliptica* and its constituents. The first reported results with rotenone (*10*).

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[3] Since the preparation of the present manuscript, a structure for toxicarol has been proposed by Heyes and Robertson, *J. Chem. Soc.*, **1935**, 681.

Owing to the paucity of data dealing with the toxicity and pharmacology of derris, the present studies were undertaken for the purpose of determining its effects toxicologically and physiologically upon laboratory animals. Most of the studies were confined to one sample of the dried root of *Derris elliptica* (sample No. I. D. 2221), finely powdered (No. 200 mesh) and containing 28.5 per cent total carbon tetrachloride extractives, including 9.6 per cent rotenone. In addition, a limited number of acute toxicity tests were made with three other finely powdered specimens of derris and one of cube (*Lonchocarpus nicou*), all containing different amounts of rotenone and total carbon tetrachloride extractives. When any of this latter group is discussed in the following report, they will be specially indicated.

Studies on Acute Toxicity

In the determination of acute oral toxicity, the powdered drugs were fed to the experimental animals in aqueous suspension by stomach tube, unless otherwise indicated. In all instances food was withheld for 24 hours prior to the administration of the derris. Water was allowed ad libitum. The diets of the experimental animals were as follows: rabbits and cavies were fed Purina Rabbit Chow; rats, Purina Dog Chow; and dogs, table scraps. All animals were kept under observation for at least 15 days because it has been established in this laboratory that about 11 days are required for the elimination, as judged by fecal excretion, of a single large dose of rotenone given orally to rabbits. Actually, however, when fatalities did occur, they most frequently took place within the first 24 to 48 hours.

Rabbits were given amounts of derris varying from 30 mg. to 1 gram per kg. body weight,[4] and the lethal dose[5] (Table I) was found to be about 600 mg. The symptoms of intoxication appeared within an hour when fatal doses were employed and were characterized by an initial respiratory stimulation, followed by signs of a generalized depression occasionally punctuated by convulsive seizures of a clonic type. Later the animal would lie on its side, unresponsive to sensory stimulation, and finally die of respiratory failure. Rabbits recovering from the initial intoxication of nonfatal doses refused food for several days and frequently gave evidence of temporary diarrhea; otherwise no untoward sequelae were noted. In animals dying within 24 hours, no gross postmortem change along the gastrointestinal tract or in any of the intrathoracic or intraabdominal organs was noted. However, in many animals dying later than 24 hours, gross examination revealed some irritation on the mucous membrane of the stomach and small intestine. No differences were observed in either the qualitative or quantitative response to derris in the three varieties of rabbits employed—red, gray, and white. Young adults weighing about 1.5 to 2 kg. were used in all experiments.

Upon the administration of derris to white rats (100 days old) and to adult cavies, the lethal dose was found to be 100 mg. for the former and 75 mg. for the latter, demonstrating that these animals are much more susceptible to derris than are rabbits. Autopsy in fatal instances showed no significant gross changes in either of these species.

When dogs were fed derris by stomach tube or in capsules in amounts from 100 to 500 mg., its only action was to provoke almost immediate emesis. However, when the vomiting center had been previously depressed by morphine (2 mg. intramuscularly), dogs tolerated amounts up to 75 mg. without manifesting any apparent systemic effects. Quantities above this value elicited definite symptoms of intoxication similar to those occurring in rabbits. The lethal dose for dogs was found to be about 150 mg. However, in one instance in a group of six dogs receiving 200 mg., one dog survived two other similar subsequent feedings at 30-day intervals without showing any demonstrable effects. This dog was still in good health more than 5 months after the last administration of derris. In a few instances where the animals (two) did not die within 24 hours after the administration of a fatal dose, they remained comatose for several days without recovering from the effects. One dog receiving 150 mg. remained alive for 9 days but was stuporous throughout the entire period. Gross post-mortem examination of the fatalities among these animals showed no apparent changes other than a slight irritation of the gastric mucosa. Table I gives a composite picture of the results obtained in these acute toxicity experiments.

[4] All doses will be given, unless otherwise indicated, in terms of "per kg. body weight;" for the sake of brevity this term will be subsequently omitted.

[5] The dose which proved fatal to about 70 per cent of the animals within 15 days was arbitrarily selected as the "lethal dose."

Table I. Acute Oral Toxicity of Derris for Rabbits, Rats, Cavies, and Dogs

	No. of Animals	Weight, Mg./Kg.	Percentage Deaths within: 24 hr.	15 days
Rabbits	6	1000	100	100
	9	700	100	100
	9	600	67	90
	6	500	17	50
	6	400	17	17
	9	300	22	22
	14	200	28	28
	4	150	0	0
	8	100	0	0
	4	75	0	0
	5	50	0	0
	3	30	0	0
Rats	3	400	100	100
	13	200	85	100
	5	100	80	100
	5	75	0	0
Cavies	5	200	100	100
	2	150	100	100
	3	100	100	100
	6	75	50	83
	5	50	0	0
Dogs	3	500	100	100
	2	400	100	100
	5	300	80	80
	2	250	100	100
	6	200[a]	67	83
	3	150	67	100
	7	100	43	43
	2	75	0	0
	2	50	0	0

[a] One survived after three consecutive feedings 30 days apart.

Haag (*10*) found that, when frogs (*Rana pipiens*) were placed in water containing rotenone (1 part per 500,000), they soon died of respiratory failure. This experiment was repeated substituting derris for rotenone; in concentrations of 1 part per 400,000 or stronger it was toxic in about 24 hours. The frogs all showed paralysis of respiratory movements, after which the heart continued to beat for several hours. In these experiments aquariums were used; each contained two frogs in 500 cc. of the various derris dilutions. This volume, which was somewhat greater than that employed by Haag, was sufficient to submerge the frogs partially.

Because of the pronounced insecticidal activity of rotenone, some workers have thought that the insecticidal effectiveness of derris might be evaluated by determining its rotenone content. This appeared an interesting proposal because Haag (*10*), as well as the writers, has found that, upon oral administration, dogs and rabbits can tolerate well over one gram of rotenone, although these animals succumb from much smaller amounts of derris. This naturally suggests that rotenone is not the only constituent present in derris to which might be ascribed its physiological action. Recently Haller and LaForge (*11*) stated that the insecticidal action of extracts of derris root is due not only to rotenone but also to other constituents which remain in the uncrystallizable residue. In order to determine whether or not any relation exists between the rotenone content of a specimen of derris and its toxicity, a

series of experiments was performed in which several samples of derris root and one of cube, all with different amounts of extractive, were administered orally to rabbits and rats. Table II lists the specimens employed, the percentage of total carbon tetrachloride extractives and rotenone found in each, as well as the individual lethal oral dose for rabbits and rats as obtained from Tables I, III, and IV.

TABLE II. ANALYSES OF SPECIMENS[a]

Sample No.	Total CCl_4 Extractives	Rotenone	Lethal Dose Rabbits	Lethal Dose Rats
	%	%	*Mg.*	*Mg.*
Derris I. D. 2288	21.0	0.0	2000	700
Derris I. D. 2539	17.3	3.1	1500	500
Derris I. D. 2470	20.6	6.6	700	200
Derris I. D. 2221	28.5	9.6	600	100
Cube	21.4	4.7	1000	200

[a] The analyses reported were kindly furnished by the Insecticide Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

TABLE III. ACUTE ORAL TOXICITY OF DERRIS SPECIMENS

Sample No.	No. of Animals	Weight, Mg./Kg.	Percentage Deaths within: 24 hr.	15 days
		Rabbits		
I. D. 2288	2	2500	100	100
	6	2000	50	100
	4	1500	25	50
	2	1000	0	0
I. D. 2539	2	1500	100	100
	4	1000	25	50
	6	800	17	33
	2	700	0	0
I. D. 2470	2	1000	100	100
	2	700	100	100
	4	500	25	25
	2	400	0	0
		Rats		
I. D. 2288	2	1000	100	100
	2	900	100	100
	6	800	67	67
	6	700	67	67
	5	600	40	40
	6	500	67	67
	6	400	50	50
	6	300	33	33
	4	200	0	0
	4	100	0	0
I. D. 2539	2	900	100	100
	4	800	100	100
	2	700	100	100
	2	600	100	100
	6	500	67	67
	2	400	0	0
	4	300	25	25
	2	200	0	0
I. D. 2470	3	500	100	100
	5	400	80	80
	5	300	60	60
	6	200	67	67
	8	100	25	25
	3	75	0	0

Tables III and IV show that, as the rotenone content of derris increases, so does its toxicity although not always in a direct ratio. The results obtained with sample I. D. 2288, which contains no rotenone, illustrate strikingly, however, that the toxicity of derris does not depend solely upon its rotenone content. This belief is further strengthened by the fact that, if the toxicity of derris were dependent directly upon its rotenone content, then, since specimen I. D. 2221, for instance, contains 9.6 per cent rotenone and since the fatal dose of rotenone for rabbits is certainly more than 1 gram, the lethal dose of this sample should have been over 10 grams instead of 0.6 gram. The total carbon tetrachloride extractives likewise are no true criterion of the relative toxicity of derris.

Acute Toxicity of Derris Extracts

One of the most characteristic properties of the active principles yet isolated from derris is their insolubility in water. To determine whether whole derris might yield an active water extract, an aqueous preparation was prepared as follows: Fifty grams of derris were digested with 500 cc. of distilled water at about 50° C. for one hour. The mixture was then centrifuged and the milky, colloid-like, supernatant portion, which contained approximately 20 per cent solids, was tested orally upon rats, and orally and parenterally upon rabbits.

The lethal dose of this water extract for rats was found to be about 10 cc., equivalent to 1 gram of derris or 200 mg. of the water-soluble residue. In rabbits the lethal dose was about 20 cc., corresponding to 2 grams of derris or 400 mg. of water-soluble residue. In both rats and rabbits this preparation provoked the same train of symptoms as the whole derris. Intravenously in rabbits the fatal dose of the water extract was found to be 0.4 cc., intramuscularly 1 cc., and subcutaneously 2.5 cc.

The aqueous extract was placed in a dialyzing bag of animal membrane and dialyzed against water for 24 hours; the dialyzing water was practically nontoxic (5 cc.) upon intravenous administration to rabbits, while the dialyzate retained its original toxicity (0.4 cc.).

The water-insoluble residue was dried and ground to a fine powder (No. 80 mesh) and administered orally to both rats and rabbits as an aqueous suspension. The lethal dose was approximately 150 mg. for rats and 800 mg. for rabbits.

From these observations it is obvious that water can extract some toxic principles, perhaps in a colloidal, nondialyzable state, from derris. Comparison of the potency of the water extract and the water-insoluble residue upon rabbits shows that the total toxicity of these two equals the previously established value for the toxicity of whole derris. In the case of rats the figures are not so convincing.

It is usually assumed that, upon acetone extraction, derris yields in its entirety all of its "active" compounds. Derris was exhaustively extracted with acetone by Soxhlet extraction and the solvent was removed. The dry acetone-soluble residue was powdered and dissolved in the smallest possible measured volume of ethyl alcohol; water was then added so that the finished preparation contained about 10 per cent alcohol. The lethal dose of the residue so prepared, when given to rabbits orally, was 200 mg. In amounts of 2 grams, the acetone-insoluble residue was nontoxic to rabbits when given per os; hence it appears that acetone definitely removes the toxic principle from derris. Incidentally, the fatal dose (for rabbits) of 200 mg. for the acetone-soluble residue is what we might expect from the toxicity of the sample of derris (600 mg.) with a total extractive content of 29 per cent.

A sample of this same acetone-soluble fraction was dissolved in a minimal amount of ether and the rotenone allowed to crystallize from solution. The ethereal solution was then evaporated to dryness and dissolved in alcohol as in the case

TABLE IV. ACUTE ORAL TOXICITY OF CUBE ROOT

	No. of Animals	Weight, Mg./Kg.	Percentage of Deaths within: 24 hr.	15 days
Rabbits	3	2000	100	100
	3	1500	100	100
	5	1000	60	80
	5	900	20	60
	5	800	0	20
	10	700	20	50
	11	600	9	19
	8	500	12	12
	14	400	7	7
	6	300	0	0
	6	200	0	0
Rats	3	400	100	100
	3	300	67	67
	3	200	67	67
	6	100	34	34
	3	75	0	0
Cavies	3	250	100	100
	3	200	67	67
	3	150	0	0
	3	100	0	0
Dogs	3	1000	100	100
	3	500	100	100
	6	300	33	50
	2	200	0	0

of the residue above. When given orally to rabbits the lethal dose of this uncrystallizable residue, largely rotenone-free, was 200 mg. This experiment demonstrates again that rotenone cannot be regarded as the only toxic agent of derris.

Inasmuch as rotenone and its related compounds are somewhat soluble in olive oil, 50 grams of derris were digested with 500 cc. of olive oil for 1 hour on a steam bath at about 50° C. The mixture was then centrifuged and, when given orally, the lethal dose of the clear oil extract was found to be 5 cc. (equivalent to 500 mg. of derris) for both rabbits and rats. When given to rabbits by intramuscular injection, the lethal dose was 1 cc., the same as that obtained for the aqueous extract.

Effect of Fats upon Derris Toxicity

McClosky (*17*) has shown that, when rotenone is dissolved in olive oil and administered to rats by stomach tube, its toxicity is increased about twenty fold; this observation was corroborated by the present authors in a limited number of experiments. To account for this phenomenon, we might theorize that the oil increases the ease of absorption of rotenone. These results prompted the subsequent experiments in which derris was given orally to rabbits and rats in a water suspension followed immediately by olive oil. Table V demonstrates the results obtained. The outcome of the control administrations of olive oil to rabbits was rather surprising. These animals appeared to tolerate the fat rather poorly, frequently developing diarrhea even after small doses; amounts of 30 cc. proved fatal. The reason for this toxicity is obscure and deserving of further study. Rats seem resistant to olive oil up to amounts of 20 cc.

Table V. Effect of Olive Oil on Oral Toxicity of Derris

No. of Animals	Derris, Mg./Kg.	Olive Oil, Cc./Kg.	Percentage Deaths within: 24 hr.	15 days
		Rabbits		
8	0	10	0	13
8	0	20	13	38
4	0	30	25	75
4	0	40	0	75
4	25	5	0	0
4	50	5	0	0
4	100	5	0	50
12	200	5	0	0
4	300	5	50	75
4	400	5	100	100
2	50	10	0	0
2	75	10	0	0
2	100	10	0	0
2	150	10	0	100
7	200	10	0	30
7	300	10	43	71
4	400	10	75	100
2	100	20	0	50
3	200	20	34	34
3	300	20	0	0
3	400	20	0	0
4	200	10[a]	0	25
4	300	10[a]	50	75
		Rats		
4	0	10	0	0
3	0	20	0	0
12	50	10	8	8
9	75	10	67	67
6	100	10	67	67
5	150	10	60	80
4	200	10	100	100

[a] Mineral oil.

The lethal dose of derris, when given to rabbits with either 5 or 10 cc. of olive oil, was about 300 mg., in contrast to 600 mg. for derris alone. When, however, the amount of oil was increased to 20 cc., rabbits apparently tolerated 400 mg. of derris. This dose of olive oil (not itself without toxicity) when given with the derris provoked a pronounced diarrhea. It is possible that the cathartic effect of this mixture rushes the intestinal contents on so hurriedly that the normal utilization of either of these substances cannot properly take place.

An interesting result was obtained with six rabbits to which 5 cc. of oil was given daily for 2 months. At the end of this period these animals had gained markedly in weight and had become as tolerant to derris as fresh controls without olive oil. In amounts of 10 cc., mineral oil influenced the toxicity of derris in a manner similar to olive oil.

In rats, olive oil in amounts of 10 cc. apparently did not influence the potency of derris to the same extent; 75 mg. proved fatal as compared to 100 mg. for derris alone.

The results of these experiments do not permit of definite conclusions and clearly point to the need of further work in this direction.

Acute Toxicity of Derris by Inhalation

In commercial milling operations and often in its practical use as an insecticidal dust, the possible health hazard to human and animal life in breathing finely powdered derris becomes of considerable importance.

To determine the extent of this hazard, a series of experiments was conducted in which several species of animals were exposed to various concentrations of derris: to acetone-extracted derris; as a control, to talc (U. S. P.) which was used as a diluent in preparing the various concentrations of derris; and finally to a 1 per cent rotenone dilution.

The animals were placed in a glass chamber measuring 24 × 18 × 12 inches, and the various dusts were blown in at intervals of 5 minutes for a duration of 30 seconds. The animals were exposed to a thin cloud of dust at all times throughout the period of the experiment. These conditions may appear somewhat exaggerated when compared to average field conditions; however, similar conditions may be encountered when derris dust is employed in confined quarters or in manufacturing plants where derris is being ground or diluted.

In the first set of experiments undiluted derris was employed. The nineteen rats exposed promptly developed signs of derris poisoning, dying from respiratory failure within one hour. A small series of rats was likewise subjected, but for only about 10 minutes, and then removed from the chamber. These all died within several hours. Two small dogs were similarly treated with derris, and after about 20 minutes in the chamber they became nauseated and vomited. They were then placed in a well-ventilated metabolism cage where, after an interval of about 10 minutes, they showed marked incoördination, became markedly depressed, and within an hour died of respiratory failure.

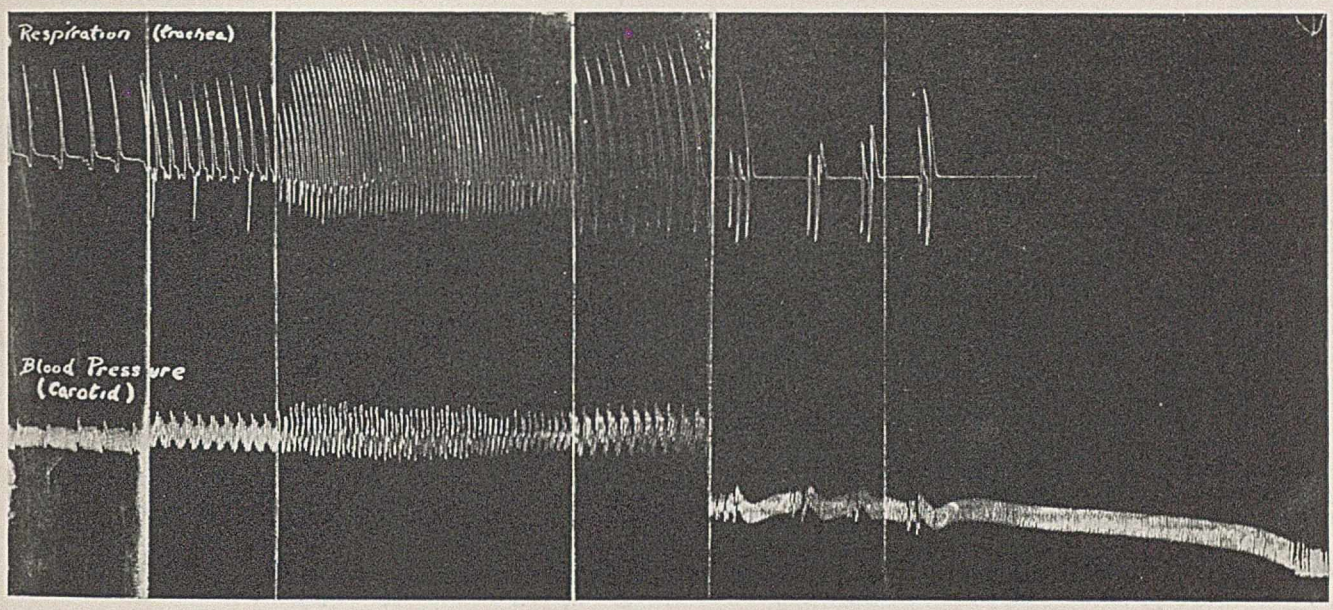
Pigeons (three) seemed to be equally sensitive and reacted similarly: cavies (six) were somewhat more tolerant. Four died after an hour and a half, one died after 7-hour exposure, and one survived although in the chamber for 7 hours.

Of four cats, one died after an hour in the chamber. The rest were exposed to the dust for 6 hours. Two died 18 hours later, and the other in 8 days. Three rabbits were subjected to the derris cloud for 7.5 hours. One of them died within 6 days and another 9 days later; one survived. Of all the animals studied, cats and rabbits seemed least susceptible. This finding for rabbits is in accord with the observed low oral toxicity of derris for these animals.

In the next series of experiments, derris diluted to 10 per cent with talc was employed as a dust upon two dogs and six rats. The results with the dogs were less striking than when the undiluted preparations were used; one animal became stuporous after a total exposure of 7 hours and died within 24 hours; the other, treated similarly, survived for 8 days in a semi-stuporous state and was then killed.

The rats all died after 2 hours of treatment. When the derris was diluted to 5 per cent with talc and used upon eight rats, three died after 4.5 hours and three after 5.5 hours. The other two, after 5.5 hours in the dust chamber, were observed for 30 days, during which time they appeared normal.

Dusts consisting of (*a*) 2.5 per cent derris in talc, (*b*) the acetone-insoluble residue of derris, and (*c*) talc U. S. P.,



Control 3 minutes later 18 minutes later 35 minutes later 53 minutes later 55 minutes later

FIGURE 1. EFFECT OF DERRIS ON THE RESPIRATION AND BLOOD PRESSURE OF A DOG

Dog anesthetized by intravenous injection of sodium amytal (50 mg. per kg.); 750 mg. derris per kg. in water administered by stomach tube.

seemed to be tolerated by rats (six or seven for each test) for 7 hours. These were kept under observation for 30 days; at the end of this period they seemed entirely normal and at no time manifested any signs of intoxication.

In considering the results of these dusting experiments, we must take into account that intoxication could result (*a*) from the absorption of the active principles from the buccal membranes and the mucosa of the respiratory tract, (*b*) from the gastrointestinal tract due to swallowed derris, and finally (*c*) from a combination of these routes of absorption. Certainly when intoxication and death ensued within an hour from the beginning of the experiment, we should feel justified in concluding that the major amount of the poison had been absorbed from the respiratory and buccal mucous membranes, because even with tremendous doses administered by stomach tube, the onset of toxic symptoms and the fatal outcome seldom occurred with such rapidity. Again, in weighing the amounts of derris insufflated into the chamber and that remaining after the animal had died, it was found that only a fraction of a fatal dose could have been swallowed.

In those experiments necessitating prolonged exposure to the dust, particularly where the symptoms were delayed in appearing and fatality occurred only after several hours or days, in all probability absorption had taken place from both the digestive and the respiratory tracts. Here, also, a possible local irritating action upon the respiratory mucosa is worthy of consideration as a contributory factor.

Finally a series of rats was exposed to a dust of 1 per cent rotenone in talc for 10 hours. They were all living and healthy after 30 days. These results are in marked contrast to those obtained where derris diluted to 1 per cent of its rotenone content was employed. In these, 100 per cent fatality occurred after 2 hours of exposure. This again indicates that the toxic action of derris does not alone depend upon its rotenone content.

General Pharmacological Considerations

In order to determine any possible local effect of derris, the finely powdered preparations were applied to the shaved arm pits of four volunteers twice daily for 30 days. At the end of this time one had developed a mild rash at the site of application; this disappeared within 24 hours. The others suffered no inconvenience except that one noted a very mild smarting. When applied in the form of a 10 per cent ointment in anhydrous wool fat for several days on the forearms of these volunteers, no local irritation or anesthesia was observed. The back and flanks of a series of white rats were shaved and slightly scarified and then anointed thoroughly with the ointment daily for 10 days without any manifestations of local or systemic effect. The scarified areas on the treated animals healed just as rapidly and perfectly as those upon controls.

Derris was dusted into the right eyes of a series of six rabbits, the left eyes being used as controls. Within several hours signs of a conjunctivitis were beginning in the treated eyes. Twenty-four hours later pus had formed abundantly; after several days the eyes became completely normal. At no time was any appreciable local anesthesia noted. Acetone-extracted derris produced only a mild degree of irritation; hence it appears that the local irritant effect was due largely to a specific action of the principles of derris rather than to a mechanical effect of the dust. The instillation of the aqueous extract of derris into eyes of rabbits at regular hourly intervals for 2 days provoked no irritation or anesthesia.

It is common experience among those working with derris that the dust is prone to produce a slight obtunding sensation in the mouth and throat, associated with a slight metallic taste. Haag (*10*) had previously observed that rotenone, when applied to the mucous membrane in the mouth of man, produces a similar effect. The writers have applied derris, as such and also in the form of the water extract, to the tongues of a series of volunteers. About 10 minutes after the application, a slight sensation of numbness as well as a metallic taste, affected all; these effects persisted for 3 or 4 hours. No appreciable degree of anesthesia was produced nor was there any change in temperature or taste sensation.

The local effect of the water extract of derris upon frogs was studied according to Türck's method. In these experiments, after immersion of the leg in the derris preparation for an hour, there was marked retardation in the response of the treated leg to 0.1 *N* hydrochloric acid. Constant washing of the test leg for an hour did not restore its control sensitivity. A series of nerve-muscle preparations of the sciatic nerve and the gastrocnemial muscle of the frog was prepared. Employing the Claude Bernard technic, analysis was made for

the site of action of the aqueous derris extract. The water extract had no influence upon the muscle or upon its motor plate, but it definitely depressed (completely at times) conductivity in the sciatic nerve as determined by faradic stimulation. The nerve failed to recover even though washed continuously with Ringer's solution for an hour.

When the water extract was applied to the vagus of dogs anesthetized with dial (60 mg. per kg. intraperitoneally), after about an hour faradic stimulation above and in the block provoked no cardiac response, indicating that the derris had exerted a paralyzing effect. Similar stimulation prior to application of the derris extract showed that dial had not abolished the functional activity of the vagus. In spite of continued washing of the blocked area for several hours, there was no return of its normal response to the electrical stimulation.

These effects could not have been due to an anisotonicity of the derris solution since this same solution was found to be isotonic as tested against mammalian red cells. The pH of the water extract of derris was 5.98 as determined potentiometrically.

From these experiments it appears that derris can exert a definite anesthetic effect when brought in intimate contact with nerve structures or when exposed to mucous membranes (as judged by the Türck experiment) in a concentrated form for a somewhat prolonged period. Recovery from such effects seems to be slow. Efferent fibers seem to be more sensitive than the afferent.

Figure 1 is a typical illustration of the effect of derris upon blood pressure and respiration in the dog. The animal was anesthetized with sodium amytal (50 mg. per kg. intravenously); 750 mg. of derris (I. D. 2221) per kg. in water was administered by stomach tube. The most pronounced effect was upon respiration which was initially stimulated and then depressed. Only in the later stages of the derris intoxication was the blood pressure somewhat depressed. Death was due to respiratory failure, circulation maintaining itself for rather long periods after respiratory cessation. The intravenous injection of the water extract of derris elicited the same type of response. Stimulation of the phrenic nerve immediately after death was effective in provoking a contraction of the diaphragm, indicating that the respiratory stoppage was not due to a curare effect. The administration of atropine and section of the vagi did not influence these physiological effects of derris.

Upon being injected into the ventral lymph sac of frogs, the water extract initially stimulated respiration and then suppressed it completely; the heart continued to beat for long periods afterward.

The convulsive seizures produced by large doses of derris in rabbits resembled somewhat those resulting from the administration of insulin. In about 50 per cent of both the rabbits and dogs, derris seemed to cause a hypoglycemia which approached convulsive levels after fatal amounts. The administration of glucose to these animals, however, did not prolong life. Other animals either showed no change in blood sugar after derris or actually, in some cases, a hyperglycemia. The results obtained in starved animals and those on a high-carbohydrate diet were identical. It might be that one of the constituents of derris affects carbohydrate metabolism, first producing a hyperglycemia and later a hypoglycemia. The relation of these changes to the toxic action of derris is a matter of conjecture.

The method of Gross and Smith (*9*) for detecting rotenone (and deguelin) in the excreta of animals fed rotenone and derris was modified slightly. The material is extracted with ether; the ether is removed and the residue taken up with acetone. To this is added one-third volume of freshly prepared 10 per cent alcoholic potassium hydroxide, and the resulting mixture is warmed; if rotenone (or deguelin) is present, a wine red color develops to its maximum in about 15 minutes.

Although this test is sensitive to 1 part of rotenone in 35,000, no positive reaction has been obtained in the excreta of rabbits unless 600 mg. of rotenone, or more, have been fed; then it persists for 10 to 12 days. Inasmuch as quantities below 600 mg. consistently gave negative results, it is probable that, in the rabbit at least, rotenone is considerably changed.

Even after repeated feeding of large doses of derris to both rabbits and dogs, no positive test has been obtained upon either single or combined extracts of the excreta. This behavior is somewhat understandable in view of the fact that at least 600 mg. of rotenone must be administered before a positive test in the excreta is established; this would correspond to a dose of 6000 mg. of derris to a rabbit.

Stability

Derris stored in a well-closed tin container, frequently opened, appeared to lose about 15 per cent of its toxicity after 7 months. When kept in a flint glass bottle, exposed to daylight and agitated daily, the powder was found to be about 50 per cent less toxic after 110 days. When derris powder was exposed to the rays of a General Electric Type S2 sun lamp at a distance of 12 inches and frequently stirred, a 50 per cent loss in toxicity occurred in 41 hours; after 281 hours no further deterioration was noted. These toxicity tests were all made upon rats by oral administration. Jones et al. (*12*) observed that, when derris was subjected to an electric arc light for 240 hours, its toxicity for gold fish (*Carassius auratus*) practically disappeared.

Derris was boiled in water (10 gm. in 250 cc.) for half an hour; the mixture was then cooled and administered orally to a series of rabbits. The toxicity was unaltered, demonstrating that boiling under conditions comparable to household cooking probably has no effect upon the toxicity of derris.

Summary

The acute oral toxicity of derris and cube (one sample) containing varying amounts of rotenone and total extractives has been determined for various laboratory animals. One specimen of derris, particularly studied, had a fatal oral toxicity of 600 mg. for rabbits, 100 for rats, 75 for cavies, and 150 for dogs.

Derris appears to exert its most profound effect upon respiration, which is initially stimulated and then, after fatal doses, completely depressed, with death resulting.

The oral toxicity of derris does not depend solely upon its rotenone or total acetone-extractive content.

Water appears definitely capable of extracting from derris some of its active principles, probably in a colloidal state. Acetone removes all the toxic principles from derris.

Preliminary experiments indicate that, when administered in certain doses, olive oil increases the toxicity of derris for rabbits and to some extent for rats.

The inhalation of derris powder and dust containing derris powder in amounts of 5 per cent and above was found to be fatal to several species of animals. Talc containing 1 per cent rotenone, administered to rats by inhalation, was quite without effect after 10-hour exposure.

When derris dust was applied to the arm pits of four individuals, it provoked a mild evanescent irritation in one instance. In the form of a 10 per cent ointment it appeared to have no local irritant or anesthetic action upon the skin of humans or rats. There was no evidence of absorption after such application. The dust provoked a severe conjunctivitis when insufflated into the eyes of rabbits. In man it produces a sensation of numbness when brought in contact with the buccal mucous membranes.

As tested by the Türck experiment, and as indicated by its effect upon the isolated sciatic nerve of frogs and upon the vagi of dogs, derris seems to have a definite anesthetic effect, slow in its onset but persistent in its action. There was no evidence of a curare effect either upon the sciatic nerve of frogs or upon the phrenic nerve of dogs.

A test for rotenone is described which has been used to study the mode of excretion of rotenone and derris.

One sample of finely powdered derris lost about 15 per cent of its toxicity in 7 months when kept in a well-closed tin container. When exposed to daylight in a flint glass bottle, it lost about 50 per cent of its activity in 110 days. Upon exposure to a sun lamp, it lost 50 per cent of its toxicity in 41 hours. Further exposure for 281 hours caused no further loss in potency.

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SELENIUM IN HAWAII AND ITS PROBABLE SOURCE IN THE UNITED STATES

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Courtesy, Geophysical Laboratory
Dome from Which Gases Were Collected within the Active Pit, Halemaumau

THE occurrence and distribution of selenium in certain soils in the United States, particularly of the semi-arid areas, have been reported by one of the authors (*1*, *2*). In the course of these investigations, at the suggestion of C. A. Browne of the Bureau of Chemistry and Soils, a sample of lava covered with a sulfur deposit was secured near Kilauea, on the island of Hawaii, through the kindness of T. A. Jaggar, of Hawaii. The association of selenium with sulfur is well recognized and has recently been demonstrated in volcanic emanations from the Valley of Ten Thousand Smokes by Zies (*13*). The sulfur sample from Hawaii was a portion of a larger sample which, by reason of its color, was presumed to be seleniferous. It was ground, and the lava and sulfur together were tested for selenium. The quantity found was 0.14 per cent. Since these sulfur deposits must be considered as sublimed onto cooler surfaces from the hot gases of the vents, the inference must be drawn that selenium is present in the volcanic gases and, by further inference, that it should be present in the soils and perhaps in the vegetation on the mountain slopes. Through the kindness of O. C. Magistad, then of the Hawaiian Pineapple Growers Association, and Leslie R. Smith, of the Division of Soil Survey, seven soil profiles from the island of Hawaii, five from Maui, one from Molokai, and one from Kauai were obtained and examined for selenium with

positive results (Table I). Through R. V. Allison, of the Soil Conservation Service, two profiles were obtained from the Erosion Experiment Station on the Island of Oahu. The results of examining them are also given in Table I. The soil survey of Hawaii, undertaken by the Bureau of Chemistry and Soils, has furnished, through the courtesy of Mark Baldwin, two profiles from Hawaii itself and with three from the island of Maui. These were examined and the results are included in Table I. Thus, one or more soil profiles from each of the five major islands of the Hawaiian group are included in this report.

In addition, samples of gases collected from the Kilauea Crater in 1917 by Day and Shepherd (*8*) were secured. These gases had been preserved in three sealed glass tubes and aggregated about 600 cc. in volume. They still showed a slightly diminished atmospheric pressure. One of the three samples had been passed through a barium hydroxide tube in the process of collection. This was not the case with the other two. This quantity of gas and the tube washings showed the presence of 0.005 mg. of selenium.

E. S. Shepherd was also able to furnish a sample of sulfur collected by T. A. Jaggar in 1921 from the Southwest Crack at the great Solfatara near Halemaumau before the great overflow of March 7, 1921. The examination of this sample showed the presence of 2200 p. p. m. of selenium.

Analytical Methods and Data

The methods used in examining the samples were those described by Robinson and co-workers (*6*) and by Williams and Lakin (*12*) except in the case of the sulfur samples. In the examination of sulfur it is convenient to digest the sample in sulfuric acid at boiling temperature until the sulfur has completely oxidized. The issuing gases are passed through a condenser and an absorption bulb containing hydrobromic acid and bromine. To the cooled sulfuric acid in the distilling flask is added the contents of the absorption bulb and enough hydrobromic acid to make up the total hydrobromic acid to 100 cc. The distillation and determination are carried out in the usual way.

TABLE I. ANALYTICAL DATA ON THE PRESENCE

Lab. No.	Field No.	Location	Material	Depth *Inches*	Selenium *P. p. m.*
		Island of Hawaii			
B17989	....	Kilauea	Gas (approx. 600 cc.)	...	0.005 mg.
B17910	....		Lava of 1919 acted upon by solfatara gases, 1920	...	1400
B17985	....		Sulfur from vent in the great Solfatara	...	2200
C1188	610101	3.1 miles W./N. W. of Hakalau, elevation 200 feet, rainfall 150 inches	Kaiwiki silty clay loam	0–9	4
C1189	610102			9–14	2
C1190	610103			14–26	3.5
C1191	610104			26–28	3
C1192	610105			28–30	3
C1193	610106			38–50	5
C1194	610107	1 mile N. of Papaikou, elevation 1100 feet, rainfall 200 inches	Hilo silty clay loam	0–9	3.5
C1195	610108			9–19	4
C1196	610109			19–22	3
C1197	610110			22–25	3
C1198	610111			25–35	5
C1199	610112			35–54	3
C1200	610113			54–67	3
		Island of Maui			
B5787	9396	156° 37′ 40″ W., 20° 56′ 20″ N., elevation 2500 feet, rainfall 100 inches	Red clay	0–6	7
B5788	9397			6–9	15
B5789	9398			9–30	18
B5790	9399		Lava and soil	30–40	8
C938	HT56	5 miles N./N. E. of Lahaina, elevation 2550 feet, rainfall 100 inches	Silty clay loam	0–7	8
C939	HT57			7–15	26
C940	HT58			15–22	3
C941	HT59			22–30	2
C942	HT60	About 5 miles N./N. E. of Lahaina, elevation 1950 feet, rainfall unknown	Reddish silty clay loam	0–7	14
C943	HT61			7–19	18
C944	HT62			19–31	14
C945	HT63			31+	14
C946	HT64	About 5 miles N./N. E. of Lahaina, elevation 1250 feet, rainfall unknown	Reddish silty clay loam	0–7	1.5
C947	HT65			9–13	2
C948	HT66			13–35	2
C949	HT67			25–41	1
C950	HT68			41–60	1
C951	HT69			60+	1

The data given in Table I show definitely the presence of selenium in the volcanic gas and in the material derived by sublimation upon colder surfaces. These observations are sufficient to warrant the conclusion that selenium is ejected from volcanoes in considerable quantities and is found among the more volatile components. It is not known how large the selenium component may be or to what extent it varies in different eruptions and in different localities, although variation seems probable. Samples of lava and volcanic ash so far examined are essentially free from selenium, possibly by reason of the high temperature of ejection (*8*) and relatively high solidifying temperature.

Table I reveals the presence of selenium in every soil sample examined from each of the five major islands of the Hawaiian group. There is, however, no evidence submitted on the selenium content of vegetation. Samples have been requested but are not at hand at the time of writing. It has been shown, through data as yet unpublished, that highly ferruginous soils convert absorbed selenium to a highly insoluble form, a basic ferric selenite. All the Hawaiian soils reported in Table I are highly ferruginous, and for this reason it may be possible that low selenium in the vegetation will be found. However, several of the profiles reported contain quantities of selenium which, if present in such soils as are found in South Dakota or Wyoming, would render many forms of vegetation decidedly toxic.

The most important relation found in the data is that between rainfall and selenium content. In the seleniferous areas previously reported (*1*, *2*), it appears that, when soils derived from shales contain selenium, the quantity present in derived soils is decreased by percolating waters (*1*, *3*, *11*) and therefore becomes lessened by drainage in areas of high rainfall. In the Hawaiian Islands, on the contrary, it appears, in general, that the higher the rainfall the higher the soil content in selenium. Thus, the estimated annual rainfall in the case of profile B5791–B5794 is 20 inches, whereas that of the two profiles B5787–B5790 and C938–C941 is 100 inches. No estimates of rainfall for profiles C942–C945 and C946–C950 are available, but the elevation of the former is 1950 and of the latter 1250 feet. Presumably the rainfall is higher at the greater elevation since the profiles are taken on the same slope.

The sample taken on Molokai Island has an estimated annual rainfall of 20 inches; that of profile B3717–B3721 on Kauai Island is 100 inches. Profiles C787–C791 and C792–C795 have an estimated annual rainfall of 100 and 26 inches, respectively. The two profiles from the island of Hawaii

OF SELENIUM IN THE HAWAIIAN ISLANDS

Lab. No.	Field No.	Location	Material	Depth	Selenium
				Inches	*P. p. m.*
		Island of Maui (*Cont'd*)			
B5791	9392	156° 40′ 24″ W., 20° 58′ 24″ N., elevation 450 feet, rainfall 20 inches	Clay loam	0–2	1
B5792	9393			2–7	3
B5793	9394			7–28	0.6
B5794	9395			28–50	1
		Island of Molokai			
B3712	...	157° 14′ 30″ W., 21° 8′ 30″ N., elevation 500 feet, rainfall 20 inches	Red silty clay	0–3	1
B3713	...			3–13	2.5
B3714	...			13–35	3
B3715	...			35–46	3
B3716	...			46–60	1
		Island of Oahu			
B17948	A-1	Wahiawa Erosion Expt. Sta., elevation unknown, annual rainfall presumably about 50 inches	Soil profile, top section	.....	10
B17949	A-2		Middle section	.....	10
B17950	A-3		Bottom section	.....	10
B17966	1		Top section	.....	12
B17967	2		Middle section	.....	10
B17968	3		Bottom section	.....	12
		Island of Kauai			
B3717	A	159° 27′ 48″ W., 22° 12′ 36″ N., elevation 500 feet, rainfall 100 inches	Red clay	0–4	15
B3718	A_2			4–16	15
B3719	B			16–33	12
B3720	C			33–50	12
B3721	D			20 feet	0.4
C784	37158	2 miles S. of Kalihiwai, rainfall 90 inches	Kalihikai silty clay	0–6	10
C785	37159			12–20	6
C786	37160			20–54	2
C787	37161	Highlands above Waimea Canyon, rainfall 100 inches	Kainamanu silt loam	5–5	6
C788	37162			5–9	14
C789	37163			9–15	16
C790	37164			15–20	12
C791	37165			20–40	1.5
C1201A	37166	2 miles S. W. of Kilohana Lookout, rainfall 100 inches	Kumuweia gravelly loam, dead vegetation	0–1	7
C1201	37167			1–3	20
C1202	37168			3–9	20
C1203	37169			9–15	12
C1204	37170			15–41	20
C792	37171	0.75 mile N. of Hanapepe, rainfall 25–30 inches	Hanapepe	0–8	1
C793	37172			8–14	1
C794	37173			14–32	1
C795	37174			32–42+	1

have annual rainfall estimated for C1188–C1194 and C1195–C1200 of 200 and 150 inches, respectively.

Therefore the conclusion appears warranted that the selenium of the Hawaiian soils is derived chiefly from the volcanic gases or sublimates, and is carried down into the soils by rain and there held in a highly insoluble form.

Primary Source of Selenium in the U. S.

These observations, coupled with those made in many other areas (*1*, *3*), lead to a rather broad general hypothesis concerning the primary source of the selenium in the soils of the United States. It appears very highly probable that the selenium is of volcanic origin and was brought down by rainfall into the seas in which the shales of the upper Cretaceous period were formed. If this is correct, apparently those formations in which selenium is most abundant were deposited contemporaneously with periods of high volcanic activity in the Rocky Mountains.

Some support is given to the hypothesis through the fact that the upper portion of the Niobrara formation and the lower portions of the Pierre formation, which are particularly rich in selenium, contain numerous strata of bentonite. Bentonite is presumed to be derived from volcanic ash or similar material (*4*, *5*, *7*, *9*). It may be presumed, therefore, that deposits of such material should be preceded, accompanied, and followed by material absorbed from volcanic gases and dust, formed by cooling of moderately volatile material. This assumption seems the more probable because it has been shown by Strock (*10*), and abundantly confirmed in this laboratory, that ferric hydroxide absorbs and precipitates selenium from even extremely dilute solutions. Added validity is given also through the fact that apparently no soils, and particularly no highly ferruginous soils, exist in which selenium cannot be found. The distribution of dust and gaseous material of volcanic origin may safely be assumed to be world wide. The hypothesis is useful in that it points to the probability that no great areas of selenium-bearing soils of materially higher selenium content than those already discovered will be found and emphasizes the suggestion (*2*) that it is impossible to make sharp definition between seleniferous and nonseleniferous soils. It would seem probable that, while some selenium is present in almost all forms of vegetation, yet because of the wide variation in the selective absorption by plants (*1*, *2*, *3*), differences in solubility of the selenium compounds in the soil, and variation of the quantity of selenium present, it is the exception rather than the rule that seleniferous vegetation is seriously harmful to animals. The total area of soils materially affected is certainly very great, and more detailed information is urgently needed.

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DESIGN OF

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The over-all plate efficiency in commercial petroleum columns treating gasoline or light naphthas under efficient operating conditions is close to 100 per cent. With close plate spacing or short path of reflux on plates, the efficiency is decreased to about 80 per cent. In lower sections of petroleum columns, or when operating on less volatile fractions, the plate efficiency is progressively reduced. With poor operating conditions, such as large quantities of water on plates, the plate efficiency is seriously limited and may be reduced to about 15 per cent.

The graphical method of computing the number of equilibrium plates required to separate complex mixtures, such as petroleum, is convenient and reliable when limited to a section containing not more than six or eight equilibrium plates, and may be used in conjunction with over-all plate efficiencies to compute the number of actual plates required in a petroleum fractionating column.

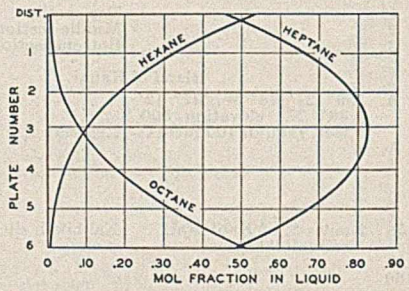

FIGURE 1. UNDERWOOD'S LIQUID COMPOSITIONS FOR TOTAL REFLUX PROBLEM

WHERE sharp separation between components is required, as is usually the case in gas and gasoline fractionation, a procedure similar to that previously described (*4*) is recommended for computing the number of equilibrium plates, or a more complete procedure (*26*) may be used, when time permits, for checking an assumed operation. In cases where less sharp separation between adjacent components, or a smaller number of plates between products, is required, as in current commercial practice in petroleum fractionation, the procedure to be described offers the advantage of greater simplicity.

The graphical method of McCabe and Thiele (*19*) is most satisfactory for its intended application to binary mixtures when the reflux ratio may be assumed to be constant. Attempts to apply an equivalent graphical procedure to complex mixtures have not been successful.

Fenske (*6*) and Garton and Huntington (*9*) have assumed that the fractionation between two cut components in the complex mixture is the same as though the two cut components alone were present in the same proportion, and that the reflux ratio of all components for the complex mixture is equivalent to the same reflux ratio for the two cut components alone for the equivalent binary mixture. This simplification is valid only for total reflux or for an infinite number of plates (*3*, *28*), and is generally unreliable.

Obryadchikov (*21*) and Peters and Obryadchikov (*23*) used a single equilibrium curve based on the composition of the feed to a fractionating column to compute, by a graphical method similar to that of McCabe and Thiele (*19*), the number of plates required to separate the feed into overhead and bottom fractions containing certain percentages boiling below (or above) a chosen cut temperature. Adjustments in the slope of the operating lines were made at each plate for the changes in reflux ratio, and apparently satisfactory results were obtained by a somewhat obscure procedure, using Engler distillation data. Attempts to apply the method, as described, to an entire column on the basis of either A. S. T. M. or so-called true-boiling-point distillation analyses have been unsuccessful. The difficulty lies in the attempted use for all plates of a single equilibrium curve based on the feed composition, which can express accurately the equilibrium conditions only for a mixture of the same composition as the feed. Since the shape of the equilibrium curve depends upon the composition of the material (*13*), which differs from plate to plate throughout the column and is at no point therein the same as the feed, successful application of this method requires the use of equilibrium curves depending upon the composition on the plates where the equilibrium is supposed to exist and not upon the composition of the feed.

Application to Underwood's Data

For example, the solution given by Underwood (*28*) for the fractionation of a mixture of five components may be correctly solved by a simple graphical procedure only if the proper equilibrium curve is used for each equilibrium plate. The conditions of this problem as solved by Underwood are given in Table I, and the compositions on plates 1 through 6, as computed by Underwood, are plotted in Figure 1.

TABLE I. SPECIFICATIONS FOR UNDERWOOD'S PROBLEM (*28*)

Component	Mole Fraction in: Feed	Overhead	Bottoms
Hexane	0.3100	0.5360	...
Heptane	0.2600	0.4600	0.00126
Octane	0.1870	0.00406	0.4370
Nonane	0.1250	...	0.2960
Decane	0.1120	...	0.2660
Moles/mole of overhead	1.7310	1.0000	0.7310

Total pressure = 14.7 lb./sq. in.; column operated at total reflux ($L/V = 1$).

FRACTIONATING COLUMNS

III. Plate Efficiency and Number of Plates for Petroleum Columns[2]

Figure 2 is a plot, or graphical solution, of the composition on each of plates 1 through 6 according to the conditions set up in Table I, using the equilibrium curve for each plate as determined by Raoult's law from the known composition and temperature of the vapor rising from that plate. Since the column is operated with total reflux ($L/V = 1$), the composition of the liquid overflowing from any plate is the same as that of the vapor rising to that plate. The composition of the overhead vapor is given in Table I. By means of the equations (*13*),

$$\Sigma\left(\frac{y}{K}\right) = 1$$

$$\text{and} \quad y = Kx$$

where $K = \frac{p}{P}$ when Raoult's law is used

p = vapor pressure of a particular component at equilibrium temp.

P = total pressure of equilibrium

the temperature of the top plate and the composition of the liquid overflowing from that plate are determined.

The numbered points in Figure 2 refer to the composition on the plate of that number for a particular cut temperature. The plain numbers (toward the upper right-hand corner) indicate the combined mole fraction of hexane plus heptane as a single component, while the primed numbers (toward the lower left-hand corner) indicate the mole fraction of hexane. The cut in the former case is made between heptane and octane, and in the latter between hexane and heptane; i. e., the two arbitrary components of the equivalent binary mixture are, in the first case, octane and all more volatile material; and in the second instance, hexane and all less volatile material.

By the use of the two series of steps, one representing the cut between octane and more volatile material (hexane and heptane) and the other between hexane and less volatile material (heptane and octane), the entire composition on each plate is represented by Figure 2 in a manner similar to that used by McCabe and Thiele for binary mixtures. The equilibrium curve for plate 2 only is drawn in its entirety, but it is clear that reliable results could not be obtained if any one of the six equilibrium curves were used to represent the conditions on all plates. When the correct equilibrium curve is used for each plate, the graphical principle of McCabe and Thiele, with all of its conveniences can be applied with accurate results to the fractionation of complex mixtures. But the difficulties in constructing a separate equilibrium curve from the composition of the vapor or liquid for each plate rob the method of all its conveniences.

Over a limited number of plates such as a short fractionating column or a section of a tall column, including usually not more than about six or eight equilibrium plates, it was found that the equilibrium curves for the materials on the intermediate plates are usually intermediate to, and lie within the area bounded by, the equilibrium curves for the first and last plates of the section. It was also found that such intermediate curves may be located with sufficient accuracy in this intermediate zone by proportional spacing of the abscissas (or ordinates), according to the number of intermediate plates.

This procedure was applied to a second problem set up by Underwood (*28*) in which the feed, overhead, and bottoms are of the same composition as given in Table I, but the reflux ratio (L/V) is 0.75. Underwood also computed the composition of the liquid on plate 6, which will be used as the lower terminal plate. The proposed binary mixture method is illustrated in Figure 3 in which the graphical solution is given for the mole fraction of hexane on the various plates in solid lines. The number of equilibrium plates required for this separation between hexane and the less volatile material (heptane and octane) as computed by the graphical method is six, the same as computed by Underwood.

The number of equilibrium plates required for the separa-

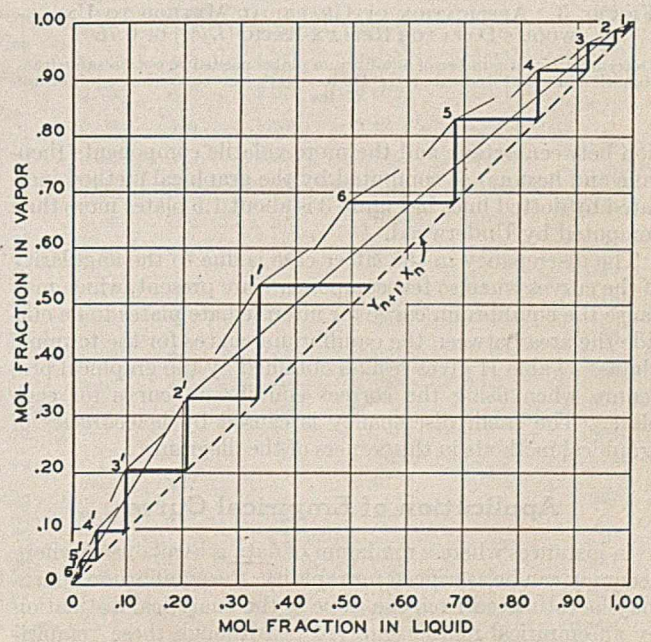

FIGURE 2. PLOT OF PLATE-TO-PLATE CALCULATIONS FOR UNDERWOOD'S TOTAL REFLUX PROBLEM

Plain numbers refer to equilibrium plate compositions for hexane plus heptane, as a single component. Primed numbers refer to equilibrium plate compositions for hexane.

[1] Present address, Standard Oil Company, Casper, Wyo.

[2] Part I appeared in January, 1934, and Part II in April, 1935.

TABLE II. VAPOR AND LIQUID COMPOSITIONS FOR UNDERWOOD'S EXAMPLES (*28*)

Method 1 = Underwood's calculation for total reflux (L/V = 1.0).
Method 2 = Hausbrand plate-to-plate calculation for total reflux (L/V = 1.0).
Method 3 = graphical calculation for total reflux (L/V = 1.0), using empirical curves of Figure 4.
Method 1A = Underwood's calculation for internal reflux (L/V) of 0.75.
Method 2A = graphical calculation for internal reflux ratio (L/V) of 0.75.
Method 3A = graphical calculation for internal reflux ratio (L/V) of 0.75, using empirical curves of Figure 4.

Component	Method	Mole Fraction of Component														
		y_1	x_1	y_2	x_2	y_3	x_3	y_4	x_4	y_5	x_5	y_6	x_6	y_7	x_7	y_8
C_7H_{16} +	1	0.9960	0.9860	....	0.9670	....	0.9175	....	0.8310	....	0.6820	....	0.4985	....	....	....
C_8H_{14}	2	0.9960	0.9860	0.9860	0.9650	0.9650	0.9175	0.9175	0.8300	0.8300	0.6830	0.6830	0.4975	....	....	....
	3	0.9960	0.9925	0.9925	0.9815	0.9815	0.9600	0.9600	0.9200	0.9200	0.8465	0.8465	0.7245	0.7245	0.5535	0.5535
C_8H_{14}	1	0.5325	0.3360	....	0.1850	....	0.0930	....	0.0400	....	0.1500	....	0.0040	....	....	....
	2	0.5325	0.3325	0.3325	0.2040	0.2040	0.0980	0.0980	0.0410	0.0410	0.0185	0.0185	0.0060	....	....	....
	3	0.5325	0.3525	0.3525	0.2060	0.2060	0.1115	0.1115	0.0580	0.0580	0.0310	0.0310	0.0195	0.0195	0.0120	0.0120
C_7H_{16} +	1A	0.9960	0.9860	....	....	....	....	....	....	....	....	....	0.7010	....	....	....
C_8H_{14}	2A	0.9960	0.9860	0.9880	0.9660	0.9735	0.9275	0.9440	0.8610	0.8954	0.7775	0.8315	0.6725	....	....	....
C_8H_{14}	1A	0.5325	....	....	....	....	....	....	....	....	....	....	0.0910	....	....	....
	2A	0.5325	0.3325	0.3810	0.2395	0.3100	0.1870	0.2705	0.1515	0.2440	0.1225	0.2200	0.0910	....	....	....
	3A	0.5325	0.3530	0.3980	0.2400	0.3125	0.1790	0.2670	0.1500	0.2450	0.1300	0.2300	0.1200	0.2200	0.1140	....

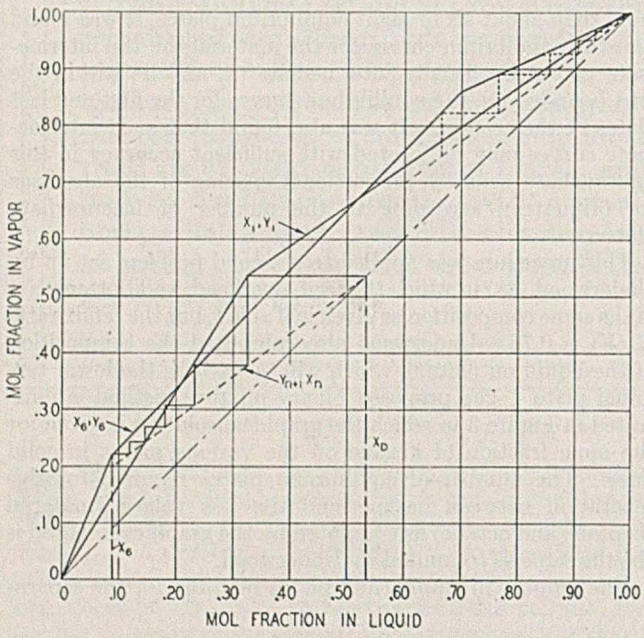

FIGURE 3. APPLICATION OF GRAPHICAL METHOD TO UNDERWOOD'S DATA FOR REFLUX RATIO (L/V) OF 0.75

Determination of number of equilibrium plates needed to obtain same fractionation as that indicated by Underwood's six computed equilibrium plates

tion between octane and the more volatile components (heptane and hexane) as computed by the graphical method indicated by dotted lines in Figure 3 is about 1.5 plates more than computed by Underwood.

The discrepancy in the latter case is due to the angularity of the curves when so few components are present, which may cause the equilibrium curve for intermediate plates to lie outside the area between the equilibrium curves for the terminal plates. Table II gives results obtained by the graphical procedure when using the correct equilibrium curve for each plate. The small discrepancy is caused by inaccuracies of graphical methods in the corners of the diagram.

Application of Empirical Curves

In instances where a minimum of data is available or where accuracy can be sacrificed for rapidity, the equilibrium curves may be estimated from the slope of the analytical distillation by an empirical relationship (*13*). Although these "empirical" curves, plotted in Figure 4, were originally based on the weight fraction of the feed material for an equilibrium vaporization, they may be used on a mole fraction basis when applied to the vapor or liquid in a section of a petroleum column, and in the same manner as the more reliable equilibrium curves computed (*13*) from the actual composition of the liquid or vapor leaving the plate.

For example, the graphical solution of Underwood's problem for a reflux ratio (L/V) of 0.75 was made on Figure 4 (dotted lines) for the separation of hexane from the less volatile material (heptane and octane). Since the slope of the distillation curve of the material present on plate 6, according to Underwood's computations, would be zero if computed from the temperatures of the 10 and 70 per cent points, the slope was taken as between the initial and end points, or 102° F. per 100 per cent, or 1.02° F. per per cent. Both the overhead product and liquid on plate 6 have such slopes of 1.02; hence the one curve serves both the terminal and intermediate conditions.

It may be suggested that, because of the difficulty of properly interpolating for equilibrium curves of materials having distillation-curve slopes of less than 1.0, the curve for a slope of 1.0 be used for all fractions having slopes of 1.0 or less.

The dotted lines on Figure 4 suggest a difficulty that is sometimes experienced with these empirical curves. The operating line intersects the equilibrium curve at or before the point where the desired lower terminal composition is reached, because the equilibrium curves represent only approximately the terminal plate materials. Consequently the result of the determination in this instance is somewhat in doubt, approximately seven or eight plates being indicated as

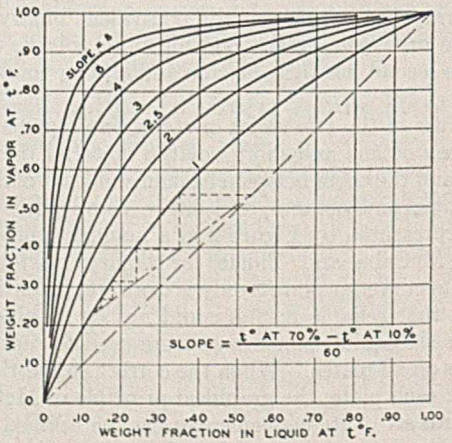

FIGURE 4. EMPIRICAL EQUILIBRIUM CURVES OF KATZ AND BROWN

Numbers on the curves refer to the slope of the so-called true-boiling-point distillation curves, in ° F. per per cent. Dotted lines indicate application of the curves to the graphical determination of the number of equilibrium plates required for the problem set up by Underwood (*28*) for reflux ratio (L/V) of 0.75

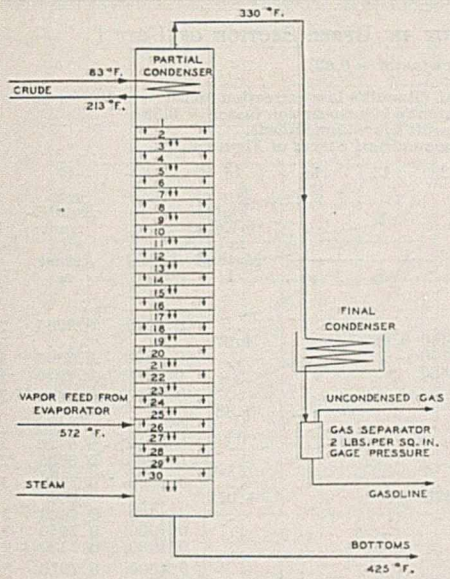

FIGURE 5. FLOW DIAGRAM OF UNIT 1 UNDER TEST

necessary to accomplish the desired separation, as against six computed by the more accurate methods.

Application to Petroleum Columns

The practical value of any method can be determined only by successful application to commercial operations. Complete test data were obtained on a commercial column, designated as unit 1, operating on a naphtha fraction of a California crude. Figure 5 gives a diagrammatic flow sheet of this unit under test. This fractionating column is 8 feet 7 inches in diameter and contains thirty plates spaced 12 inches apart. Vapors were supplied from an evaporator in which the crude was separated into 51 per cent residuum and 49 per cent vapor feed which entered the column between plates 25 and 26, and was fractionated into an overhead product and bottoms. Reflux for the separation was furnished by passing the cold crude through a partial condenser located in the vapor space above plate 1.

The operating test data are presented in Figures 6 and 7, and Table III. The molecular weights were determined from published data (*7, 18*), as were the specific, sensible, and latent heats (*8, 14, 30, 31*).

The usual equations (*29*) employed in making the Hausbrand type (*12*) of plate-to-plate computation were applied to the experimentally determined composition of the liquid overflowing from plate 1 to compute the composition and quantity of the vapor rising from plate 2 rather than attempting to use the undetermined composition of the stream from the reflux condenser as a starting point. The composition and temperature of the liquid on equilibrium plate 2 was next computed by the application of a corrected Raoult's law (*1*) to the composition of the vapor rising from plate 2, in the manner shown in Table IV (*13*). This procedure was then repeated for equilibrium plates 3, 4, and 5. The results of these calculations are given as method 1 in Table V and in Figure 8.

The graphical method was then applied to the same problem, using identical vapor-liquid equilibrium data for equilibrium plates 2 and 5, as illustrated in Figure 9. The value of

TABLE III. TEST DATA FOR UNIT 1

Stream	Gravity, ° A.P.I.	Temp., ° F. Liquid	Temp., ° F. Vapor	Quantity/Hr.	Gage Pressure, Lb./Sq. In.
Crude	31.1	614	...	209 bbl.	..
Residuum	19.8	566	...	107 bbl.	..
Naphtha feed	44.9	572	...	102 bbl.	..
Bottoms	33.7	425	...	335 bbl.	..
Distillate	51.6	...	330	68.4 bbl.	..
Liquid on:					
Plate 1	42.3	363	359	...	6.5
Plate 2	41.8	397	...	...	..
Plate 3	40.8	414	...	...	..
Plate 5	40.3	423	...	...	..
Plate 9	39.9	436	...	...	..
Plate 13	39.5	440	...	...	..
Plate 16	39.4	441	...	...	..
Plate 19	39.2	447	...	...	..
Plate 21	38.5	...	455	...	..
Plate 23	37.6	461	467	...	..
Plate 25	35.5	485	492	...	..
Plate 26	35.0	481	527	...	18.0
Plate 28	34.2	...	...	...	..
Plate 30	35.2	455	444	...	..
Steam	..	...	...	530 lb.	..

L/V for use in this analysis was obtained by averaging the L/V ratios found for plates 2, 3, and 4 by the plate-to-plate calculations. Using this average value of 0.568 for the slope, the operating line was laid off, passing through the point (x_1, y_2) for the arbitrarily selected cut temperature, and the number of equilibrium plates required was stepped off as previously described. The two operating lines in Figure 9 represent the two cut temperatures of 425° and 390° F. Similar operating lines were laid off for each cut temperature shown in Table V, and the required number of equilibrium plates was stepped off to obtain the same separation as in the case of the four equilibrium plates of the plate-to-plate calculation. The

TABLE IV. COMPUTATION OF VAPOR-LIQUID EQUILIBRIUM ON PLATE 5 OF UNIT 1

Temp. ° F.	Mole Fraction in Liquid x	Δx	Av. Atm. B. P. ° F.	Vapor Pressure (2) at 425° F. Mm. Hg	$K^* \Delta x$	Mole Fraction in Vapor Δy	y
160	0						0
		0.02	202	10,550	0.1690	0.1663	
228	0.02						0.166
		0.02	250	6,200	0.0984	0.0969	
265	0.04						0.263
		0.02	282	4,290	0.0680	0.0670	
293	0.06						0.330
		0.02	305	3,255	0.0516	0.0509	
317	0.08						0.381
		0.04	335	2,273	0.0721	0.0710	
353	0.12						0.452
		0.04	365	1,600	0.0508	0.0500	
374	0.16						0.502
		0.06	383	1,265	0.0602	0.0593	
390	0.22						0.561
		0.06	395	1,100	0.0524	0.0515	
399	0.28						0.613
		0.06	402	992	0.0473	0.0465	
405	0.34						0.669
		0.06	409	930	0.0443	0.0435	
414	0.40						0.713
		0.06	422	775	0.0369	0.0363	
424	0.46						0.749
		0.06	425	760	0.0362	0.0356	
426	0.52						0.785
		0.06	429	730	0.0348	0.0342	
430	0.58						0.819
		0.06	433	695	0.0330	0.0324	
436	0.64						0.851
		0.06	439	648	0.0308	0.0303	
441	0.70						0.882
		0.06	442	605	0.0288	0.0283	
445	0.76						0.910
		0.06	447	575	0.0273	0.0268	
449	0.82						0.927
		0.04	449	555	0.0176	0.0173	
450	0.86						0.944
		0.04	450	550	0.0173	0.0170	
450	0.90						0.961
		0.04	451	545	0.0171	0.0168	
452	0.94						0.978
		0.04	456	515	0.0162	0.0159	
465	0.98						0.994
		0.02	474	400	0.0063	0.0062	
492	1.00						1.000
				Total	1.0164	1.0000	

* $K = 0.88\, p/P$; P = 1110 mm. Hg.

TABLE V. EQUILIBRIUM PLATES AND PLATE EFFICIENCY IN UPPER SECTION OF UNIT 1

Method 1 = plate-to-plate calculation for 4 equilibrium plates (Raoult's law correction factor = 0.88).
Average reflux ratio (L/V) = 0.568 for following methods:
Method 2 = graphical calculation using same terminal plates as found by method 1 (Raoult's law correction factor = 0.88).
Method 2A = graphical calculation from actual plate 2 through actual plate 5 (Raoult's law correction factor = 0.88).
Method 2B = graphical calculation from actual plate 2 through actual plate 5 (Raoult's law unmodified).
Method 3 = graphical calculation from actual plate 2 through actual plate 5, using empirical curves of Figure 4.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
		Mole Fraction of Arbitrary Component												No. of Plates to Equal x_5 of Method 1	Actual x_5	y_5 in Equilibrium with Actual x_5	No. Equilibrium Plates	Plate Efficiency %
Cut Temp. ° F.	Method	x_1	y_2	x_2	y_3	x_3	y_4	x_4	y_5	x_5	y_6	x_6	y_7					
445	1	0.9895	0.9926	0.9655	0.9791	0.9191	0.9023	0.7369	0.8478	0.6318	....	....	....	..	0.7600	0.8995	3.05	76
	2	0.9895	0.9926	0.9655	0.9790	0.9185	0.9520	0.8340	0.9040	0.7310	0.8460	0.6270	....	4.97	....	....	..	..
	2A	....	0.9926	....	0.9810	....	0.9565	....	0.9200	....	0.8790	....	....	..	0.7600	0.8995	4.50	111
	2B	....	0.9926	....	0.9815	....	0.9600	....	0.9275	....	0.8880	....	....	..	0.7600	0.9025	4.63	116
440	1	0.9385	0.9629	0.8623	0.9199	0.7610	0.8622	0.6535	0.7988	0.5429	....	....	....	..	0.6950	0.8690	2.88	72
	2	0.9385	0.9629	0.8623	0.9190	0.7515	0.8560	0.6370	0.7910	0.5310	....	....	....	3.88	....	....	..	..
	2A	....	0.9629	....	0.9195	....	0.8640	....	0.8075	....	....	....	....	..	0.6950	0.8690	2.93	73
	2B	....	0.9629	....	0.9200	....	0.8650	....	0.8100	....	....	....	....	..	0.6950	0.8720	2.87	72
	3	....	0.9629	....	0.9120	....	0.8380	....	....	....	....	....	....	..	0.6950	0.8975	2.20	55
425	1	0.9125	0.9416	0.7975	0.8768	0.6658	0.7994	0.5372	0.7253	0.4241	....	....	....	..	0.4900	0.7620	3.50	88
	2	0.9125	0.9416	0.7975	0.8765	0.6645	0.8010	0.5385	0.7295	0.4280	0.6670	....	....	4.07	....	....	..	..
	2A	....	0.9416	....	0.8750	....	0.8025	....	0.7340	....	....	....	....	..	0.4900	0.7620	3.59	90
	2B	....	0.9416	....	0.8755	....	0.8050	....	0.7375	....	....	....	....	..	0.4900	0.7650	3.59	90
	3	....	0.9416	....	0.8640	....	0.7710	....	....	....	....	....	....	..	0.4900	0.7850	2.85	71
415	1	0.9057	0.9194	0.7408	0.8264	0.5671	0.7247	0.4178	0.6385	0.3042	....	....	....	..	0.4000	0.7070	3.21	80
	2	0.9057	0.9194	0.7408	0.8270	0.5755	0.7325	0.4245	0.6460	0.3150	0.5670	....	....	4.09	....	....	..	..
	2A	....	0.9194	....	0.8255	....	0.7300	....	0.6480	....	....	....	....	..	0.4000	0.7070	3.28	82
	2B	....	0.9194	....	0.8270	....	0.7350	....	0.6510	....	....	....	....	..	0.4000	0.7095	3.18	80
405	1	0.8953	0.9075	0.7153	0.8059	0.5317	0.6986	0.3819	0.6119	0.2823	....	....	....	..	0.3380	0.6645	3.39	85
	2	0.8953	0.9075	0.7153	0.8065	0.5375	0.7045	0.3835	0.6175	0.2815	0.5600	....	....	4.10	....	....	..	..
	2A	....	0.9075	....	0.8070	....	0.7060	....	0.6205	....	....	....	....	..	0.3380	0.6645	3.49	87
	2B	....	0.9075	....	0.8070	....	0.7080	....	0.6245	....	....	....	....	..	0.3380	0.6655	3.51	88
	3	....	0.9075	....	0.7850	....	0.6700	....	....	....	....	....	....	..	0.3380	0.6780	2.94	74
394	1	0.8151	0.8540	0.6157	0.7416	0.4399	0.6378	0.3091	0.5620	0.2208	....	....	....	..	0.2400	0.5835	3.72	93
	2	0.8151	0.8540	0.6157	0.7415	0.4305	0.6370	0.2995	0.5620	0.2208	....	....	....	4.00	....	....	..	..
	2A	....	0.8540	....	0.7375	....	0.6350	....	0.5600	....	....	....	....	..	0.2400	0.5835	3.69	92
	2B	....	0.8540	....	0.7415	....	0.6390	....	0.5640	....	....	....	....	..	0.2400	0.5875	3.69	92
390	1	0.6615	0.7639	0.4578	0.6490	0.3159	0.5631	0.2250	0.5101	0.1700	....	....	....	..	0.2180	0.5620	3.02	75
	2	0.6615	0.7639	0.4578	0.6480	0.3070	0.5620	0.2220	0.5125	0.1715	0.4860	....	....	4.09	....	....	..	..
	2A	....	0.7639	....	0.6490	....	0.5640	....	0.5130	....	....	....	....	..	0.2180	0.5620	3.04	76
	2B	....	0.7639	....	0.6500	....	0.5660	....	0.5135	....	....	....	....	..	0.2180	0.5680	2.98	75
	3	....	0.7639	....	0.6230	....	0.5550	....	0.5400	....	....	....	....	..	0.2180	0.5530	3.12	78
360	1	0.5512	0.6728	0.3312	0.5478	0.2074	0.4728	0.1423	0.4343	0.1090	....	....	....	..	0.1320	0.4625	3.27	82
	2	0.5512	0.6728	0.3312	0.5470	0.2050	0.4755	0.1435	0.4410	0.1140	0.4250	....	....	4.64	....	....	..	..
	2A	....	0.6728	....	0.5485	....	0.4750	....	0.4425	....	....	....	....	..	0.1320	0.4625	3.38	85
	2B	....	0.6728	....	0.5520	....	0.4785	....	0.4400	....	....	....	....	..	0.1320	0.4800	2.98	75
	3	Operating line intersected equilibrium curve before reaching necessary x_5																
340	1	0.3628	0.5420	0.2010	0.4507	0.1306	0.4048	0.0973	0.3845	0.0802	....	....	....	..	0.0930	0.4010	3.19	80
	2	0.3628	0.5420	0.2010	0.4515	0.1300	0.4115	0.1030	0.3965	0.0895	0.3880	0.0825	0.3840	5.89	....	....	..	..
	2A	....	0.5420	....	0.4500	....	0.4070	....	0.3920	....	....	....	....	..	0.0930	0.4010	3.40	85
	2B	....	0.5420	....	0.4510	....	0.4085	....	0.3905	....	....	....	....	..	0.0930	0.4185	2.77	69
	3	Operating line intersected equilibrium curve before reaching necessary x_5																
300	1	0.1972	0.3909	0.0962	0.3339	0.0664	0.3115	0.0533	0.3030	0.0465	....	....	....	..	0.0650	0.3410	1.88	47
	2	0.1972	0.3909	0.0962	0.3350	0.0675	0.3180	0.0575	0.3130	0.0520	0.3090	0.0485	0.3070	6.00	....	....	..	..
	2A	....	0.3909	....	0.3335	....	0.3155	....	0.3120	....	....	....	....	..	0.0650	0.3410	1.87	47
	2B	....	0.3909	....	0.3345	....	0.3175	....	0.3120	....	....	....	....	..	0.0650	0.3520	1.59	40

compositions of the individual streams so computed are indicated under method 2 of Table V. The number of plates determined by this method, necessary to give the same fractionation as indicated by the four equilibrium plates of the plate-to-plate analysis are indicated in Table V, column 15.

A comparison of the composition of each stream as obtained by these two procedures, methods 1 and 2, indicates good agreement in all but a few cases at the extreme corners of the equilibrium curves. This difficulty encountered in the upper corner is due in part to the high sensitivity to small changes in the vapor composition, and in part to the difficulty in making sufficiently accurate geometrical construction in the small dimensions of the corner. Similar errors are also introduced in the lower corner.

A study of Table V indicates that cut temperatures with fractions of more than 0.97 or 0.98 in the material rising from the top terminal plate should not be used. Similarly, cut temperatures with fractions less than 0.08 or 0.10 in the liquid on the lower terminal plate should not be used for reliable results. The average of the results of this graphical procedure (method 2, Table V), omitting the obviously incorrect values of the 445°, 340°, and 300° F. cuts for these reasons, indicates 4.12 plates required to accomplish the same fractionation as obtained by 4 plates as computed by the plate-to-plate procedure (method 1, Table V).

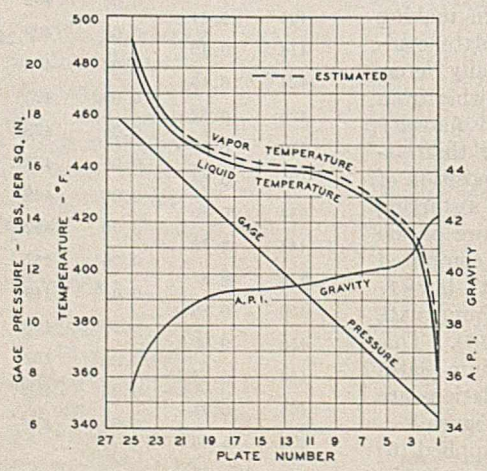

FIGURE 6. OPERATING CONDITIONS FOR UNIT 1 UNDER TEST

Another comparison of equilibrium plates was made in the lower section of the same column. In this case the plate-to-plate computations were begun with the liquid leaving plate 19 (Figure 7) and continued for three equilibrium plates. The procedure for calculating the vapor-liquid equilibria was somewhat modified from that followed in the upper section of the column. In this instance the equilibrium plate temperature was approximated and Raoult's law was applied, provisions being made for arbitrarily introducing on

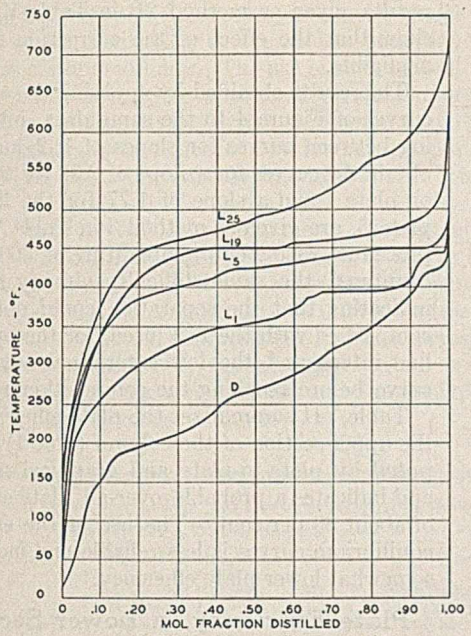

FIGURE 7. TRUE-BOILING-POINT DISTILLATION ANALYSES FOR UNIT 1

Compositions for overhead distillate and liquid leaving plates 1, 5, 19, and 25

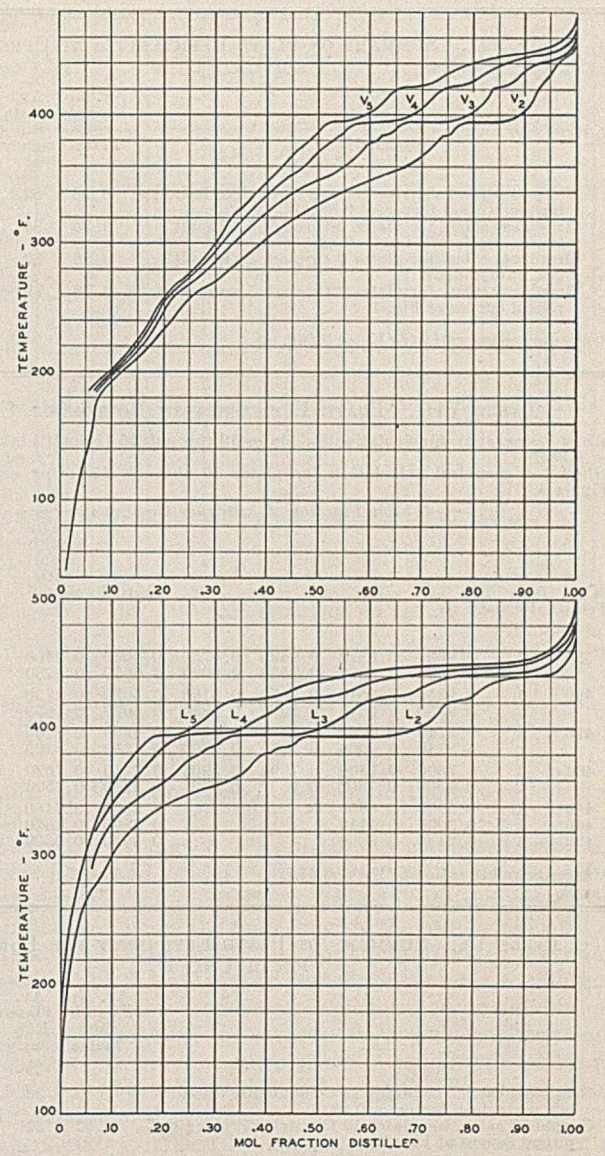

FIGURE 8. DISTILLATION CURVES FOR VAPORS AND LIQUIDS IN UPPER SECTION OF UNIT 1 AS CALCULATED BY PLATE-TO-PLATE METHOD

(*Above*) Computed vapors rising from equilibrium plates 2, 3, 4, and 5
(*Below*) Computed liquids leaving equilibrium plates 2, 3, 4, and 5

each plate a proportional part of the heavier component present in the liquid from actual plate 25, but not appearing in the analysis of the liquid on plate 19. The results of the computation are given as method 1 in Table VI and in Figure 10.

The graphical method was applied to the identical equilibrium data as were used in these plate-to-plate computations for the lower section of the column, with the results given as method 2 in Table VI. The cut temperature of 555° F. gave excellent agreement with the plate-to-plate calculations, although representing more than 0.98 of the vapor rising from the upper terminal plate. The cut temperature of 400° F. represents less than 0.10 of the liquid on the lower terminal plate, and, for the reasons stated, is not expected to give reliable results. Excluding the cut temperature of 400° F., the graphical method indicates an average of 2.70 equilibrium plates for the same fractionation as calculated for 3 equilibrium plates by the plate-to-plate method.

The graphical calculations presented for the determination of the number of equilibrium plates required to effect a given separation agree within about ±10 per cent with the plate-to-plate computations. The equilibrium curves for the material on the top and bottom terminal plates of a short section of any column may be used as the limits for the equilibria on intermediate plates, and these equilibria on intermediate plates may be estimated in the manner described. However, there is a limitation in selecting the cut temperatures to be used, because of the limitations of accuracy with which drawings and analyses can be made.

TABLE VI. COMPARISON OF EQUILIBRIUM PLATES IN LOWER SECTION OF UNIT 1

Method 1 = Hausbrand's plate-to-plate calculation for 3 equilibrium plates.
Method 2 = graphical calculation for same terminal plates as used in method 1 (average L/V = 0.515).

Cut Temp. °F.	Method	Mole Fraction of Arbitrary Component x_1	y_2	x_2	y_3	x_3	y_4	x_4	No. Equilibrium Plates
555	1	0.9962	0.9925	0.9466	0.9725	0.8482	0.9231	0.6315	3.00
	2	0.9962	0.9925	0.9466	0.9715	0.8500	0.9225	0.6270	2.95
488	1	0.9390	0.9677	0.8570	0.9264	0.7116	0.8539	0.4639	3.00
	2	0.9390	0.9677	0.8570	0.9260	0.7000	0.8445	0.4495	2.85
475	1	0.8480	0.9199	0.7462	0.8694	0.6014	0.7981	0.3799	3.00
	2	0.8480	0.9199	0.7462	0.8670	0.5625	0.7725	0.3460	2.75
460	1	0.6585	0.8202	0.5588	0.7730	0.4494	0.7211	0.2832	3.00
	2	0.6585	0.8202	0.5588	0.7685	0.4545	0.6895	0.2460	2.60
452	1	0.4986	0.7352	0.4180	0.6996	0.3144	0.6518	0.2067	3.00
	2	0.4986	0.7352	0.4180	0.6945	0.3030	0.6350	0.1900	2.70
439	1	0.3002	0.6295	0.2601	0.6171	0.2112	0.5982	0.1531	3.00
	2	0.3002	0.6295	0.2601	0.6085	0.2030	0.5785	0.1365	2.35
400	1	0.1694	0.5235	0.1446	0.5194	0.1207	0.5136	0.0921	3.00
	2	0.1694	0.5235	0.1446	0.5100	0.1130	0.4945	0.0820	1.65
				Average, method 1 (excluding 400° F. cut)					3.00
				Average, method 2 (excluding 400° F. cut)					2.70

Plate Efficiency

The matter of plate efficiency has been investigated from two distinctly different approaches, the average individual plate efficiency (*20*), and the over-all plate efficiency. The former is derived from a consideration of the individual plate efficiency of each plate in a column. The latter is the quotient of the total number of

TABLE VII. SUMMARY OF PLATE EFFICIENCIES AT UPPER SECTION OF UNIT 1[a]

	Method	Av. No. Equilibrium Plates	Av. Plate Efficiency %	Cut Temp. Included in Av. ° F.
1.	Plate-to-plate calcn. for plates 2 through 5 (Raoult's law correction factor = 0.88)	3.28	82	440, 425, 415, 405, 394, 390, 360
2A.	Graphical calcn. for plates 2 through 5 (Raoult's law correction factor = 0.88)	3.35	84	440, 425, 415, 405, 394, 390, 360
2B.	Graphical calcn. for plates 2 through 5 (Raoult's law unmodified)	3.26	82	440, 425, 415, 405, 394, 390, 360
3.	Graphical calcn. for plates 2 through 5, using empirical curves of Fig. 1	2.78	70	440, 425, 405, 390

[a] Average reflux ratio (L/V) = 0.568.

TABLE VIII. PLATE EFFICIENCY IN BOTTOM OF UNIT 1[a]

Method 1 = graphical calculation for plates 19 through 25 (Raoult's law correction factor = 0.88).
Method 2 = graphical calculation for plates 19 through 25, using empirical curves of Figure 4.

Cut Temp. ° F.	Method	Mole Fraction of Arbitrary Component x_{19}	y_{20}	y_{21}	y_{22}	Actual x_{25}	y_{25} in equilibrium with actual x_{25}	No. Equilibrium Plates	Plate Efficiency %
520	1	0.9800	0.9820	0.9490	0.8750	0.6650	0.9400	2.13	36
	2	0.9800	0.9820	0.9550	0.9000	0.6650	0.9280	2.49	42
490	1	0.9350	0.9510	0.9080	0.8190	0.5070	0.8720	2.40	40
	2	0.9350	0.9510	0.8900	0.7820	0.5070	0.8650	2.23	37
476	1	0.8740	0.9000	0.8435	0.7605	0.4250	0.8280	2.19	37
	2	0.8740	0.9000	0.7970	0.6700	0.4250	0.8220	1.76	29
464	1	0.7300	0.7800	0.7090	0.5960	0.3210	0.7620	1.25	21
	2	0.7300	0.7800	0.6350	0.5325	0.3210	0.7500	1.21	20
456	1	0.5980	0.6850	....	....	0.2590	0.7180	<1	..
440	1	0.3000	0.4110	....	....	0.1890	0.6620	<1	..
420	1	0.2130	0.3630	....	....	0.1510	0.6300	<1	..

[a] Average reflux ratio (L/V) = 0.515.

TABLE IX. SUMMARY OF PLATE EFFICIENCY FOR LOWER SECTION OF UNIT 1[a]

	Method	Av. No. Equilibrium Plates	Av. Plate Efficiency %	Cut Temp. Included in Av. ° F.
1.	Graphical calcn. for plates 19 through 25 (Raoult's law correction factor = 0.88)	1.99	33	520, 490, 476, 464
2.	Graphical calcn. for plates 19 through 25, using empirical curves of Fig. 1.	1.92	32	520, 490, 476, 464

[a] Average reflux ratio (L/V) = 0.515.

equilibrium plates required to perform a desired separation, divided by the total number of actual plates required, and is the plate efficiency considered in the following calculations.

Plate Efficiency in Upper Section of Unit 1

In graphically determining the plate efficiency in the top section of unit 1, the equilibrium curves were computed for the actual materials on the second and fifth plates by means of Raoult's law, with a correction factor of 0.88. Operating lines were constructed for the cuts shown in Table V, using the average operating-line slope of 0.568. The number of equilibrium plates necessary to arrive at the actual fractionation effected in the column were stepped off between these operating lines and the computed equilibrium curves for the terminal plates, estimating the equilibria for the intermediate plates in the manner previously described. The results are given as method 2A in Table V, with the over-all plate efficiencies given in column 19.

In order to determine the effect of the Raoult's law correction factor (*1*) on computed plate efficiency, the same determinations were repeated, but with equilibrium curves computed by Raoult's law without a correction factor. The results, given as method 2B in Table V, clearly show that the effect of the correction factor is negligible.

The results obtained by applying the empirical curves of Figure 4 to the same data, interpolating between curves for slopes of 1, 2, and 2.5 to obtain the curves for a slope of 2.33 for the liquid on plate 1 and a slope of 1.77 for the liquid on plate 5, are given as method 3 in Table V. This procedure with a cut temperature of 360° F. encountered the same difficulty already noted in indicating that the separation could not be accomplished with the L/V used, for the operating line intersected the lower terminal equilibrium curve before reaching the composition required.

Table VII summarizes the plate efficiencies for the upper section of the column (unit 1) as computed by plate-to-plate and graphical methods, and indicates a probable over-all plate efficiency of about 80 per cent. The use of the empirical equilibrium curves is less reliable and indicates a somewhat lower plate efficiency.

Plate Efficiency in Lower Section of Unit 1

In the lower section of the fractionating column (unit 1) the actual compositions of the vapor rising from plate 20 and of the liquid on plate 25 were used as the terminal conditions. Equilibrium curves calculated from these compositions were used in conjunction with an average operating line having a slope of 0.515. The results of the graphical solution are given as method 1 in Table VIII.

In applying the empirical equilibrium curves to this section of the column, the same procedure was followed as in the analysis of the top section of the unit. The slopes of 2.10 and 2.58, respectively, served as bases for determining the terminal equilibrium curves, and the operating lines used had the same slope of 0.515, as before. The results of this solution are indicated as method 2 in Table VIII.

The results for cut temperatures of 520°, 490°, 476°, and 464° F. are averaged in Table IX and indicate good agreement between the graphical procedures at an apparent over-all plate efficiency of about 33 per cent, being less than half that indicated for the upper section of the same column.

Plate Efficiency in Unit 2

Lewis and Wilde (*17*) tested a commercial column, 9 feet in diameter and containing ten plates spaced 20 inches apart; each of the plates above the feed was equipped with 115 Badger bell caps 6 inches in diameter. The total slot area per plate was 10 per cent of superficial cross section. Slots were 0.25 inch wide and 1 inch high, and the minimum seal was 1 inch. The vapor space above the top plate contained a partial condenser through which circulated cold oil to furnish reflux for the column, the remaining vapors passing to a total condenser. The column was part of a continuous battery of shell stills operated on a Midcontinent crude. The vapor fed to the column from the shell still entered below the bottom plate; the liquid fed to the column (the bottoms from the preceding shell still of the battery) entered on the eighth plate from the top.

The so-called true-boiling-point distillation curves of the overhead distillate (product) and of the liquid on plate 6 are represented by the solid lines in the upper section of Figure 11.

Lewis and Wilde computed plate efficiencies by utilizing

individual key components boiling in narrow ranges rather than the whole distillation curve, as has been done in the cases so far considered here. The use of such individual components makes the method entirely dependent upon the accuracy of a small section of the true-boiling-point curves which are generally not satisfactory for this purpose except when treating the more volatile fractions of less complexity (*4*).

On the basis of two key components, Lewis and Wilde found the average individual plate efficiency above the feed plate to be 65 per cent. However, for the two components so selected, deviations of from 0.15 to 0.26 mole fraction existed between the actual compositions and the corresponding computed compositions on certain plates when using this plate efficiency of 65 per cent. Lewis and Smoley (*16*) stated that such a plate efficiency is too low.

Table X. Comparison for Determining Plate Efficiency of Partial Condenser in Unit 2

Temp. ° F.	Mole Fraction in Liquid in Equilibrium with Actual Vapor Leaving Partial Condenser	Mole Fraction in Actual Liquid Leaving Partial Condenser
242	0	0
290	0.048	0.045
300	0.071	0.066
310	0.117	0.113
320	0.162	0.160
330	0.223	0.208
340	0.326	0.321
350	0.425	0.425
360	0.547	0.541
370	0.669	0.650
380	0.791	0.792
390	0.900	0.914
400	0.976	0.975
436	1.000	1.000

Before applying the graphical method to these data of Lewis and Wilde, the change in composition brought about by the reflux condenser was considered separately. It was found (Table X) that the overhead distillate was within the limits of error of the analysis, in equilibrium with the liquid reflux returned to the column by the partial condenser. Therefore, the terminal plates chosen for the graphical determination of the number of equilibrium plates were the partial condenser as top terminal plate, and actual plate 6 as lower terminal plate. This procedure is equivalent to using the partial condenser as the top equilibrium plate, with the reflux to the column furnished by returning a portion of the totally condensed overhead distillate to the top equilibrium plate.

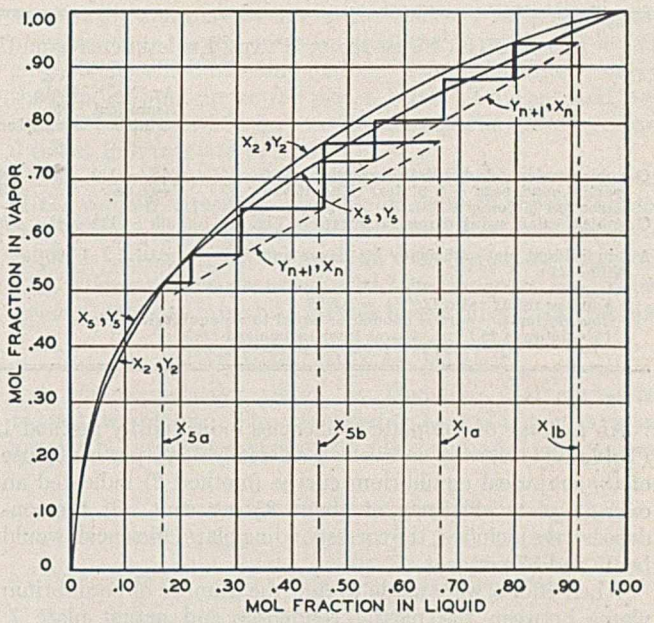

Figure 9. Application of Graphical Method to Data of Unit 1

Determination of number of equilibrium plates required for same fractionation as was obtained between actual plates 2 and 5

Using the average L/V of 0.815 (as computed from the data of Lewis and Wilde) for the operating lines and a Raoult's law correction factor of 0.88 (as used by Lewis and Wilde), the graphical solution of the problem gave the results indicated as method 1 in Table XI. The equilibrium plates are numbered in Table XI so that the partial condenser is equilibrium plate 1. Since this condenser is equivalent to an equilibrium plate, the efficiency of the actual plates should be determined by subtracting one from the number of equilibrium plates required, before dividing this number by the six actual plates in the section of the column.

The results obtained by applying the empirical curves of Figure 4 are given as method 2 in Table XI. The slopes of the distillation curves for the distillate and the liquid on plate 6 were 1.30 and 1.00, respectively, and corresponding curves were interpolated from Figure 4. The average slope of the operating line of 0.815 was used as before.

Table XI. Plate Efficiency in Unit 2[a]

Method 1 = graphical calculation for distillate through plate 6 (partial condenser + 6 actual plates; Raoult's law correction factor = 0.88).
Method 2 = graphical calculation for distillate through plate 6, using empirical curves of Figure 4.

Cut Temp. ° F.	Method	Mole Fraction of Arbitrary Component y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	Actual x_6	y_6 in equilibrium with actual x_6	No. Equilibrium Plates	Plate Efficiency %
408	1	0.9950	0.9900	0.9780	0.9550	0.9120	0.8450	0.7620	....	0.6160	0.7730	6.87	98
	2	0.9950	0.9900	0.9800	0.9605	0.9275	0.8800	0.8190	0.7410	0.6160	0.7710	7.62	110
396	1	0.9810	0.9645	0.9315	0.8775	0.8000	0.7120	0.6250	....	0.4640	0.6380	6.85	98
	2	0.9810	0.9560	0.9100	0.8300	0.7250	0.6060	0.5150	....	0.4640	0.6450	5.67	78
388	1	0.9460	0.9020	0.8330	0.7445	0.6490	0.5605	0.4885	....	0.3500	0.5260	6.48	91
	2	0.9460	0.8825	0.7810	0.6600	0.5500	0.4685	0.4150	....	0.3500	0.5300	5.25	71
380	1	0.8920	0.8125	0.7120	0.6065	0.5130	0.4385	0.3850	....	0.2430	0.4080	6.57	93
	2	0.8920	0.7800	0.6400	0.5150	0.4250	0.3700	0.3430	....	0.2430	0.4025	5.41	74
372	1	0.8270	0.7185	0.5990	0.4910	0.4075	0.3490	0.3110	....	0.1740	0.3240	6.66	94
	2	0.8270	0.6770	0.5250	0.4125	0.3450	0.3100	0.2990	....	0.1740	0.3050	6.45	91
364	1	0.7610	0.6300	0.5035	0.4015	0.3310	0.2870	0.2625	....	0.1330	0.2680	6.78	96
	2	0.7610	Operating line intersected equilibrium curve before reaching necessary x_6										
356	1	0.6810	0.5340	0.4080	0.3195	0.2620	0.2310	0.2150	....	0.1030	0.2220	6.56	93
	2	0.6810	Operating line intersected equilibrium curve before reaching necessary x_6										

[a] Average reflux ratio (L/V) = 0.815.

TABLE XII. SUMMARY OF PLATE EFFICIENCIES FOR UNIT 2[a]

Method	Av. No. Theoretical Plates	Av. Plate Efficiency %	Cut Temp. Included in Av. ° F.
Graphical calcn. for distillate through plate 6 (partial condenser + 6 plates) (Raoult's law correction factor = 0.88)	(6.68 − 1)[b] = 5.68	95	408, 396, 388, 380, 372, 364, 356
Graphical calcn. using empirical curves of Fig. 1	(6.08 − 1)[b] = 5.08	85	408, 396, 388, 380, 372
Av. individual plate efficiency by Lewis and Wilde (*17*)	.....	65[c]	.....

[a] Average reflux ratio (L/V) = 0.815.
[b] Considering the partial condenser equal to an equilibrium plate.
[c] This figure is too low, as was later recognized (*16*).

An average of the plate efficiencies indicated by method 1 (Table XII) showed an over-all efficiency of 95 per cent; use of the empirical equilibrium curves (method 2) indicated an over-all plate efficiency of about 85 per cent. If the condenser were included, the corresponding plate efficiencies would be 95 and 87 per cent.

When efforts were made to find the number of equilibrium plates between the partial condenser and actual plate 7, many of the cut temperatures chosen gave uncertain solutions; but when actual plate 6 was chosen as the bottom terminus of the section, the solutions were satisfactory. This behavior was due to the fact that an attempted analysis over a range equivalent to eight plates of 95 per cent efficiency was, in this case, too large a section of the column. It is generally true that the greater the slope of the distillation curves, the greater the curvature of the equilibrium curves. Inspection of the distillation curves originally presented by Lewis and Wilde for the individual plates of the column shows that the slopes of the curves pass through a minimum at about 5 or 6, which should therefore be taken as a lower terminus in order that the equilibrium curves of intermediate plates may lie between those of the terminal plates.

Plate Efficiency in Unit 3

In order to eliminate several fundamental errors believed to have caused the deviations noted in Lewis and Wilde's work, Lewis and Smoley set up a laboratory column (*16*), 8 inches in diameter with 10 plates equally spaced 16 inches apart; each plate was occupied by one rectangular bubble cap 2 inches wide and extending entirely across the column. The column was operated at total reflux (L/V = 1) and was jacketed with a warm-air circulating system to minimize radiation losses.

Tests were run on a West Texas cracked naphtha with a distillation range of 70° to 480° F. Other runs were also made with other materials and with the addition of small amounts of foreign materials, used as "key components."

The results were analyzed by the type of calculation employing cut components (*17*), with the exception that the Raoult's law deviation factor was not fixed. In fact, several values were chosen for the factor, and the corresponding plate efficiencies were calculated; for the straight naphtha run a factor of 1.03 gave a good check, corresponding to a plate efficiency of about 80 per cent. But 1.03 differs from unity by less than the experimental error involved, and a correction factor of unity is sufficiently accurate.

When aniline, as the key component, was added to a naphtha of a slightly higher boiling range, a plate efficiency of

TABLE XIII. PLATE EFFICIENCY IN UPPER SECTION OF UNIT 3[a]

Method 1 = graphical calculation for distillate through plate 6 (Raoult's law unmodified).
Method 2 = graphical calculation using empirical curves of Figure 4 for distillate through plate 6.

Cut Temp. ° F.	Method	Mole Fraction of Arbitrary Component y_1	y_2	y_3	y_4	y_5	y_6	Actual x_6	y_6 in equilibrium with actual x_6	No. Equilibrium Plates	Plate Efficiency %
250	1	0.9900	0.9710	0.9210	0.8240	0.6840	0.5360	0.5120	0.6400	5.30	80
	2	0.9900	0.9660	0.9000	0.7550	0.5600	0.3790	0.5120	0.6870	4.35	73
242	1	0.9700	0.9160	0.8040	0.6410	0.4660	0.3160	0.3310	0.4530	5.08	85
	2	0.9700	0.9000	0.7270	0.4875	0.2825	0.1600	0.3310	0.5630	3.68	61
236	1	0.9500	0.8670	0.7190	0.5320	0.3500	0.2180	0.2350	0.3430	5.05	84
	2	0.9500	0.8350	0.6050	0.3540	0.1850	0.0990	0.2350	0.3920	3.85	64
229	1	0.9200	0.8040	0.6230	0.4195	0.2500	0.1440	0.1020	0.1680	5.77	96
	2	0.9200	0.7500	0.4790	0.2500	0.1170	0.0615	0.1020	0.1920	4.44	74
222	1	0.8820	0.7310	0.5260	0.3160	0.1710	0.0910	0.0800	0.1370	5.43	90
	2	0.8820	0.6620	0.3790	0.1825	0.0870	0.0450	0.0800	0.1520	4.32	72

[a] Average reflux ratio (L/V) = 1.0.

TABLE XIV. PLATE EFFICIENCY IN LOWER SECTION OF UNIT 3[a]

Method 1A = graphical calculation for plates 6 through 10 (unmodified Raoult's law).
Method 2A = graphical calculation using empirical curves of Figure 4 for plates 6 through 10.

Cut Temp. ° F.	Method	Mole Fraction of Arbitrary Component y_7	y_8	y_9	y_{10}	y_{11}	Actual x_{10}	y_{10} in equilibrium with actual x_{10}	No. Equilibrium Plates	Plate Efficiency %
311	1A	0.9800	0.9500	0.8785	0.7425	....	0.7000	0.8625	3.12	78
	2A	0.9800	0.9600	0.9200	0.8475	0.7250	0.7000	0.8300	4.14	103
295	1A	0.9490	0.8915	0.7815	0.6175	....	0.5700	0.7606	3.13	78
	2A	0.9490	0.9000	0.8110	0.6700	....	0.5700	0.7350	3.54	89
278	1A	0.8600	0.7600	0.6170	0.4470	....	0.4090	0.5990	3.11	78
	2A	0.8600	0.7450	0.5810	0.3985	....	0.4090	0.5900	2.95	74
265	1A	0.7600	0.6400	0.4915	0.3340	....	0.2350	0.3825	3.65	92
	2A	0.7600	0.6010	0.4190	0.2560	....	0.2350	0.3920	3.16	79
259	1A	0.6750	0.5480	0.4020	0.2620	....	0.1750	0.2960	3.76	94
	2A	0.6750	0.4980	0.3220	0.1850	....	0.1750	0.3080	3.10	77
242	1A	0.3310	0.2150	0.1270	0.0680	0.0350	0.0250	0.0500	4.55	114
	2A	0.3310	0.1900	0.1020	0.0540	0.0300	0.0230	0.0450	4.37	109

[a] Average reflux ratio (L/V) = 1.0.

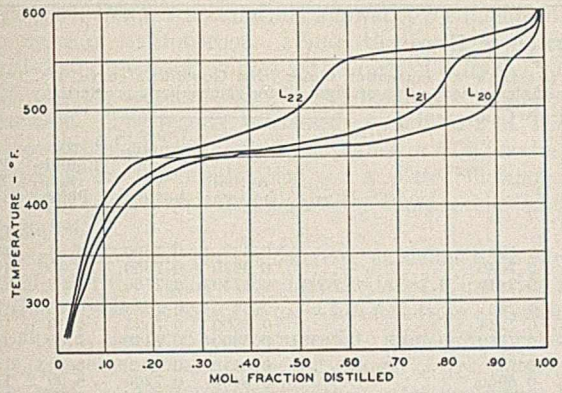

FIGURE 10. DISTILLATION CURVES FOR LIQUIDS IN LOWER SECTION OF UNIT 1 AS CALCULATED BY PLATE-TO-PLATE METHOD

Computed liquids leaving equilibrium plates 20, 21, and 22

95 per cent agreed with the experimental results. When pinene was added as the key component, a plate efficiency of 85 per cent was obtained in dilute solutions, and about 90 per cent in more concentrated solutions. Runs on benzene-toluene and benzene-toluene-xylene mixtures indicated plate efficiencies of about 59 and 75 per cent, respectively, using the same apparatus for all determinations.

For the present consideration of complex mixtures, the naphtha run made without any additional component is of greatest interest. The distillation curves for the overhead distillate (external reflux) and the liquids on the sixth and tenth plates of the column are shown in the lower section of Figure 11.

In applying the graphical method, the column is considered in two sections: (*a*) plates 1 through 6 and (*b*) plates 6 through 10. The distillation curves show the same characteristic of passing through a minimum slope as those of Lewis and Wilde, and the column requires more than six or eight equilibrium plates. Equilibrium curves were computed for the overhead distillate and the liquid on plates 6 and 10, using Raoult's law unmodified (Figure 12). Using L/V equal to 1, the equilibrium plates were stepped off, with the results given as method 1 in Table XIII.

Similarly, empirical equilibrium curves were applied to this same section, using the curves corresponding to slopes of 1.88 and 1.00, since the distillate and liquid on plate 6 had slopes of 1.88 and 0.58, respectively; the results of this computation are recorded as method 2 in Table XIII.

The lower section of the column was treated in the same manner, using both graphical procedures; the results are given in Table XIV.

The summary of these data (Table XV) indicates the close agreement between the results of the graphical method and those computed by Lewis and Smoley. The upper six plates of the column have an average over-all plate efficiency of 89 per cent, compared with 85 per cent for the lower four plates. A weighted average of these efficiencies indicates an over-all plate efficiency of 87.5 per cent, which is identical with the average of the individual plate efficiencies of 80, 85, 90, and 95 per cent reported by Lewis and Smoley for the various naphtha runs.

Using the single cut temperature of 242° F. throughout the column, from plates 1 to 10 as indicated in Figure 12, an average over-all plate efficiency of about 97 per cent is obtained. This higher average efficiency is in good agreement with the higher efficiencies obtained by Lewis and Smoley and may be due to the choice of cut temperature or possibly to the low mole fraction of this cut in the liquid on plate 10 which was only 0.0250. Figure 12 shows clearly that equilibrium curves for plates 1 and 10 alone could not be used to give satisfactory results because the curve for plate 6 is not intermediate to 1 and 10.

The empirical results are satisfactory in the lower section of the column, covering only four plates. In the upper section of the column an equilibrium curve corresponding to a slope of 1.0 was used for a material with a computed slope of 0.6; this condition, coupled with the range of six plates covered, tends to introduce greater uncertainty in the results.

Plate Efficiency in Unit 4

A commercial unit tested by Goodliffe (*11*) contained twenty-two plates. The vapor fed to the column entered at a point below the twenty-second plate and at a temperature

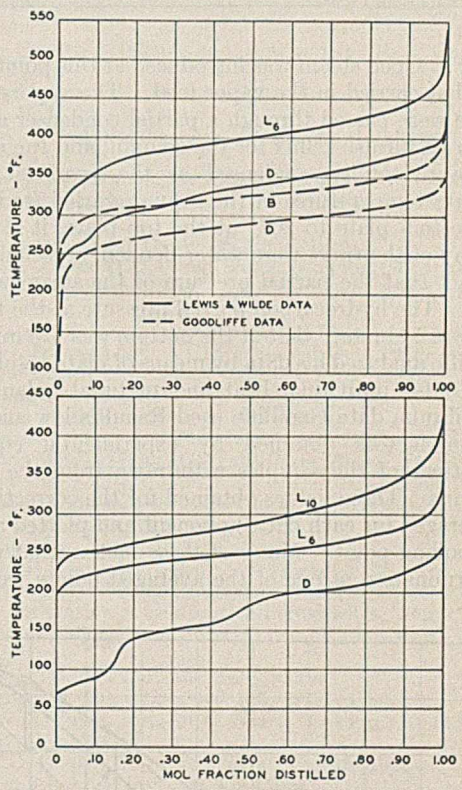

FIGURE 11. TRUE-BOILING-POINT DISTILLATION ANALYSES

(*Above*) Full lines show composition of distillate and liquid leaving plate 6 of unit 2; dashed lines show composition of distillate and bottom product of unit 4

(*Below*) Composition of distillate and liquid leaving plates 6 and 10 of unit 3

TABLE XV. SUMMARY OF PLATE EFFICIENCIES FOR UNIT 3[a]

	Method	Av. No. Equilibrium Plates	Av. Plate Efficiency %	Cut Temp. Included in Av. °F.
1.	Graphical calcn. for distillate through plate 6 (Raoult's law unmodified)	5.32	89	250, 242, 236, 229, 222
2.	Graphical calcn. using empirical equilibrium curves of Fig. 4 for distillate through plate 6 (Raoult's law unmodified)	4.13	69	250, 242, 236, 229, 222
1A.	Graphical calcn. for plates 6 through 10 (Raoult's law unmodified)	3.41	85	311, 295, 278, 265, 259
2A.	Graphical calcn. using empirical equilibrium curves of Fig. 4 for plates 6 through 10	3.41	85	311, 295, 278, 265, 259
	Av. of individual plate efficiencies reptd. by Lewis and Smoley (*16*)	..	87.5	.....

[a] Average reflux ratio (L/V) = 1.0.

TABLE XVI. PLATE EFFICIENCY IN UNIT 4

Method 1 = graphical calculation from overhead distillate through bottoms (Raoult's law correction factor from Goodliffe's curve, *11*).
Method 2 = graphical calculation from overhead distillate through bottoms, using empirical curve of Figure 4 for atmospheric pressure.

Cut Temp. °F.	Method	$\frac{L}{V}$	Mole Fraction of Arbitrary Component y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	Actual bottoms	Vapor in equilibrium with bottoms	No. Equilibrium Plates	Plate Efficiency %
333	1	0.605	0.9800	0.960	0.932	0.892	0.847	0.808	0.779	....	....	0.623	0.7850	6.8	18
	1	0.635	0.9800	0.9590	0.9255	0.8840	0.8400	0.7980	0.7640	....	....	0.6230	0.7850	6.40	16
	2	0.635	0.9800	0.9650	0.9470	0.9230	0.8950	0.8610	0.8440	0.7850	0.7500	0.6230	0.7760	8.26	25
330	1	0.605	0.9700	0.941	0.901	0.855	0.807	0.769	0.746	....	....	0.58	0.7525	6.7	17.6
	1	0.635	0.9700	0.9390	0.8950	0.8450	0.7960	0.7550	0.7235	....	....	0.5800	0.7525	6.10	15
	2	0.635	0.9700	0.9500	0.9250	0.8945	0.8565	0.8160	0.7760	0.7380	0.7050	0.5800	0.7440	7.84	23
328	1	0.605	0.9600	0.923	0.874	0.822	0.775	0.737	0.718	....	....	0.54	0.72	6.9	18.5
	1	0.635	0.9600	0.9200	0.8670	0.8100	0.7600	0.7200	0.6930	....	....	0.5400	0.7200	6.00	14
	2	0.635	0.9600	0.9325	0.8995	0.8590	0.8250	0.7800	0.7380	0.700	0.6700	0.5400	0.7110	7.71	22
323	1	0.605	0.9300	0.870	0.805	0.745	0.700	0.667	0.650	0.641	0.637	0.445	0.638	8.75	27
	1	0.635	0.9300	0.8665	0.7965	0.7330	0.6830	0.6480	0.6290	....	....	0.4450	0.6380	6.60	17
	2	0.635	0.9300	0.8850	0.8325	0.7775	0 7250	0.6800	0.6450	0.6180	0.6000	0.4450	0.6270	7.67	22

of 265° F. Open steam was introduced at this point, in addition to that carried in the vapor feed. The vapors from the top plate were passed through a partial condenser and water separator to furnish reflux for the column, and the remaining vapors were totally condensed as the overhead product. Since plate temperatures in the column varied from 219° F. at the bottom plate to 207° at the top plate, it is apparent that many of the trays were water-flooded, especially in view of the fact that the partial pressure of the steam was about 700 mm. The hydrocarbon partial pressure at the top of the column was 144 mm.; that at the bottom was 123 mm.

Goodliffe analyzed his data by means of plate-to-plate equations (*29*) for individual heat and material balances. For his equilibrium data Goodliffe used Raoult's law and applied correction factors obtained by experimental equilibrium vaporizations of the samples withdrawn from the plates of the column. These values obtained for the correction factor were averaged for each cut component and plotted as a function of boiling point. Many of these factors that went into the determination of one of the averaged points varied from

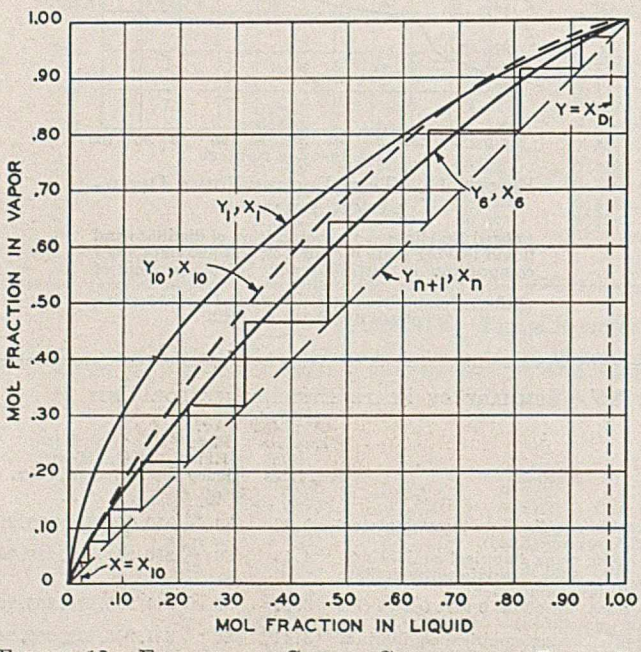

FIGURE 12. EQUILIBRIUM CURVES COMPUTED BY RAOULT'S LAW UNMODIFIED AND GRAPHICAL CALCULATION OF THE NUMBER OF EQUILIBRIUM PLATES IN UNIT 3 USING CUT TEMPERATURE OF 242° F. FROM DISTILLATE TO PLATE 10 WITH EQUILIBRIUM CURVES FOR PLATES 1, 6, AND 10

the average by amounts greater than the total range of the curve, and the correction factors so obtained have no more significance than those of Brown and Caine (*1*).

Goodliffe (*11*) computed over-all plate efficiencies on the basis of key components of 18° F. boiling range each, using a simplified procedure (*27*), and arrived at a value of 3.88 equilibrium plates to be equivalent to the 21 actual plates between the first and twenty-second, with $L/V = 0.605$. The average over-all plate efficiency, then, was 3.88/21, or 18.5 per cent, an extremely low value due to poor operating conditions with such large amounts of water present on the plates. In the earlier advance copy (*11A*) a slightly higher reflux ratio ($L/V = 0.635$) was used in the calculation of plate efficiency, and 3.36 equilibrium plates were indicated, corresponding to a plate efficiency of 16 per cent.

In applying the graphical binary mixture method of computation, the intention was primarily to compare this method with the plate-to-plate calculation used by Goodliffe (*11A*). Consequently Goodliffe's identical reflux ratios and equilibrium data were employed without variation. The equilibrium curves for the overhead product and for the bottom product, taken as the terminal conditions, were calculated for the indicated partial pressures from the distillation curves reported by Goodliffe as shown in dashed lines on the upper section of Figure 11. The number of equilibrium plates was determined by the graphical method, using values for L/V of 0.635 (*11A*) and 0.605 (*11*). The results are given as method 1 in Table XVI.

The slopes of the distillation curves of the materials on the plates of this column also go through a minimum, but the amount of fractionation accomplished by seventeen of the twenty-two plates is so small (equivalent to only about two equilibrium plates) that satisfactory results are obtained over the entire range of plates.

In order to obtain plate efficiencies for the same twenty-one plates utilized by Goodliffe, three equilibrium plates were subtracted from the total number of equilibrium plates required by the graphical method (Table XVI) to allow for the reboiler, partial condenser, and top plate.

The resulting plate efficiencies average 15.5 and 20.3 per cent, compared with 16 and 18.5 per cent computed by Goodliffe for the two reflux ratios. Using the average plate efficiency of the top or first plate of 83 per cent as computed by Goodliffe (*11*) and considering the condenser and boiler as equivalent to one plate each, the corresponding over-all plate efficiencies average 16.6 and 21.2 per cent, respectively. The latter figure is reduced to 18.9 per cent if the 323° F. cut temperature is omitted.

The empirical equilibrium curves were applied to these

same data but without making any allowance for the low partial pressure of hydrocarbons. Since the top and bottom materials had distillation curves with slopes of 0.75 and 0.62, respectively, the empirical curve corresponding to a slope of 1.0 was used. The results, expressed as method 2 in Table XVI, show a total of 7.96 equilibrium plates, or 4.96 for the 21 actual plates under consideration, or a plate efficiency of about 23 per cent, which is not directly comparable for the reason stated.

Although individual plate efficiency, as defined by Murphree (*20*), and the highly refined methods for computing individual plate efficiencies are of most interest from a theoretical standpoint, the over-all average plate efficiency is practically of greater convenience in the design of fractionating columns, and can be determined with greater confidence on commercial equipment. The individual plate efficiencies, as computed by Goodliffe (*11*), vary from −50 to +81 per cent for the same components on different plates, and from −50 to +164 per cent for different components on the same plate. These discrepancies are probably due to difficulties in obtaining representative samples, particularly as Goodliffe attempted to sample the liquid on the plate of the column rather than to obtain a sample of the liquid overflowing from the plate to the next lower plate. It is better practice to define an equilibrium plate in terms of the average composition of the vapor leaving that plate and the composition of the liquid overflowing from that plate.

Since the average over-all plate efficiency can be determined satisfactorily by the graphical binary mixture method described over a series of not more than six or eight equilibrium plates, this method offers a convenient and reliable procedure for determining plate efficiency in petroleum fractionating columns without the necessity of taking samples from every plate.

Application to Design

If the over-all average plate efficiency is known, the number of actual plates required may be determined by dividing the number of equilibrium plates by the average over-all plate efficiency. In designing equipment, the required number of equilibrium plates may be determined by the graphical method described, by estimating or arbitrarily fixing the distillation characteristics desired in the overhead distillate and in the next lowest side stream as removed from the column; this can usually be done in a reasonably satisfactory manner by consideration of the distillation characteristics of the crude or feed to the column and the desired specifications in the overhead product. Equilibrium curves are then constructed for the products so determined. The slope of the operating line is determined from a heat and material balance over the column. The required number of equilibrium plates can then be computed readily in the manner described.

For the first approximation the empirical equilibrium curves shown in Figure 4 are more convenient, since they can be estimated directly from the slope of the distillation curves. If it is desired to base the computations upon A. S. T. M. distillation data, similar curves are available (*13*).

Acknowledgment

The plant data and samples for unit 1 were kindly furnished by the Development Department of the Union Oil Company of California, through E. G. Ragatz.

Nomenclature

D = distillate withdrawn as overhead product, moles; used as subscript to signify overhead product
L = liquid, moles
V = vapor, moles
B = bottom product, moles; used as subscript to signify bottom stream
R = reflux returned to top plate, moles; used as subscript to signify reflux stream
K = equilibrium constant for a particular component at temp. and total pressure of equilibrium
P = total pressure
p = vapor pressure of any component at temp. of equilibrium
t = temp., ° F.
x = mole fraction of any component in liquid phase
y = mole fraction of any component in vapor phase
a, b, c = individual components, of which a is most volatile, moles; used as subscripts to refer to individual components
1, 2, . . . n = First, second, third . . . . nth plate of a column, from top down

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Ammonia Catalyst Fusion Pot, Fixed Nitrogen Research Laboratory

Nature of Cigaret Smoke

Technic of Experimental Smoking

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The published results of research work on cigaret smoke show little agreement. These discrepancies are largely due to differences in the technic of smoking. A standardization of procedure is in the interest of economy of research, and harmony among the various investigators.

The criteria of a successful smoking experiment are discussed, and the factors which must be stated to characterize completely a smoking procedure are enumerated. Smoking apparatus which possesses the necessary attributes is described in detail. The puffing device, in particular, operates simply, accurately, and precisely to draw on a cigaret, and is so designed that the operator is at all times acquainted with the constants of its performance.

THE field of tobacco chemistry, prominent in scientific literature since the turn of the century, would be sterile had not investigators realized almost immediately the importance of an accurate knowledge of the constituents of tobacco smoke and the amounts in which they occur. Considerable ingenuity has been shown in devising means of securing this information. The divergence of results, with the paucity of data in many instances, has led to controversy and confusion. A desire to extend recognition of the fact that apparently contradictory findings result from differences in the conditions of smoking, and that contradictions frequently disappear when differences in technic are considered, led to the publication of this paper. It is hoped that the necessity for a standardization of technic and for inclusion of all significant details of the experimental smoking will be more widely realized, and that this will lead to a closer correlation of results among interested laboratories. Pyriki (*11*) attributed his failure to check the findings of Wenusch (*12*) to differences in technic of smoking or in the method of assaying the nicotine. Recent work (1935) of Jensen and Haley (*5*), showing the variation in the nicotine content of cigaret smoke with certain changes in smoking conditions, illustrates quantitatively the probable effect of discrepancies in the smoking procedure.

The Problem

The three criteria of a successful smoking experiment are:

1. It should be reproducible.
2. The smoking procedure, the cigarets smoked, and the environment while smoking should be definitely characterized.
3. It should sufficiently approximate the conditions of human smoking for conclusions from experiments *in vitro* to admit of interpretation *in vivo*.

The principal laboratory methods of production of cigaret smoke fall into four groups:

The application of continuous suction to the burning tobacco (*4, 7, 8*).
Puffing by mouth, with suitable absorption apparatus between the lip and the cigaret (*3*).
Suction interrupted by a stopcock or valve opened at intervals (*1, 2, 4, 5, 6, 9*).
The controlled aspiration of a definite volume of air through the cigaret (*10, 11*).

The use of continuous suction fails to fulfill criterion 3. The abnormally long glowing end produced by continuous suction is prima facie evidence of a condition of pyrolysis not existing in mouth smoking. It would not be presumptive to say that marked qualitative, as well as quantitative, differences exist between smoke so obtained and that which the smoker receives.

Mouth puffing, while answering requirement 3 almost as a mathematical identity, is not reproducible, nor are the details of puffing accurately known.

The application of interrupted suction shows, in its most refined forms, a really scientific recognition of the difficulties and factors involved. Its evolution has been rather gradual from humble beginnings to a highly precise instrument. The use of a valve whose movements are controlled by an automatic timing device and of a constant reduced-pressure regulator bring this type of smoker to its greatest perfection. This principle was employed in this laboratory in two smoking machines. The better of these, and that of Jensen and Haley (*5*), can be depended on to take a puff at the same time interval, of the same duration, and at a constant draught. However, the volume of puff will vary between cigarets of different tightness, even though carefully selected for uniformity, and will show a marked increase as the cigaret is consumed and its resistance to the flow of smoke diminished. Although the various forms of the constant-volume device will overcome this objection completely, the tedium of manual operation and the difficulty of adapting it to automatic and multiple smoking have impeded its development and restricted its use in favor of the much more simply mechanized constant pressure–time machine.

Pfyl (*10*) described in 1933 a device which accomplishes all that the best of the constant pressure–time machines can do, and which, in addition, draws a puff of the same volume each time. The high hydrostatic pressure and the resistance to the free flow of smoke developed in his absorption system require the use of mercury, which has certain practical objections. Pyriki (*11*) and others (*10*) have reported favorably on the entire technic, however, and the former, particularly, has obtained results substantially in agreement with those obtained in this laboratory.

Proposed Puffing Devices

The simple form of the apparatus employed here is not unlike that of Pfyl, but the use of gravity for deposition of smoke, with bubblers designed to minimize hydrostatic back pressure, a mere 2 inches, makes possible a somewhat simpler device with water as the operating fluid. It exists in three forms: the first form, together with a routine absorption train, is shown in Figure 1:

A reduction in pressure, resulting in puffing the cigaret, is caused by allowing the water column in buret *A* to fall to the volume of puff desired. The air so drawn is expelled through pinchcock *I* with *J* closed by raising the leveling bottle, *C*. When the zero mark is reached, and pinchcocks *I* and *J* are returned to their original positions, the apparatus may take the next puff when desired. The duration of puff is controlled by a suitable jet in the water line. It has not been thought advisable to replace pinchcock *I* with a check valve, as described by Pfyl, because of the danger of occasional unobserved leakage, which would prevent close agreement between experiments.

While the apparatus is simple in construction and operation, its manipulation is tedious and time-consuming. It is not practicable for an operator to smoke more than one cigaret at a time. Where much smoking is to be done, one of the other forms of the apparatus is recommended.

The second device (Figure 2) employs the identical principles of the first:

Fresh water is used to fill buret *A* each time, however, and, when admitted from a constant-level source of supply, *B*, the volume is automatically controlled. A float, *C*, ground to fit a constriction, *D*, at the bottom of the buret, checks the flow of water, terminating the puff. A mechanical arrangement, *E*, provides for manipulating the four pinchcocks, *F*, with one motion. Each pair of valves acts as a fulcrum by means of which the lever raises the dogs to open the other pair. It is thus impossible for the four cocks to be open simultaneously. A screw valve, not shown, on the water outlet, controls the rate of fall as desired. The volume of smoke drawn is found by collecting the water from the outlet in a graduated vessel.

For mass smoking, the robot shown in Figure 3, with the improved bubblers, is recommended. The substitution of rotary valves of metal, operated by an electric motor actuated by a synchronous timer, for the pinchcocks of the second apparatus, and inclusion of a rotating "distributor" or "selector" valve, permit alternate puffing on as many as four cigarets with the same precision as obtained in the first two forms. The operation of the machine may best be seen from the skeleton drawings of the three valves in Figure 4:

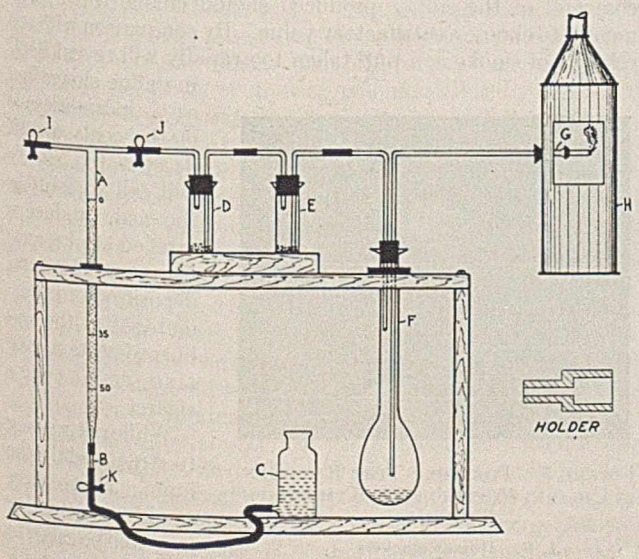

FIGURE 1. FIRST FORM OF PUFFING DEVICE

The absorption trains are connected at 1, 2, 3, and 4 on the distributor valve (Figure 3). *A* is connected to *B*, *C* is open to the air. *D* and *G* are connected, respectively, to the top and bottom of the buret. *E* drains into a graduated vessel, and *F* is connected to the constant level. The shaft connecting the air and water valves rotates through 90°, pauses, and returns. With the valves in the position shown, water enters the buret through *F* and *G* until the constant level is reached, forcing the previous puff out through *D* and *C*. When the shaft is rotated to its alternate position, water leaves the buret through *G* and out at *E* to a graduated vessel until checked by the ground float. Replacing the water, an equal volume of air is pulled through the cigaret and absorption train (No. 1), and enters the apparatus at 1, through *A*, *B*, and *D*, to the top of the buret. As the shaft makes this 90° rotation, a pawl slides along a disk attached to the rotor of the distributor until, at the limit of motion, it engages a notch. On returning the shaft to its original position, the rotor moves through 90° into position for puffing on cigaret 2. In this manner the air and water valves go through their cycle once every 15 seconds, puffing on each cigaret in turn once a minute. (Machine drawings and details of construction, omitted for brevity in these diagrams, are available to interested persons.)

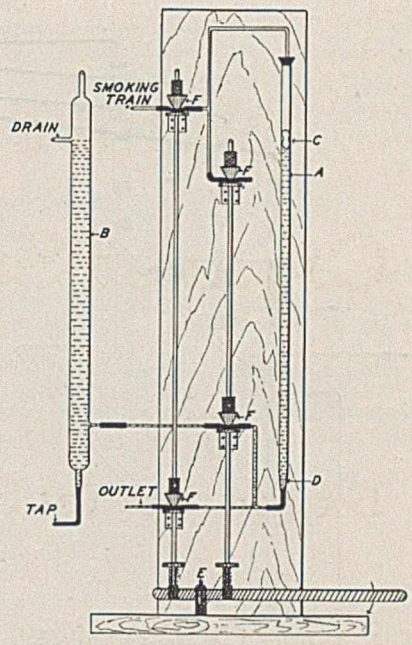

FIGURE 2. SECOND FORM OF PUFFING DEVICE

Smoke Collection

The problem of collection of smoke has such a simple solution that it has escaped attention in many cases. However, no universal system of smoke collection has yet been found. The complex nature of the mixture, in respect to state, molecular aggregation, and contrasting chemical affinities, permits certain components to escape while others are retained. The colloidal nature of the smoke cloud prevents collection by the usual wash-bottle train, unless it be of ridiculous length. Gravity is an excellent agent for depositing smoke, and is the cause of the deposition of the greater portion of all smoke solids in flask *F*, Figure 1. Saturation of the residual particles by bubbling through alcohol and precipitation by bubbling through water complete the deposition of semi-solid material. Apparently, in passing through alcohol, the minute particles, largely alcohol-soluble, accumulate in or on themselves a quantity of the solvent. The great mutual affinity of water and alcohol then causes the particles to precipitate when they come in contact with water. This behavior has been an invaluable aid in collecting side-stream smoke where the gravity separation is not practicable. Very volatile material is retained by the addition of suitable reagents to the contents of the flask and bubbling tubes.

Cigaret Holder

Making an air-tight contact between the cigaret and holder that will neither compress nor distort the cigaret end is a neat problem. Few investigators have reported treatment of this phase. A not unnatural error to one who failed to recognize the factors involved would be to screw a cigaret tightly into

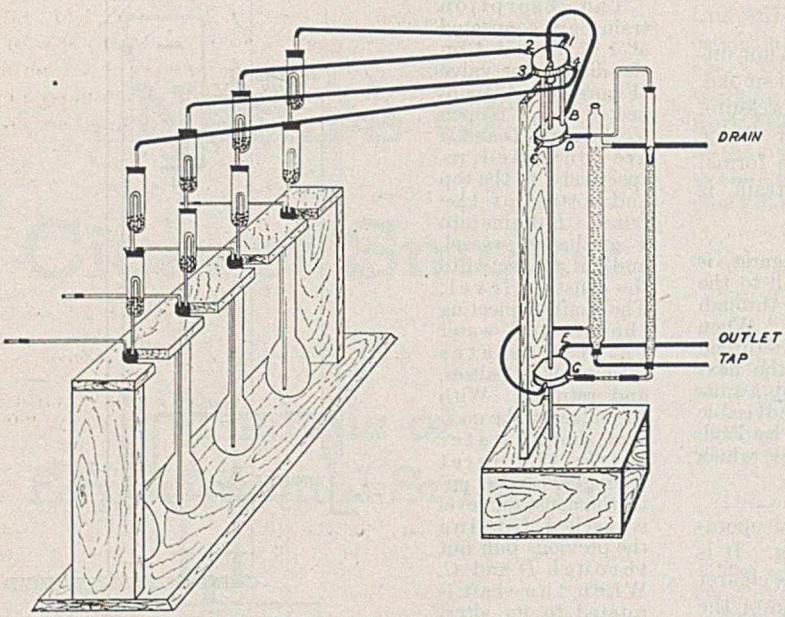

FIGURE 3. ROBOT FOR MASS SMOKING

one of the tapered commercial holders. Kenyon (*6*) shows a device which is a distinct improvement. Figure 1 shows a cross section of a machined Bakelite holder. The cylindrical opening allows a slide fit for a cigaret. The seal is then made with a dextrose sirup concentrated *in vacuo* to a consistency that does not wet the cigaret paper.

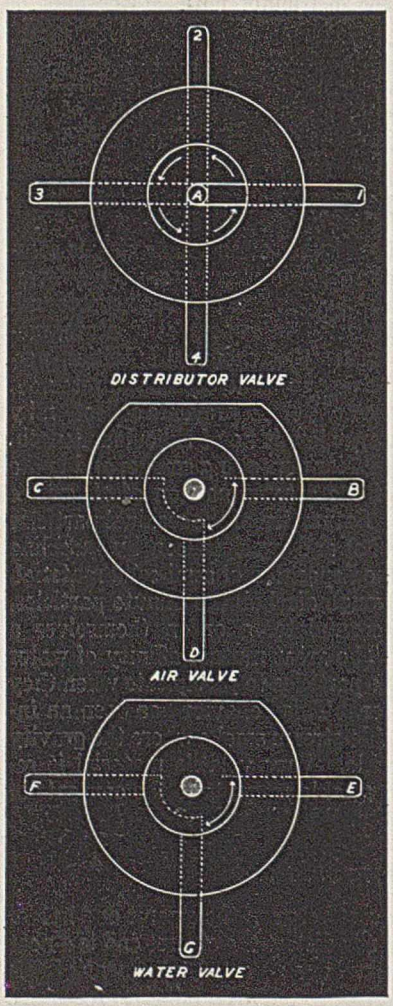

FIGURE 4. DIAGRAMS OF VALVES

Draught Shield

Obviously, changes in the draught to which a cigaret is exposed, by altering the ventilation to the combustion zone, can raise or lower the temperature of the burning end, as well as change the proportion of cigaret material entering the main and side stream. The draught shield proposed (Figure 1), a simple tin can with removable windows of celluloid, open at top and bottom, excludes any influence of extraneous air movement, and permits only such circulation as is provided by the convection currents due to the heat of the coal. Enclosing a cigaret in a horizontal shield confines an oxygen-poor atmosphere about the tip and reduces free burning, thus increases the proportion of the cigaret from which main-stream smoke is derived, and contaminates the main-stream smoke with products from the side stream, which, confined about the glowing end, are reaspirated through the cigaret. The entire apparatus may be constructed simply and economically from stock glassware and material easily obtainable.

Characterization of Smoking

The operation of the puffing machine furnishes the following data: (1) the volume of smoke taken at each puff, (2) the length of time required to take the puff, and (3) the frequency with which puffs are taken.

It is of the utmost importance to secure the following additional information: (1) the weight of the cigarets used for the test (each test should consist of cigarets of uniform weight), (2) the circumference and air resistance of the cigarets, (3) the moisture content of the cigarets, (4) the length of unburned butt, and (5) the relative humidity and temperature of the atmosphere in which smoking takes place.

When this information accompanies a smoke analysis (together with the assurance that the stated puff has actually passed through the cigaret, that the butt portion of the cigaret has retained its natural shape, and that the coal has been neither unnaturally fanned nor smothered), the data obtained by different investigators in both chemical and biological experiments should be compatible, taking into consideration such unavoidable personal factors as seem to enter the most precise experimental work.

Choice of Rate

Even though the constants of the smoking procedure are carefully determined, it is still necessary that the puffing rate fall within certain limits. A puff should not exceed in size the capacity of the mouth, but should be large enough to produce a generous smoke. Results will not be duplicable unless, between puffs, sufficient time elapses to return the coal to a free-burning condition. Finally, the puff should avoid either extreme in duration. Inspection of the glowing coal and of the smoke produced should enable the experimenter to choose a satisfactory value. By comparison with the cigarets of smokers, a puff taken too rapidly will reveal itself in undue elongation and incandescence of the coal; a puff drawn too slowly will fail to kindle the coal, produce a rarefied smoke, and, through unnatural deposition of smoke material in the unburned portion, give rise to a soggy cigaret.

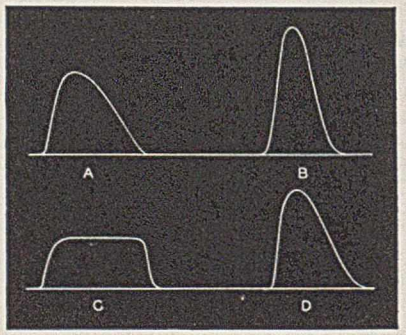

FIGURE 5. PRESSURE-TIME RELATION IN CIGARET PUFFING FROM KYMOGRAPH TRACINGS

A, B. Human smokers
C. Constant pressure
D. Constant volume

While not wishing to stress unduly the human method of smoking, attention may well be called to what constitutes a

definite superiority of the constant-volume buret smoker over the constant pressure–time device. If the "suction" and consequent rate of flow through the cigaret be plotted against time during the puff, it will be seen that in the latter the flow rises to a maximum as the valve opens, depending upon the rapidity with which this is accomplished, remains constant until the valve begins to close, and then diminishes to zero as the valve closes. In the former, the flow quickly reaches a maximum and diminishes with the head of water in the buret. This behavior corresponds closely to the diminished suction in mouth puffing as the buccal cavity becomes filled with smoke. A graphical representation of this phenomenon is shown in Figure 5, the volume taken being the same in each case.

Pfyl (*10*) studied the smoking habits of several individuals in the effort to choose as realistic a rate as possible. The difficulty of obtaining such information under normal conditions is great and, when obtained, shows wide variation between individuals and between different times for the same individual. Also, the subjects under examination are apt to be nervous and smoke somewhat more vigorously than normally. Pfyl, as a result of his investigation, took a 40-cc. puff of 2-second duration twice a minute; Pyriki (*11*) adhered to Pfyl's rate. The present writers' arbitrarily selected rate is a 35-cc. puff of 2-second duration taken once a minute. It is comparatively simple to correlate data so similarly obtained, when all the facts in the case are presented, and this has been done.

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COLLOIDAL FUEL

DESCRIPTION OF DIFFERENT PROCESSES

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DURING the recent years since the World War (1914–18) great attention has been given, particularly in Great Britain, to what is called "colloidal fuel." In nearly all cases, however, this name is grossly misleading, since the fuel is not in the true colloidal condition; that is, the solid particles are not in that extremely fine state of division where settling by gravity is impossible, as is the case in a "solution" of glue in water.

Colloidal fuel may be defined as a mixture of finely pulverized coal, or other solid fuel, and a liquid fuel, such as petroleum oil, coal tar, lignite tar, or shale oil fractions, in such a condition that the solid particles will not separate out by gravity for a long period. About 30 to 50 per cent by weight of solid fuel is generally used so that the mixture remains liquid, and the object is to substitute the product for oil fuel, whether for combustion by atomization at burners or for internal combustion engines.

The main advantage claimed is that a liquid fuel of equal heating value is obtained containing much less oil. Obviously colloidal fuel is of no practical value to countries such as the United States and Soviet Russia with abundant oil supplies, but may be important to Great Britain, France, Germany, Japan, and other countries that possess little or no petroleum.

The subject, however, is of considerable scientific interest in the field of fuel technology, and American fuel technologists have played a prominent part. Accordingly, the present contribution will attempt to give, for reference purposes, a concise description of all the colloidal fuel processes.

Methods of Manufacture

Three general methods have been used in the manufacture of colloidal fuel. The first is to grind the coal or other solid fuel in the liquid fuel under such conditions—for example, with a colloid mill—that the coal is converted into the true colloidal condition and therefore cannot separate by gravity. This method, however, is not at present commercially economical because of the high cost and general difficulties of colloidal grinding for the bulk production that would be necessary.

Generally, therefore, the principle of a stabilizer or *fixateur* is used, as well as a peptizer. That is, the coal or other solid fuel in the ordinary pulverized condition is merely mixed with the oil or tar fractions, and the stabilizer, generally a colloid, is added in small amount to delay a separation of the solid particles by gravity. The stabilizers have included soaps of all kinds, alkalies such as sodium silicate, gelatin, glue, gum arabic, olein oil (sodium salt of sulfonated castor oil), dextrin, and stannic acid. Mostly, however, lime-rosin soap mixed with oil has been employed, the average composition being 84 per cent oil, 10 per cent rosin, 5 per cent lime,

and 1 per cent water. This mixture is used in the colloidal fuel in an amount corresponding to about 0.5–1.5 per cent of rosin on the weight of the coal. In some cases the *fixateur* employed has been kept secret; hundreds of colloids can, of course, be used for the purpose. Coal tar or other carbonization tar fractions are generally employed as peptizers. It is remarkable that such fractions can be mixed intimately with petroleum fractions and stabilized by using pulverized coal as a stabilizer or *fixateur;* that is, a solid acts as a stabilizer for two liquids that otherwise will not mix. A typical colloidal fuel which is not too pasty, made on the peptizer principle, is 30 per cent coal, 10 per cent tar products, and 60 per cent petroleum products, with about 1 per cent lime-rosin soap as a *fixateur*, although the latter is not essential.

A third method is to adopt mechanical means, such as continually moving agitators in the store tanks, to prevent undue separation of the solid particles.

Nature of Colloidal Fuel

A solid, such as coal, in a liquid, such as petroleum oil, may exist in three conditions—true solution, colloidal solution, and suspension. In a true solution, such as sodium chloride in water, the solid particles are less than 0.001 micron in size. In a colloidal solution, however, the individual particles of the solid in the liquid (such as coal in oil or glue in water) are within a range of 0.001 to 0.10 micron in size. Under such conditions the particles can be seen in the solution by the ultramicroscope but not by the ordinary microscope.

Further, as already mentioned, particles of solid material in the colloidal solution will never separate by gravity on standing and are equal in this respect to those of a true solution. Simple suspension means a state where the solid particles in the liquid are larger than 0.10 micron and can easily be separated by means of filter paper or cloth. In a colloidal solution, however, the solid particles are much too large to pass through parchment, whereas, when the particles are in true solution, they go through the microscopic interstices of parchment as easily as the original liquid.

When pulverized coal is ground with oil in an ordinary ball or roller mill for a reasonable length of time, the result is a very small proportion of true solution and some colloidal solution, but mostly simple suspension. Consequently the greater part of the coal particles separate by gravity in a few hours. The role of stabilizers or *fixateurs* is to delay this action; such a fuel is, of course, not in colloidal solution but is mostly in delayed suspension which is entirely different.

The work that has been carried out in the field of colloidal fuel is described in order of date. No commercial success has yet been achieved by any process, mainly because the net cost of manufacture is too high in competition with petroleum, and the product gives more or less trouble in burners and pipes.

Smith and Munsell Method

Great interest attaches to the patent of two Americans (*4*), which is one of the first references in the literature to colloidal fuel. It describes the manufacture of liquid fuel by pulverizing any solid fuel in the dry condition and mixing it with the liquid fuel for use at burners, simple mechanical agitation being employed to prevent separation.

The patentees believed they were the first to make an artificial liquid fuel composed of a mixture of solid particles and liquid, and apparently their claim is correct. The object was to produce a cheap and easily manipulated fuel for use in steam boilers, furnaces, gas manufacture, metallurgical operations, and other purposes. The inventors point out clearly that any solid fuel, such as coal, coke, charcoal, or oil shale, could be used, as well as any liquid; generally, a 50 to 50 mixture was preferred.

They understood thoroughly, more than half a century ago, the principles of colloidal fuel, and one of their proposals was to carbonize coal at the mines and mix the resulting tar with pulverized coal or other solid product to make colloidal fuel. Nothing is known, however, as to whether Smith and Munsell carried out this work on a large scale.

Spelman Method

Another interesting early patent issued to an American (*6*) describes a "composite" fuel—that is, a mixture of pulverized solid fuel and crude petroleum or other liquid hydrocarbon in which pulverization of the solid takes place in the presence of the liquid, followed by the addition of a thinner such as alcohol or light hydrocarbons.

The solid fuels preferred included anthracite or bituminous coal, but peat, charcoal, and sawdust could also be used. In addition to crude petroleum or similar inflammable liquids, reference was made to the utilization of molasses. No details, however, were given as to the method and degree of grinding the solid in the presence of the liquid, and it is possible that the resulting product was more or less in the true colloidal condition.

Curiously enough, however, Spelman does not seem to have been concerned so much with producing a stable colloidal fuel as with preventing dust explosions by grinding dry solid coal; this was a serious problem about thirty years ago. Here again there is no record as to whether this method was carried out on a large scale, and obviously the idea of using molasses instead of heavy oil is an impracticable proposition as far as rapid and efficient combustion is concerned.

Plauson Process

The practical pioneer of colloidal fuel, as well as the colloid mill, is Herman Plauson, an Estonian fuel technologist resident for a long time in Hamburg. His original British patent (*3*) was taken out in 1913 when he lived in Leningrad, and describes in lucid language the whole principle of the colloid mill and the manufacture of true colloidal fuel.

Essentially his method is to grind pulverized coal, charcoal, or other solid fuel with liquids, especially hydrocarbons such as petroleum oil fractions, for a long period (about 1 to 2 hours), using two polished metal plates operating at high speed until the solid is reduced to the true colloidal solution. In addition, Plauson describes the beneficial action of adding to the mixture a small amount (around 1 to 3 per cent) of another colloid, such as soap, gelatin, and albumen, which enables the action to be considerably accelerated.

This work was based on the Acheson process for the manufacture of colloidal graphite, as used for lubricants; Plauson also points out that other investigators have reduced metals to the colloidal condition. From this he developed the idea of converting solid fuel, such as coal, into the colloidal condition suspended in liquid fuel so that the product could be employed at burners in place of oil or for internal combustion engines of the Diesel or other type.

Research by Submarine Defense Association

This well-known work on colloidal fuel (with that of Plauson, the most important ever undertaken) was begun in New York in 1918, under the presidency of Lindon W. Bates, for the production of colloidal fuel from pulverized coal and heavy petroleum fractions using a stabilizer or *fixateur*, and also if necessary according to the peptizer principle, with the addition of coal-tar fractions such as creosote. The object was to find a liquid fuel for the British Navy during the war in order to reduce the amount of petroleum that had to be taken across the Atlantic, in view of the activities of German submarines. The stabilizer used was lime-rosin soap, and gen-

erally the fuel consisted of about 33 parts by weight of coal, first pulverized to pass through a 200-mesh screen, and 63 parts by weight of heavy petroleum fractions, along with 1 per cent rosin soap.

When a peptizer was used, with or without a *fixateur*, usually 10 per cent of coal-tar fractions was added to the petroleum. Colloidal fuel of this type, with a heating value of 17,000 B. t. u. per pound, was used on a large scale during the period April to July, 1918, on the U. S. Navy scout vessel *Gem*, fitted with Normand water-tube boilers, but the war came to an end before the British Navy could take advantage of the work. Attempts were then made to develop the fuel in the United States for commercial use both on land and sea but without success.

A large number of patents, dating from 1919, were taken out, and considerable differences of opinion exist as to the stability and general efficiency of the fuel.

Coalinoil Process

A mixture of pulverized coal and oil, using a stabilizer such as lime-rosin soap, was produced by Charles Jason Greenstreet, an American fuel technologist now resident in Great Britain. This fuel was called "Coalinoil" and seems to be identical with the colloidal fuel of the Submarine Defense Association.

According to patents dating from 1920, the principle is to mix coal or other solid fuel, pulverized to pass through a 200-mesh screen, with heavy liquid fuel (petroleum or carbonization products) of around 22–25° Bé., and to use as a stabilizer or *fixateur* oleates, stearates, and palmitates (that is, soap) as well as paraffin wax or other wax substance.

Greenstreet appears to have started work on the subject in 1918 and at first tried to prevent separation by gravity of the solid particles from the liquid by blowing in hot air to cause thickening by oxidation. Later, about 1920, stabilizers were employed.

The proportions given by Greenstreet are 20 to 35 parts of solid fuel, and 100 parts of liquid fuel, with 2 parts of soap. Later there was developed the Greenstreet process for the carbonization of colloidal fuel.

Calvert or Coloil Process

Another method suggested in 1920 in Great Britain for the use of pulverized coal suspended in petroleum oil or other liquid fuel was that of George Calvert of Twickenham (London). This consisted in mixing the pulverized coal with the oil, giving a more or less simple suspension; the fuel was in special tanks provided with compressed-air equipment or other apparatus for continual agitation, neither colloidal grinding, stabilizers, or *fixateurs* being used. It is claimed that by mechanical agitation, combined with a special design of pipe circuits and burners, no practical difficulty resulted from separation of the solid particles, but the process never reached the commercial stage.

United Coal Oil Corporation Process

Another British colloidal fuel process was developed, dating from 1920, by a company called United Coal Oil Corporation Ltd., of London, with which was prominently associated Sir Sam Fay, formerly chief engineer of the Great Central Railway in Great Britain (now merged in the London and North-Eastern Railway Group).

The basic principle, like that of the Coloil process, is the simple mixing of pulverized coal or other solid fuel with petroleum oil or other liquid fuel, combined with the use of a special arrangement of tanks, agitators, pipes, and burners, so as to prevent the solid particles from separating by mechanical means.

In this case, however, the bulk of the liquid fuel, such as oil, was kept in a separate storage tank, and a very thick mixture of oil and pulverized coal was kept in another storage tank. When ready for use at the burners, the thick product was then mixed with the oil in a third small tank provided with agitators and was used direct before it had time to settle.

Large-scale experimental work with this fuel was carried out on one of the locomotives of the Great Central Railway in runs between Manchester and various other places. This work was also combined with pulverized fuel firing. In general the results were favorable, but the net cost of preparing the colloidal fuel was too high and the work was abandoned.

Leadbeater Process

Some work on the manufacture of colloidal fuel was undertaken during 1921–22 by John W. Leadbeater at the works of the Coal, Peat & Oil Company Ltd. of Earlstown (Lancashire). The general principle was to use the higher grade black peat from the bottom of bogs as a stabilizer or *fixateur*, along with a small amount of fatty substance such as tallow or soap.

Several British patents were taken out in this connection; essentially the process consisted in using 5 to 10 parts of the wet black peat and 1 part of tallow or soap, added to a mixture of 30 parts of pulverized coal and 70 parts of petroleum oil or other liquid fuel. Nothing further has been heard of this process.

French Process

A patent was taken out in 1923 by the Société Anonyme des Pétroles, Houilles, et Dérivés (*5*) and assigned to Emile B. G. Bascou. The principle consists in using colloidal fuel, not for combustion at burners or in internal combustion engines, but for injecting into the charge of either low- or high-temperature carbonization retorts or ovens, in order to obtain a more dense solid fuel. For example, the colloidal fuel is made by grinding 100 parts of mazout (heavy petroleum fractions) and 30 parts of pulverized fuel, the temperature being raised to about 60° C. to give increased fluidity. Then 15 to 20 per cent of the colloidal fuel is sprayed into the charge in the retorts or ovens, and a current of inert gas is passed through at the same time.

Balcke Process

Interesting work has been carried out by the Maschinenbau A. G. Balcke of Bochum, Germany, in producing a product called *Fliesskohle* (flowing or liquid coal). Essentially this consists of finely divided coal (generally anthracite or anthracitic) suspended in heavy coal-tar fractions (usually anthracene oil) in the average proportion of 50 to 60 per cent coal and 40 to 50 per cent tar oil by weight.

Full details including the date of origin cannot be obtained, but no stabilizer or *fixateur* is employed, and apparently grinding is carried out in some form of colloid mill. Whether this results in true colloidal grinding or only gives what may be termed a partial colloidal fuel is not known. The main point is that heavy carbonization tar oils are used, and not petroleum products, forming a smooth thick liquid of about 14,500 to 14,800 B. t. u. per pound with 3.5 per cent or less ash.

Nothing is known as to how long this fuel will stand without separation of the coal particles by gravity. Performance tests on firing steam boilers are contained in a report issued by

the Verein zur Ueberwaching der Kraftwirtschaft der Ruhrzechen (Association for the Scientific Control of Boiler Plants in the Ruhr Mines) of Essen, but no commercial development seems to have resulted, in spite of great interest in Germany in every method capable of reducing dependence upon imported petroleum.

Cunard Process

A great sensation was caused in Great Britain, starting in June, 1932, by hundreds of articles, notices, and letters (mostly rubbish) in the British press, concerning the production of a secret colloidal fuel by the Cunard Steam Ship Company Ltd. This fuel was first tested on one boiler of the Cunard oil-fired liner *Scythia*, which left Liverpool for New York June 11, 1932, but no detailed information has ever been made public concerning the results obtained. The matter has long since been forgotten by the daily press but finally the British patent appeared in 1934 (*2*).

The essential claim is for the manufacture of colloidal fuel, without a *fixateur* or stabilizer, by mixing coal pulverized to pass through a 200-mesh screen, with petroleum oil or tar fractions that contain not less than 5 per cent, and preferably 6 per cent, fixed carbon. The latter is determined by heating a weighed proportion of the oil or tar for 7 minutes over a Bunsen burner flame in a fused-silica crucible under certain standard conditions. For the liquid fuel any product can be used so long as there is 5 or 6 per cent fixed carbon, such as cracked petroleum fuel oil or noncracked straight-run petroleum oil fractions blended with cracked fuel oil, or coal-tar fractions containing a high proportion of fixed carbon Generally also bituminous coal is used (for example, 40 parts by weight with 60 parts of the cracked fuel oil), apparently made merely by mixing the pulverized coal with the oil. Whether the claims for stability by these methods can be substantiated is a matter of conjecture, and no large-scale development has yet taken place.

Some of the statements made in the patent, however, are vague, including reference to passing the fuel through a "homogenizer." No explanation is given as to what this means, although it obviously refers to some kind of grinding; apparently neither a stabilizer nor a colloid mill is considered necessary.

Wyndham Mobile Fuel

This invention (*7*) attracted considerable attention in the daily papers in South Wales in 1932. At that time the colloidal fuel was made from pulverized fuel, using a stabilizer or *fixateur* which was at first kept secret. However, the British patent appeared in 1934, and the colloidal fuel in its present form consists in grinding pulverized coal with liquid fuel, such as petroleum oil or tar fractions, in a mill consisting of a pair of metal rollers almost in contact, driven in opposite directions at different speeds; one roller runs five times quicker than the other. No stabilizer is now employed, and apparently the liquid fuel is in the partially colloidal condition. It is also understood that a commercial-sized mill has been erected.

The stabilizer or *fixateur* originally used, and then abandoned, consisted of a small amount of paraffin wax. For this purpose the colloidal fuel had to be made by grinding the coal with hot oil to melt the wax so that each solid particle was covered with a film of wax, to delay separation by gravity. However, paraffin proved to be of little value in this connection.

Processes for Carbonization of Coal-Oil Mixture

An entirely new development in the field of colloidal fuel is concerned with various processes for the carbonization of coal-oil mixtures. The basic principle (*1*) is to heat a mixture, generally 50 to 50, of pulverized coal or other solid and liquid fuel, such as petroleum or coal-tar fractions or the mixed heavier oils from the process, to temperatures varying within a wide range—about 392° to 2000° F. (200° to 1095° C.)—either at atmospheric or higher pressures which may reach 200–300 pounds per square inch. The claim is that by this means a higher yield of valuable light oil is obtained than if the coal and the liquid are heated separately. However, there is great difference of opinion about this claim.

In two of these processes (Bluemner and the Carbonol or Woidich) the coal-oil mixture is heated to within a range of about 302° to 806° F. (150° to 430° C.) under pressure conditions up to several hundred pounds per square inch, in such a manner as to drive off only the light oils and leave a heavy thick liquid in which the solid particles are partly carbonized coal. Also the operation is carried out by forcing the coal-oil mixture, using a pump in the circuit, between the narrow concentric space of two steel cylinders or pipes which are externally heated.

It is claimed that this thick residual liquid is more or less in the true colloidal condition because of the extreme subdivision of the already finely pulverized coal particles obtained as the result of carbonization and partial solution of the bituminous content in the hot oil.

Incidentally, the Bluemner process also includes in the circuit a simple form of colloid mill, but this is intended only to finish the subdivision of the partly carbonized particles; no reference to such supplementary treatment is made in the Woidich process.

Therefore, according to these claims the manufacture of true colloidal fuels may be combined with low-temperature carbonization and the production of a high yield of light oil in a manner that involves practically no colloidal or other costly grinding.

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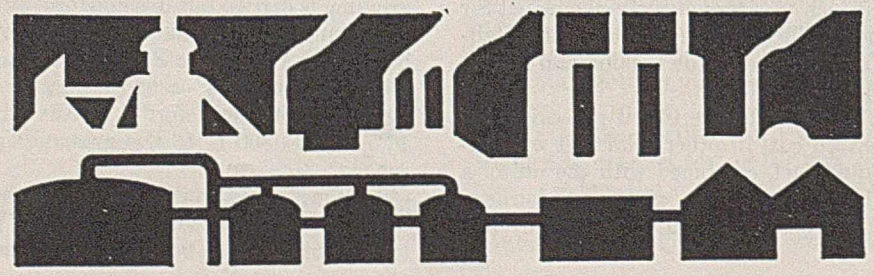

OIL-IMPREGNATED PAPER

Effect of Anhydrous Oxidation Products on Power Factor and Conductivity

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Power factor and conductivity measurements were made on oil-impregnated papers contaminated with each of ten compounds selected to represent common types of oxidation products formed by oxidation of hydrocarbons. The oil-soluble compounds of medium and high molecular weight caused very little increase in either the power factor or the conductivity of the impregnated paper. The acids of low molecular weight, however, caused large increases in the power factor but only small increases in the conductivity of the impregnated insulation.

RECENTLY the authors (*2*) described one phase of an investigation designed to determine which of the types of products that may be formed by service degradation of insulating oils cause serious dielectric losses in insulating oils at 60 cycles, and which do not. The class of degradation products with which that phase of the investigation was primarily concerned was the oil-soluble oxidation products. It was found that moderately large quantities of many chemical types of oxidation products caused only small increases in the 60-cycle power factor and the d. c. conductivity of liquid paraffin as long as the oxidation products remained in solution in the oil.

The present paper constitutes part of a similar but separate investigation concerning the effect of degradation products on oil-impregnated paper. As before, the primary interest is centered on oil-soluble oxidation products. During the course of the study several oil-insoluble oxidation products were also used. Data for these compounds are included for comparison with the data for the oil-soluble compounds.

Materials and Procedure

The paper used in the tests was a highly calendered kraft paper of American manufacture, representative of the papers used in the manufacture of high-voltage underground cables. The paper was cut in strips of a uniform size. Each strip was wound tightly over the high-voltage electrode of the electrical-measurements cell which, with the details of the test procedure common to both studies, was described in the previous paper (*2*). The roll so formed was of sufficient length to cover the high-voltage electrode and of sufficient thickness (nine layers) to fit snugly between the high-voltage electrode and the cylinder constituting the measuring electrode with its guard rings. After the apparatus was assembled, the paper was dried for one hour at 100° C. and a pressure of less than 1 mm. of mercury, which treatment was sufficient to dry the paper to constant power factor. These power factor measurements were made at atmospheric pressure attained by introducing dry nitrogen into the cell.

The usual procedure for impregnating the paper was to invert the complete apparatus, prepare the impregnating liquid in the mixing bulb, evacuate the system, place the apparatus in an upright position in the bath which was controlled to 80° C., and, by slowly admitting dry nitrogen, allow the impregnating liquid to enter the cell proper and impregnate the paper. When the test sample came to equilibrium, as indicated by constancy of the electrical measurements, the power factor and d. c. conductivity values were determined.

The impregnating liquids were of three kinds: liquid paraffin alone, solutions of the several oil-soluble compounds in liquid paraffin, and emulsions of the oil-insoluble compounds in liquid paraffin. Relevant information concerning both the liquid paraffin and most of the compounds used in the preparation of the impregnating liquids was given previously (*2*). Similar information concerning four compounds used in this work, but not in the previous work, is given in Table I.

The volume of the liquid used for impregnating each paper sample was approximately the same as that used in the investigation concerning liquids alone—that is, about 30 ml. The weight of dry paper in each sample was 14 grams. Thus the ratio between the weight of the impregnants (which had specific gravities slightly less than 0.9) and the weight of paper was nearly 2. Since in the insulation of high-voltage underground cables the "oil-paper ratio" is around 0.6, the results of the tests must be interpreted in the light of the purpose for which the work was intended—namely, to find which types of oxidation products cause appreciable increases in power factor and conductivity, rather than to estimate the quantitative effect produced by a given concentration of any definite compound.

Effect of Acids of Different Molecular Weights

The relative effect of each of five organic acid son the power factor of impregnated paper is shown in Figure 1. From the same figure a comparison can be made between the power factor of the impregnated paper and that of the impregnating liquid alone. For this comparison some of the data which were previously reported (*2*) have been replotted. In both Figures 1 and 3 some of the power factor data obtained at

TABLE I. DESCRIPTION OF FOUR COMPOUNDS USED WITH LIQUID PARAFFIN TO FORM IMPREGNATING LIQUIDS

Name of Compound	Class of Oxidation Product Represented	Origin	Treatment	Solubility in Liquid Paraffin
Acetic acid	Acid of low molecular weight	Eastman Kodak Co., "Eastman" grade	Refluxed under reduced pressure over anhydrous $CuSO_4$; distilled in same apparatus; melted, as used, at 16.4° C. (after crystallizing three times, melted at 16.6° C.)	Entirely soluble at all temperatures and concentrations used
Formic acid	Carboxylic acid of lowest molecular weight	Eastman Kodak Co., "Eastman" grade	Crystallized from its own mother liquor 3 times in closed system into which it was distilled after drying as above; melted at 8.4° C.	Only slightly soluble at temperatures as high as 80° C.
tert-Amyl alcohol	Alcohol of medium molecular weight	Eastman Kodak Co., "Eastman" grade	Dried over anhydrous $CaSO_4$, distilled under reduced pressure in all-glass apparatus	Entirely soluble at all temperatures and concentrations used
Ethyl alcohol	Alcohol of low molecular weight	U. S. I. absolute, 99.8 to 100% (scientific)	Same as acetic acid	Sparingly soluble at the lower temperatures used

60°, 40°, and 30° C. were not plotted. In all these cases the values were below the respective values determined at 80° C.

Stearic acid, the compound chosen to represent the class of oil-soluble organic acids of fairly high molecular weight, was found to cause little increase in the power factor of impregnated paper (Figure 1 *B*). Similar observations had previously been made concerning the effect of stearic acid in the oil without paper (Figure 1 *A*).

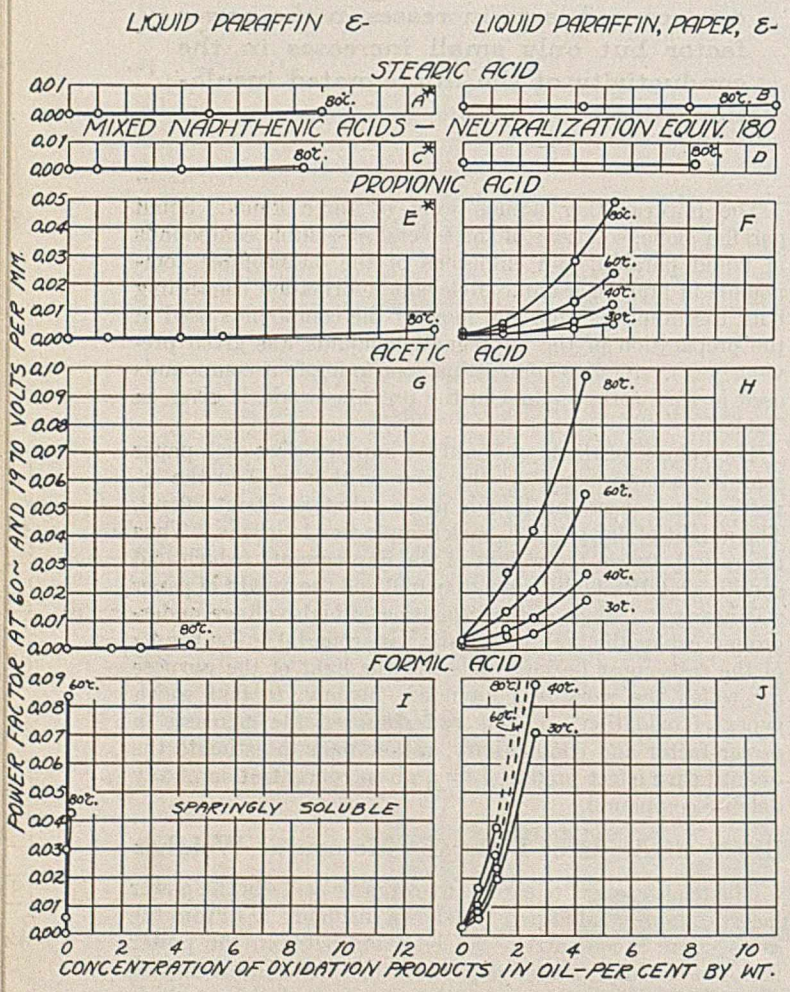

FIGURE 1. EFFECT OF ANHYDROUS ORGANIC ACIDS ON POWER FACTOR OF LIQUID PARAFFIN AND LIQUID PARAFFIN AND PAPER

* Previously reported (2)

As an example of acids of medium molecular weight, mixed naphthenic acids were chosen. These acids were chosen instead of a pure chemical compound because among some cable research workers an opinion, apparently unpublished, was held that the presence of these acids in cable insulation was a major cause of high power factor. Like the stearic acid, however, the naphthenic acids used caused little increases in the power factor of either the oil or of the oil-impregnated paper (Figures 1 *C* and *D*).

Propionic acid, the compound used to represent the class of acids of low molecular weight in the previous work (*2*), was the first acid of low molecular weight investigated in the present study. It was found that propionic acid caused a marked increase in the power factor of the impregnated paper (Figure 1 *F*), although it had previously been found that propionic acid had little effect on the power factor of the liquid paraffin alone (Figure 1 *E*). For this reason acetic acid was also studied.

As shown in Figure 1 *H*, given concentrations of acetic acid caused the power factor of the impregnated paper to be even higher than for similar concentrations of propionic acid. Like the propionic acid and the other oil-soluble compounds, the acetic acid had only a small influence upon the power factor of the liquid paraffin when no paper was present (Figure 1 *G*).

Since the effect of a given amount of acid seemed to increase with decreasing molecular weight of the acids, the carboxylic acid of lowest molecular weight—formic acid—was next selected for test. Although when carefully dried all the other acids used were readily soluble in liquid paraffin, formic acid was very sparingly soluble. Especially at the lower temperatures and higher concentrations the mixtures of formic acid and liquid paraffin formed visibly heterogeneous emulsions which had very high power factors as shown in Figure 1 *I*.

The power factors of paper impregnated with the emulsions of formic acid in liquid paraffin were very high at first but decreased rapidly until equilibrium was reached, under which conditions the cloudiness of the excess oil above the paper had practically disappeared. The resulting values, though still high, were not nearly so high as those of the emulsions, and differed further from those of the emulsions in that the higher values were at the higher temperatures. When the impregnation was carried out in the cell in the usual manner, there was a tendency for some of the formic acid droplets to be caught by a small part of the roll of paper near the inlet opening of the cell. For this reason the samples represented in Figure 1 *J* were impregnated in a special apparatus which permitted the entire paper sample to come in contact with the emulsions at practically the same time. After being

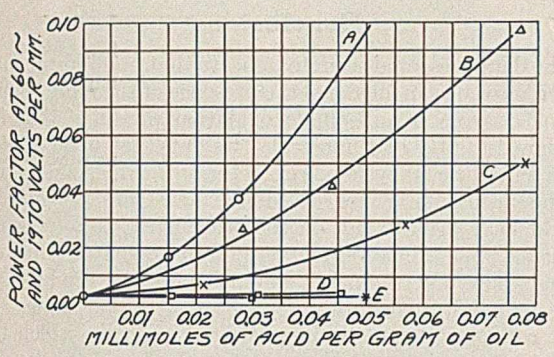

FIGURE 2. POWER FACTOR AT 80° C. OF OIL-PAPER INSULATION CONTAINING EQUIMOLECULAR QUANTITIES OF FIVE ORGANIC ACIDS

A. Formic acid; power factor, 0.10 at 0.06 millimoles per gram
B. Acetic acid
C. Propionic acid
D. Stearic acid
E. Mixed naphthenic acids

thoroughly impregnated, the samples were quickly transferred to the measuring cell.

The data for the experiments concerning formic acid, as well as those for the experiments involving acetic and propionic acids, indicate that the power factor of impregnated-paper insulation may be markedly increased by the presence in the insulation of low-molecular-weight acids such as these. As previously stated, the effects of the high-molecular-weight acid tested were very small.

The concentration values shown in the various figures are based on percentage by weight. The molar concentration for a given percentage concentration is much higher in the case of the acids of lower molecular weight than of those of higher molecular weight. That the difference in the number of functional carboxyl groups for a given percentage composition is not primarily responsible for the differences in the power factors of the impregnated paper containing the several acids is shown in Figure 2, where part of the power factor data from Figure 1 are replotted against the molar concentrations of the acids in the oil. Even on this basis the magnitude of the effect of the acids in increasing the power factor appears to be in the order of the decreasing molecular weight of the acids.

The similarity between the power factors of the paper impregnated with the emulsions consisting of the oil-insoluble formic acid suspended in liquid paraffin and those of the paper impregnated with the solutions of the oil-soluble acetic or propionic acids in liquid paraffin seem to indicate that the power factor increases caused by both classes of acids may be due to similar mechanisms. The power factors of the paper impregnated with formic acid emulsions were only about as much higher than the respective values for the paper impregnated with the acetic acid solutions as might be expected from the corresponding increase for acetic acid over propionic acid, provided the difference in solubility behavior between formic and acetic acids were ignored. As has been stated previously, after paper had been thoroughly impregnated with the oil emulsions of formic acid, the excess oil appeared clear or only slightly hazy, thus indicating that the formic acid droplets had been sorbed almost entirely by the paper. In view of the similarity of effect on power factor it seems probable that the acetic and propionic acids were also strongly sorbed by the paper. Support for this hypothesis may be given by the fact that the power factor values for the paper impregnated with the oil solutions of acetic and propionic acids rose rapidly at first and then progressively more slowly until the equilibrium values shown were attained. An investigation of the relative sorption of organic acids of different molecular weights from oil by paper is now in progress.

It may be of interest to investigators who work with high-voltage underground cables to note that a peculiar acrid odor was usually perceived whenever the paper impregnated with the formic acid–oil emulsions was removed from the power factor cell. This odor seemed to be identical with that often found in cables which have a high power factor and in which intensive oxidation has taken place. The odor was not that of formic acid itself. No investigation concerning the origin of the odor has yet been undertaken.

The d. c. conductivities of the impregnated samples described and those whose descriptions follow did not exceed 1.5×10^{-14} mho per cc. except in some of the cases involving formic acid in which the droplets of the acid were not entirely sorbed by the paper. The d. c. conductivities were determined after one minute of voltage application (*1*).

Effect of Alcohol, Aldehyde, and Ketone

Since the magnitude of the power factor of the impregnated paper increased with decreasing molecular weight of the acids used as contaminants, an attempt was made to determine whether a similar order would result from the use of other chemical classes of oxidation products such as the alcohols. As an example of an alcohol of high molecular weight, cetyl alcohol was selected. The results of the power factor measurements made upon paper impregnated with solutions of cetyl alcohol in liquid paraffin are shown in Figure 3 *B*. In the impregnated paper as well as in the liquid paraffin alone (data for the latter are reproduced for comparison in Figure 3 *A*), the presence of the cetyl alcohol caused very little increase in the power factor of the insulation as long as the alcohol did not separate from the oil. Upon separation of the cetyl alcohol as a gel, however, the power factor of the impregnated insulation was very high, though not so high as for corresponding concentrations of the cetyl alcohol in the oil alone.

As an example of an alcohol of medium molecular weight, *tert*-amyl alcohol was used. This alcohol, which was completely soluble in the oil at all temperatures and concentrations used, had little influence upon the power factor of either the oil or the impregnated paper, as shown in Figure 3 *C* and *D*.

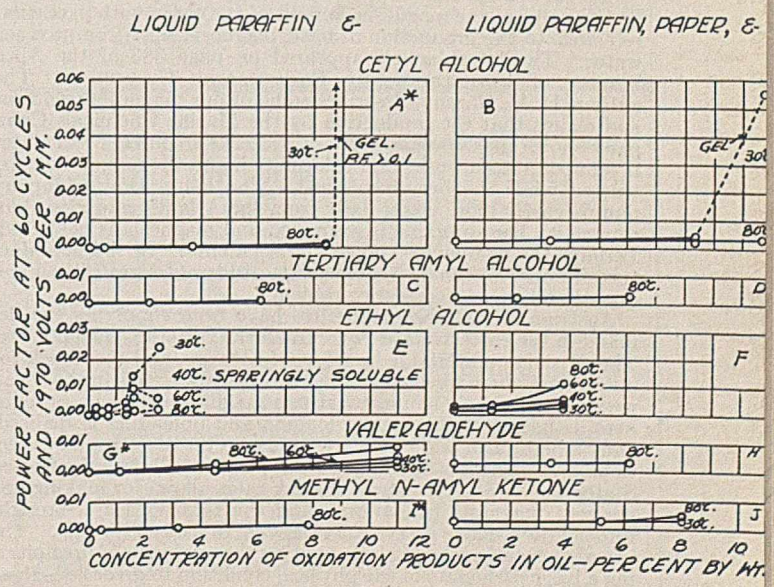

FIGURE 3. EFFECT OF ANHYDROUS OXIDATION PRODUCTS ON POWER FACTOR OF LIQUID PARAFFIN AND OF LIQUID PARAFFIN AND PAPER

* Previously reported (*2*)

For purposes of this investigation desirable properties of an alcohol to be used to represent the class of alcohols of low molecular weight would be low volatility and complete solubility in liquid paraffin. Because of the volatility requirements imposed by the vacuum technic employed, no attempt was made to use methyl alcohol. Ethyl alcohol, the compound selected, was not entirely satisfactory in that it was only sparingly soluble in the liquid paraffin but, since the property of complete solubility could be attained only by using compounds of higher molecular weight than desired, the ethyl alcohol was used.

In concentrations beyond 1.5 per cent the mixtures of ethyl alcohol and liquid paraffin were visibly heterogeneous at the lower temperatures and under those conditions had high power factors as shown in Figure 3 *E*. Difficulty was experienced in obtaining the power factor values shown since the solutions had a tendency to supersaturate before separating. The power factors of the paper impregnated with the alcohol-oil mixtures were higher than those of the paper impregnated with the oil alone, but the effect of the alcohol was not marked, as is shown in Figure 3 *F*.

Because the acid and alcohol of medium molecular weight had about the same small effect upon the power factors of the impregnated paper as had the acid and alcohol of high molecular weight, only one aldehyde and one ketone were used to represent both medium- and high-molecular-weight oxidation products of these chemical types. The compounds selected were valeraldehyde and methyl *n*-amyl ketone. As shown in Figures 3 *H* and *J*, neither compound caused any appreciable increase in the power factor of the impregnated paper in which it was used as the contaminant. The behavior of each in this respect was similar to its corresponding behavior (Figures 3 *G* and *I*) when each was used with liquid paraffin alone. Because of the high volatility of both aldehydes and ketones of low molecular weights, no examples of these types of oxidation products were investigated.

Conclusions

The data presented seem to indicate that in oil-impregnated paper, as well as in oil alone, the presence of the more common chemical types of oil-soluble oxidation products that have medium to fairly high molecular weights, has little influence upon either the 60-cycle power factor or the d. c. conductivity of the insulation. Two oil-soluble acids of low molecular weight have been found, on the other hand, to have a large influence upon the power factor of oil-impregnated paper even though they, like the other soluble oxidation products, had little influence upon the power factor of the oil alone. The d. c. conductivity of the impregnated paper in which these acids were used as contaminants was found to be little changed. In their effect upon the power factor of the impregnated insulation these two oil-soluble acids were found to be similar to a closely related but oil-insoluble acid. Judging from the single set of data available, the presence of anhydrous, low-molecular weight oxidation products other than acids contributes in a mild way to power factor increases in oil-impregnated insulation. These increases, however, are not considered sufficiently great to warrant their further investigation at this time.

The work is being continued, the major emphasis being shifted to an examination of the effect of dispersions of oil-insoluble materials on the power factor and conductivity of both oil and oil-impregnated paper.

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Received April 29, 1936. This work forms part of an investigation on the deterioration of high-voltage underground cable being conducted by The Detroit Edison Company under the direction of C. F. Hirshfeld, chief of research.

Our Magnesia Resources

Several articles have appeared recently in the technical press on the value of the magnesia content of the ocean with particular reference to the production of basic magnesia salts from raw sea water. The latest article appeared on page 383 of the April number of Industrial and Engineering Chemistry. The author, H. H. Chesny, describes some of our magnesia resources and claims that the production by the Marine Chemicals Company shows the superiority of sea water as a source. Sea water is pumped to the works and chlorinated, and the magnesia is extracted while the bromine is lost. The Ethyl Dow Company pumps vastly more water daily from the Atlantic and also chlorinates it; here bromine is recovered and magnesia is neglected. Perhaps the companies should trade patents. In the manufacture of bulky and cheap chemicals the study of freight rates is frequently the most necessary problem.

Austrian and Greek magnesites have been supplying the demand in the eastern states for refractories, plastics, cements, etc. The Austrian material is best for refractories, and the Greek for operations where freedom from iron is essential. Owing to cheap westward ocean freight rates, these magnesites can be brought here as ballast if the cost of loading and unloading is realized. Only a high tariff will prevent their use in the most populous sections. As mentioned, dolomites are plentiful all over the United States and are used (where freight rates allow) for making "85 per cent magnesia insulation," and the bicarbonate is brought into solution under pressure by blowing in carbon dioxide. The use of this old method is indicated by the necessity of precipitating a basic carbonate of the physical condition to give the highest insulating value for pipe and boiler coverings.

The German fertilizers consisting of carnallite could be worked here to concentrate the potash contents and leave a concentrated magnesium chloride which could be converted into sulfate, if the demand justified the cost of manufacturing.

Mixed calcium and magnesium chlorides are made from the residues of salt manufacture from the Ohio River and Midland, Mich., bittern or brines; they have also been made at Tulsa, Okla., from brines of about the same composition ratio but differing in total solids content. The process of separating magnesia is about the same as that described by Chesny.

The early Dow process at Midland for the by-product manufacture of magnesia is cited, but the costs of digging wells and of general operations are erroneously charged to magnesia production. These costs cannot be charged to this by-product since well digging and other general operations are already necessary in making the other chemicals. The amount of magnesia made is thus limited to the possibility of selling it for more than its manufacturing cost, which includes only the special operations for precipitating the magnesium. Magnesia has also been manufactured on the Pacific Coast from the bitterns left after salt is manufactured by solar evaporation of sea water. This is a concentrated solution of magnesia as compared with ocean water.

About 300 tons of salt are made daily at Charleston, W. Va., according to E. T. Crawford [Ind. Eng. Chem., 27, 1274, 1411 (1935)], who gives the history of salt manufacture there. Now "calcium" is sold to the coal mines for floating coal off the slate, and no separation of the calcium and magnesia is necessary. It will not be separated until there is no longer a market for the mixed product.

Thus, we have many sources of magnesia suitable for manufacture in the United States and better supplies of raw materials abroad which will be used unless a high tariff prevents.

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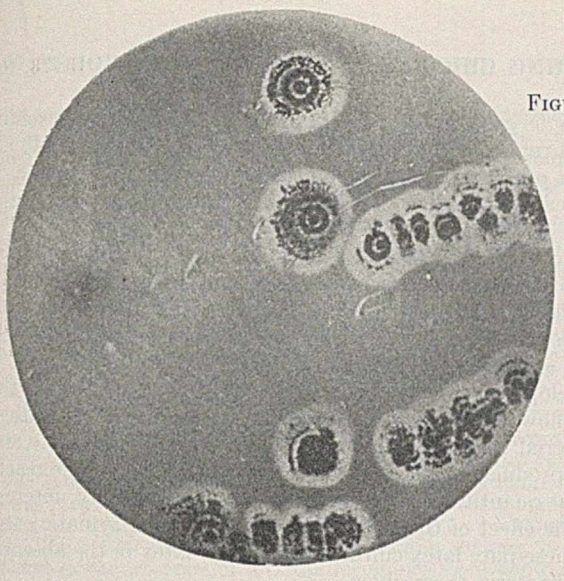

FIGURE 1. ACTINOMYCETES COLONIES ON LATEX-AGAR PLATES

Bacterial Decomposition of the Rubber in Hevea Latex

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A RECENT communication (*6*) has shown by several different means that rubber present in the living plant actually disappears under seasonal and other conditions in the life of the plant, and that it can, therefore, no longer be regarded as an excretory product of metabolism of no physiological value to the plant. The results recorded were obtained in a study of the rubber content of *Parthenium argentatum*, but they will undoubtedly be found to hold for *Hevea brasiliensis* when suitable methods of investigation are developed for the latter.

The importance of these findings in relation to the economic development of rubber is obvious and far-reaching. They have already been applied in the cultural development and exploitation of *Parthenium argentatum*.

On the scientific side they suggest a more intimate study of the behavior of the rubber hydrocarbon towards oxidation-reduction processes occurring within the living plant and to the effect of such agencies on the rubber itself *in vitro*. That rubber is readily attacked by oxidizing agents in general is now well known. But even the classical researches of Harries on the products of decomposition of the rubber hydrocarbon by means of ozone (*1*) have thrown little light on the ways and means by which the rubber in the plant is first produced and thereafter broken down and utilized in its cycle of yearly development. This is not surprising when we consider the reagents heretofore employed and the drastic character of the decompositions effected by them.

The solution to this question will probably be found in microbiological methods. Therefore, this investigation had as its object, first to determine the extent to which the rubber hydrocarbon is affected, directly or indirectly, by the action of bacteria, and subsequently to study the nature of the changes brought about by these means and by the extracellular enzymes developed therefrom. The present paper will give the first account of some striking results obtained on the decomposition of the rubber hydrocarbon of Hevea latex by means of bacteria under aërobic conditions; a subsequent paper will show how the physical character and quality of the rubber from *Parthenium argentatum* is profoundly changed, for better or for worse, by decomposition of the cortical tissue by means of pure cultures of certain organisms under anaërobic conditions.

We would hardly expect that a solid, compact mass of rubber in its coagulated state would be subject to bacterial action to the same extent as the same material in the finely dispersed condition in which it exists as latex in the plant. This probably accounts for the fact that little progress has been made since the original work of Söhngen and Fol (*2*) who showed that species of Actinomyces developed on thin films of rubber on culture plates. Similarly, the loss in weight and in physical quality observed by de Vries in moist sheets of plantation crepe on which Penicillium molds had been allowed to develop was insignificant until after five years of slow development (*7*).

Sterile Latex

The preparation of a sterile latex suitable for bacteriological study presents a problem in itself, particularly when one has to deal with the product as it arrives in this country preserved with ammonia. However, by dialyzing the latex against a strongly buffered solution, continuously renewed and of about the same pH as fresh Hevea latex (6.8–7.2), it is possible to get rid of the ammonia and water-soluble organic crystalloids present in the original latex without coagulation; furthermore, this dialyzed latex can be afterwards sterilized in the ordinary way (15 minutes at 120° C.) without coagulation taking place. Latex, so prepared and sterilized, can be kept apparently indefinitely without coagulation. On standing in the dark some "creaming" occurs in the course of time, but even after six months, gentle shaking of the contents of

That bacterial contamination of late accounts for some of the variability in plantation rubber is now recognized. Studies of the decomposition of the non-rubber constituents of latex have already appeared. This paper gives the first account of the decomposition of the rubber hydrocarbon itself by bacteria applied to latex. The results show that the hydrocarbon is readily attacked by certain organisms, producing discoloration in latex and ultimately bringing about the complete decomposition of the rubber. The practical importance of this behavior is indicated, and new means are provided of studying the role of the rubber in the living plant.

the flask will bring about a complete redispersion of the globules, provided the latex was properly buffered and sterilized in the first place.

This prepared and sterilized latex was used in the following work. By dilution with sterilized tap water, it is possible to prepare latex dispersions of any given concentration with the requisite amounts of inorganic elements for bacterial growth. Or this latex can be brought to any desired concentration and subsequently resterilized in individual flasks, provided that the pH is maintained unchanged and that ammonium chloride is not added as a source of nitrogen. Even in the small amounts (0.05 per cent) necessary for bacterial growth, this latter reagent brings about coagulation of the latex on sterilization probably because of the decomposition of the ammonium chloride at the temperature of sterilization. Later potassium nitrate was used as a source of nitrogen; it answers every requirement and at the same time overcomes the difficulty described where ammonium chloride is added prior to sterilization.

Working with latex has shown that the decomposition of the rubber hydrocarbon by certain bacteria is both rapid and profound; after a few weeks at 30° C. the greater part of the rubber originally present in the latex has vanished and what is left is a coagulum composed of a mass of bacteria in a residue which has little claim to be called rubber.

Bacteria Strains

So far only those forms of Actinomyces derived from garden soil have been used. Four strains prepared in pure culture using agar-latex plates developed for the purpose have yielded characteristic results. When one of them was used to inoculate a prepared and sterile latex, after 4 weeks at 30° C. in the dark, over 70 per cent (by weight) of the rubber hydrocarbon present in the original latex had disappeared. Large colonies of bacteria developed freely and rapidly on the surface and throughout the latex which gradually darkened in color as the decomposition proceeded. After 3 weeks the milky appearance of the latex was gone, and there remained a brownish residue in a clear, brownish, watery serum. This residue turned black on drying and was friable and hard, unlike rubber. After acetone extraction and drying, it contained roughly one-half its weight of bacteria; the remainder was partially soluble in benzene alone and gave a clear, soft, almost oily product on evaporation of the benzene. The product, insoluble in benzene but swelling in it after a time, was readily dissolved in benzene containing trichloroacetic acid and therefore probably represents "insoluble" rubber. The acetone extract of this product of the latex remaining after bacterial decomposition was over 10 per cent, representing an increase of more than 50 per cent in acetone-solubles compared with the original (sterile) controls. The water liquor from this same latex after bacterial decomposition, when filtered, evaporated to dryness, and incinerated, appeared to contain over 30 per cent by weight of the total coagulum of the original latex in the form of water-soluble organic decomposition products. With barium hydrate a copious white precipitate was formed, although no sulfates had been used in the preparation or coagulation of this latex.

Similar results were obtained with the pure cultures of all four organisms isolated and tested. Marked differences, however, appeared in their rate of development both on the original agar-latex plates and in the latex itself. Although the water-insoluble residue left after bacterial decomposition of the latex was almost black in the case of organisms 1, 2, and 3, and friable or tough but not elastic, in the case of organism 4, there was practically no discoloration in the residue which was still quite white and somewhat elastic. The analytical figures show that the bacterial development in this case was quite as great as that of organism 1. Much less "insoluble" (gel) rubber and also carbon dioxide seem, however, to have been produced in the case of organism 4, indicating a less intensive oxidation of the original hydrocarbon than in the case of the others.

No attempt has yet been made to study the products of decomposition of the hydrocarbon; present efforts were directed towards establishing the fact that the rubber hydrocarbon in latex form can be and actually is readily attacked and almost completely decomposed by bacteria and to the development of practical means to this end. The writers are now in a position to prepare much larger quantities of material than was possible in the first instance and to study the products of decomposition and the course of the reaction in a quantitative way. They are particularly interested in the effect of the addition of an aqueous enzymatic extract of these pure latex cultures upon fresh latex in the absence of the bacteria themselves.

There is every reason to believe that latex fresh from the tree will be much more susceptible to the action of bacteria than the old, ammonia-preserved material. On the practical side, the present results explain the generally poor physical quality of earth and bark scrap rubbers and their blackish color. Early sterilization should provide the remedy. That the physical quality of the rubber hydrocarbon can be profoundly affected by the action of microörganisms applied to the latex is also shown by the marked differences in viscosity here recorded between samples of rubber prepared from latex and from the same material after bacterial infection and development.

Experimental Procedure

The latex used in this work was a 40 per cent product furnished by the U. S. Rubber Company; it contained 1 per cent ammonia. For this work the removal of the ammonia and any water-soluble sugars, etc., from this latex was essential, and the method of dialysis first developed and applied some twenty-eight years ago to the purification of latex (*3*) and to its analysis (*4*) was utilized.

Considerable coagulation occurred on the walls of the dialysis tube when the latex was dialyzed against running water, so that it could not be purified in this way without considerable loss of rubber by coagulation. Although this loss was relatively unimportant in these experiments, since it was still possible to obtain a sufficiently concentrated latex for use after dialysis in this way, it was utterly impossible to sterilize the latex without coagulation. This dialyzed latex quickly became foul on standing and finally coagulated of its own accord.

The first series of experiments was carried out with 50 cc. of this dialyzed latex, diluted to 1 liter with tap water and filtered through cheesecloth and subsequently through a No. 1 Schott sintered glass funnel. Four lots of 50 cc. each of this dilute dialyzed latex were measured off, two for immediate coagulation and two for incubation at 30° C. A few drops of toluene were added to the latex in one flask before placement in the incubator and to the other was added a trace of garden soil. The flasks were provided with cotton wool plugs and a few drops of toluene were added to one flask, from time to time, to prevent bacterial growth. The flasks were left in the incubator 6 weeks. The two lots of latex serving as controls were coagulated at once by adding to each of them three drops of 10 per cent sulfuric acid and heating to the boiling point to ensure complete coagulation. The clots formed in each case were filtered, extracted with boiling acetone, kept 6 hours in the dark, and subsequently dried in vacuum over sulfuric acid in the dark until constant in weight. At the end of 6 weeks both lots of latex in the incubator had coagulated more or less completely, but the one containing the soil had turned dark in color and had a powerful, characteristic odor of moist soil. The particles of soil were removed by the centrifuge, and the liquor (with coagulum and washings) was treated with three drops of 10 per cent sulfuric acid and raised to the

boiling point. The contents of the other flask containing toluene were similarly treated to ensure uniformity and complete coagulation throughout the series. The clots in each case were extracted with boiling acetone, dried in the dark in vacuum as in the case of the two original controls, and weighed.

In order to effect a complete separation of the bacteria and/or vegetable protein from whatever rubber was still present in the various samples, the method (*5*) of dissolving the samples in benzene containing 1 per cent trichloroacetic acid was used. In this way it was possible to filter off the bacteria in a sintered glass crucible and, after washing with fresh benzene and drying, to determine the amount in each coagulum. In the case of the control samples, the figures obtained in this way represent the vegetable protein of the rubber.

In addition, and in order to illustrate the difference in quality between the rubber in the control samples and that from the latex in which the bacteria had developed, viscosity determinations were made in dilute solution. A 1 per cent solution in benzene was prepared for this purpose, due allowance being made for the bacteria and protein present in each sample by previous determination. After several weeks of constant shaking in the dark and in the absence of air, the insolubles were allowed to settle out, and the viscosity measurement was made on an aliquot portion of the clear solution which was afterwards evaporated to dryness and weighed. The results of these viscosity measurements confirm the obvious differences in physical quality between the different samples observed by rule-of-thumb tests.

The results obtained by the above methods on the preliminary sample of dialyzed but not sterilized latex subjected to the action of soil bacteria were as follows:

	Latex Coagulated at Once		Latex after 6 Weeks at 30° C. with:	
	Sample 1	Sample 2	Toluene	Soil
Total dry weight of coagulum, gram	0.4260	0.4260	0.4308	0.3840
Total dry weight of bacteria and/or protein, gram	0.0114	0.0110	0.0112	0.0504
Total residual rubber (by difference), gram	0.4146	0.4150	0.4196	0.3336
Relative viscosity, sec.	20	22	18	3

The coagulum obtained from the soil-treated latex was practically black when dry, and very soft and "dead." All the others were pale and transparent throughout and quite hard and tough. More than 20 per cent of the rubber originally present in this latex was completely decomposed, and that which remained was thoroughly deteriorated, soft, and "dead."

Preparation of Sterile Latex

After months of experimenting on the preparation of a latex which would stand sterilization without coagulation but would contain the inorganic salts and nitrogen necessary to ensure bacterial development, the following satisfactory method was developed. It is capable of wide application where the preservation of latex in general against coagulation in storage or use is desired.[1]

The latex is diluted with at least its own volume of a buffer solution made by the addition of the necessary quantity of a 0.05 *M* solution of sodium hydroxide to a 0.05 *M* solution of potassium dihydrogen phosphate in distilled water to bring the pH of the final solution to approximately 6.8 by determination. This latex can now be dialyzed (to get rid of the ammonia and otherwise be purified) into a large volume of this same buffer solution, renewed from time to time, without any appreciable coagulation. After dialysis in this way and filtration if necessary through a sintered glass filter, this latex can be sterilized by steam for 15 minutes at 120° C. without coagulation, and in this sterile condition can be kept apparently indefinitely, without change. It is necessary only to shake the contents of the flask gently if there is evidence of creaming on long standing, in order to ensure a uniform redispersion of the latex particles. In withdrawing samples for test purposes, it is obviously essential to avoid bacterial contamination from any source. Samples can be taken by sterile pipets and diluted thereafter as required for bacteriological purposes, or the latex after dialysis can be diluted as a whole to any desired concentration by means of tap water containing the necessary salts for bacterial development and then sterilized. The only difficulty experienced is in sterilizing the diluted latex in the presence of ammonium chloride. On the addition of only 0.05 per cent of this material to the diluted latex, coagulation occurs on sterilization. However, the use of potassium nitrate (0.1 per cent) overcame this difficulty. The dialyzed and sterile latex was diluted for the experiments so as to contain, before inoculation, inorganic elements approximately as follows (in per cent): potassium dihydrogen phosphate, 0.1; magnesium sulfate, 0.05; ammonium chloride, 0.05, or potassium nitrate, 0.1, with a rubber content of less than 1 per cent (determined by coagulation tests) and a pH of 6.8 to 7.

In the first experiment carried out with sterile latex prepared in this way, soil particles were again used for inoculation purposes, and the four flasks (two sterile), each containing 100 cc. of latex, were put into the incubator at 30° C. for 35 days. Long before the end of this period the soil-inoculated latex had again darkened in color and completely coagulated; the two sterile controls were still milky white and showed evidence of some agglutination of latex globules but almost no coagulation. The soil particles were removed from the two by centrifuge and all four samples were then treated alike for complete coagulation and analysis as previously outlined. The results of this experiment are shown in the following table and confirm previous findings as far as the effect of soil bacteria on latex is concerned:

	Sterile Latex Controls		Soil-Inoculated Latex	
	No. 1	No. 2	No. 1	No. 2
Final total dry weight of coagulum, gram	0.4786	0.4724	0.4238	0.4308
Dry weight of bacteria and/or protein (by detn.), gram	0.0124	0.0112	0.0648	0.0660
Total residual rubber (by difference), gram	0.4662	0.4612	0.3590	0.3648
Relative viscosity of 1% soln. of benzene-sol. fraction, sec.	14	13	4	3

Here again more than 20 per cent of the rubber originally present in the latex was completely decomposed by the action of the soil bacteria, and the rubber remaining was so deteriorated physically that a 1 per cent solution in benzene had practically the same viscosity as pure benzene (2.75). The residue after benzene extraction in the presence of trichloroacetic acid was a blackish mass which, when ground to powder and examined under the microscope, obviously consisted almost entirely of disintegrated Actinomycetes.

Enrichment of Organisms and Preparation of Pure Cultures from Soil for Latex Decomposition

Washed agar (in water) was used to which the following percentages were added: ammonium sulfate, 0.1; potassium hydrogen phosphate, 0.1; magnesium sulfate, 0.05. The warm agar solution was poured into Petri dishes and allowed to cool and harden, then covered with a thin layer of a milky white suspension of sterile latex in water-agar medium, and inoculated with soil particles. Incubation was carried out at 20°, 25°, 30°, and 37° C. Colonies, chiefly Actinomycetes, quickly appeared on all plates and developed most rapidly at 25° to 30° C. Pure cultures of four distinct strains were prepared by four repeated replatings on the same medium. All four strains showed more or less distinct clear zones in the opaque latex-agar medium surrounding the individual colonies. (Figure 1 shows a photograph made by transmitted light.) Whether this is due to extracellular enzymatic decomposition of the latex or not remains to be determined.

[1] It should now be possible to determine whether the protein of latex can be removed by digestion with trypsin and subsequent dialysis without coagulation. By digestion of sterile latex with active trypsin and subsequent dialysis into a buffer solution of the correct pH, there is some hope of arriving at a decision as to the role of the protein in connection with latex and its coagulation. The conclusions of Freundlich and Haüser [*Kolloid-Z.*, **36**, 21, Zsigmondy Festschrift (1925)] are based on entirely inadequate experimental evidence and are at complete variance with the earlier observations by one of the writers on the effects of trypsin applied both to Hevea and Funtumia latices (*4*).

TABLE I. RESULTS OF EXPERIMENTS

	Sterile Latex Controls				Latex after 28 Days at 30° C. with:			
	Coagulated at once		Coagulated after 28 days at 30° C.					
	1	2	1	2	Strain 1	Strain 2	Strain 3	Strain 4
Total dry weight of coagulum, gram	0.248	0.246	0.245	0.243	0.144	0.195	0.1494	0.1946
Appearance of coagulum	Clear, pale, and tough	Clear, pale, and tough	Clear, pale, and tough	Clear, pale, and tough	Black, crumbly mass	Black, solid mass	Black, crumbly mass	Pale, muddy, slightly elastic
Dry weight of bacteria and/or protein in coagulum, gram	0.0079	0.0076	0.0083	0.0083	0.0704	0.0378	0.0426	0.0760
Total rubber (benzene and acid sol.), by difference, gram	0.2401	0.2384	0.2367	0.2347	0.0736	0.1572	0.1068	0.1186
Benzene-sol. rubber only, gram	Not determined		....	....	0.0475, very soft and plastic	Not determined		0.1062, soft and plastic
Original rubber lost,[a] %	....	....	....	....	70	36	56	51
Water sol. in serum (loss by incineration), gram	....	....	....	....	0.0856	0.0651	....	0.0316
Acetone-sol. extracts, gram (%)	....	....	0.0074 (3.0)	0.0070 (2.88)	0.0156 (10.8)	0.0124 (6.4)	0.0150 (6.2)	0.0170 (8.7)

[a] The actual losses are undoubtedly higher because the residues left were oxidized rubber, to a greater or less extent.

Preparation of Latex for Inoculation with Pure Cultures

For this series a dialyzed latex was used and diluted with standard 0.05 *M* buffer solution to bring the rubber concentration to approximately 5 per cent. Eleven flasks, each containing a solution of 0.1 per cent potassium nitrate, 0.1 potassium hydrogen phosphate, 0.05 magnesium sulfate, and brought to a pH of 7.0 by means of potassium dihydrogen phosphate, were prepared; to each were added 5 cc. of the latex. All eleven flasks were successfully sterilized for 20 minutes at 120° C. without any coagulation. Two of these flasks of sterile latex were immediately coagulated, and the rubber content was determined. Two other flasks were set aside to be placed in the incubator with the remaining seven which were inoculated as follows: two with strain 1, two with strain 2, one with strain 3, and two with strain 4. All nine flasks were left in the incubator at 30° C. for 28 days.

In a week, bacterial growth was clearly evident, particularly in the case of strains 1 and 3. In 3 weeks, all milkiness had disappeared, and instead large colonies had developed on the surface and throughout the liquors. The colonies were smaller in the case of strain 2. Contents of 1, 2, and 3 had turned dark. After 4 weeks strain 4 alone appeared as white moldlike colonies in a clear liquor; the others were now almost black. All had the characteristic odor of moist soil. The sterile controls after 4 weeks in the incubator came out slightly coagulated, but were still milky and apparently unchanged.

The control samples of latex from the incubator and one of each of the samples containing the various strains were treated alike with five drops of 10 per cent sulfuric acid and raised to the boiling point. The clear liquor was filtered off, and the residue or coagulum well washed with boiling water, finally extracted with boiling acetone in the dark, and dried in vacuum in the dark until constant in weight. In this series the acetone extracts were also evaporated to dryness and weight. The benzene-soluble content was determined in samples of the residues from strains 1 and 4 only while the bacteria, together with any protein still present, were separated by the benzene–trichloroacetic acid method in each case and weighed. In this way the amount of benzene-insoluble rubber present in strains 1 and 4 was estimated. The water liquors from the additional flasks containing strains 1, 2, and 4 were used to determine the organic matter present in these liquors at the end of the incubation period. The bacteria and water-insolubles were filtered. The residual liquors were boiled, refiltered, and finally evaporated to dryness and weighed before and after ignition in a platinum crucible. Extensive charring occurred with strain 1, very little with strain 4. This same liquor from strain 1 gave a copious precipitate on addition of barium hydroxide, strain 2 very much less, and strain 4 only a trace. Insufficient material prevented further investigation. The results of this series are given in Table I.

It is clearly evident that the rubber hydrocarbon in the latex of Hevea is readily attacked by microörganisms of aërobic type and ultimately decomposed into products with very little physical resemblance to India rubber. That such agencies may exert a profound influence on the final quality of the rubber prepared from various latices and may help to explain the still unsolved problem of plantation rubber variation is clearly indicated from the preliminary results.

The preparation of a sterile latex from Hevea opens up ways and means for a complete investigation of this whole subject as a practical problem of the utmost importance to plantation owners and rubber manufacturers alike; also the foundation has been laid for a study of the reactions and products involved in the building up and breaking down of the rubber hydrocarbon by the living plant.

Acknowledgment

The writers wish to express their thanks to W. A. Gibbons and H. L. Fisher of the U. S. Rubber Company for their assistance in furnishing the latex used in this work. They also desire to thank H. Albert Barker for many valuable suggestions made in the course of this work and also A. W. Martin for preparing the photograph illustrating the characteristic appearance of Actinomycetes development on latex-agar plates.

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Extraction of Solids with Liquids

Multiple and Countercurrent Extraction

A complete graphical solution of problems involving the multiple and continuous countercurrent extraction of solids with liquids is presented including the case of extraction with varying entrainment. The latter condition has not been discussed in the literature heretofore. The solution of a practical problem of this type is also presented.

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MANY mathematical formulas (*1, 3, 6, 8, 9*) have been presented for the solution of extraction problems. Most of them are somewhat special in application and do not present a simple treatment when the data known are different from those for which the formulas were designed. Graphical solutions of extraction problems have also been presented (*2, 4, 5, 7*). These solutions, however, have not been worked out primarily for the extraction of solids with liquids and are not readily adaptable to these problems. Therefore, a completely graphical solution applicable to nearly all types of extraction of solids with liquids has been developed, and found to be rapid and convenient. In addition, it solves some types of problems not discussed heretofore and permits us to visualize readily the effect of changing the terminal conditions of a given system.

It will be assumed throughout this discussion that the method of extraction employed involves a thorough mixing of the solvent with the finely divided solids to give a complete solution of all of the extractant present. An equilibrium condition results in which the resulting menstruum is of uniform concentration, both that free to be removed from the sludge and that entrained by the sludge and carried by it to the next tank or operation.

Heretofore, it has been customary to assume further that the amount of menstruum entrained by the solids is constant. In many cases considerable error may be introduced by neglecting to take into consideration the variation in entrainment that may occur. This variation is particularly noticeable when the viscosity and density of the menstruum increases appreciably as the concentration of extractant present becomes larger. It is generally possible experimentally to determine the entrainment per unit of solids treated as a function of the concentration of extractant in the menstruum by mixing together various mixtures and noting the results. Each of the graphical methods here presented starts with a graph of this function. Thus, these methods are more generally applicable than those presented heretofore. Obviously if the entrainment is constant, the graph becomes a straight line which simplifies the balance of the construction somewhat but does not affect its accuracy.

Three of the commonest types of extraction of solids with liquids will be discussed:

Multiple extraction, or the treatment of one lot of solids repeatedly with fresh menstruum.

Continuous countercurrent extraction, or the moving of the sludge countercurrent to the menstruum through a tank or series of tanks.

Batch countercurrent extraction, or the treatment of each lot of solids with successively weaker batches of menstruum—that is, in countercurrent sequence.

Irrespective of the method of extraction used, it will simplify the mathematical considerations involved if all quantities of solvent, etc., are considered on the basis of one unit solids treated. The nomenclature used in the following solutions is therefore based on one pound of insoluble solids.

Multiple Extraction

The nomenclature used is as follows:

x = composition of menstruum, pounds extractant per pound menstruum
m = menstruum adhering to the solids (i. e., the entrainment), pounds
M = menstruum removed from the tank after a given wash, pounds
E_i = extractant present in solids initially, pounds
S_i = solvent present in solids initially, pounds
x_i = composition of menstruum present in solids initially
Whence $x_i = \dfrac{E_i}{E_i + S_i}$
M_0 = menstruum used for each wash, pounds
x_0 = composition of fresh menstruum used in each wash, pounds
W = waste (i. e., residual extractant present in sludge after the final wash), pounds
Whence $W = m_f x_f$

Figure 1 represents the operations performed by the nth wash in systems of this type, and the following equations may be written:

$$\text{Menstruum balance: } M_0 + m_{n-1} = M_n + \quad (1)$$

$$\text{Extractant balance: } M_0 x_0 + m_{n-1} x_{n-1} = m_n x_n + M_n x_n \quad (2)$$

In most extraction problems of this type, E_i and S_i are known from the analysis of the untreated solids; the entrainment, m, has been determined experimentally as a $f(x)$; and M_0 and x_0 are assumed to see what W will become after a given number of washes.

This problem is solved graphically as follows: On a set of x, y coördinates, as shown in Figure 2, plot the entrainment curve $y = m = f(x)$. The values of S_i and E_i are laid off above the x axis on the line $x = 1.0$. The line $x = x_i$ is located by drawing the line $y = (E_i + S_i)x$, which intersects

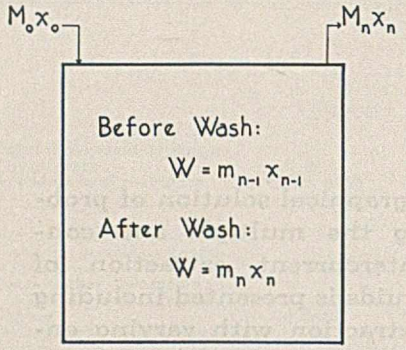

FIGURE 1. OPERATIONS PERFORMED BY THE NTH WASH IN MULTIPLE EXTRACTION

the line $y = E_i$ at $x = x_i$, by definition of x_i. The horizontal line $y = -M_0$ and the vertical line $x = x_0$ are also drawn.

Points A and B are connected as shown. Line AB crosses the x axis at $x = x_1$. This can be proved from the geometry of the figure as follows:

$$\frac{CB}{ED} = \frac{AC}{AE} \quad \text{or} \quad \frac{x_i - x_0}{x_1 - x_0} = \frac{M_0 + (E_i + S_i)}{E_i + S_i}$$

Rearranging: $M_0x_0 + x_i(E_i + S_i) = x_1(M_0 + E_i + S_i)$
From (1): $M_0x_0 + E_i = x_1(M_1 + m_1)$

which is the extractant balance similar to Equation 2 but written for the first wash.

From the intersection of the vertical line $x = x_1$ and the entrainment curve $y = m$, another triangle is constructed as shown and the value of x_2 determined. This construction is repeated for the desired number of washes. After finding the value of x_f, the intersection of the line $x = x_f$ with the entrainment curve is projected over to the line $x = 1.0$ and the line $y = m_fx$ is drawn. The value of W is read from the intersection of this line with the line $x = x_f$ as shown in Figure 2.

If the quantity of wash menstruum, M_0, varies from wash to wash, the construction can be made by using an appropriate set of lines for $y = -M_0$.

If pure solvent is used for washing, $x_0 = 0$ and the triangulation is performed on the y axis. Also, if the entrainment is constant, $y = m$ becomes a horizontal straight line and the triangulation becomes simpler again. The construction in this case is a graphical solution of the Hawley formula for multiple extraction (*1*).

General Considerations in Countercurrent Extraction

Irrespective of the details of the method of countercurrent extraction used, several mathematical considerations of the system as a whole may be written. As before, the following nomenclature is assumed on the basis of one pound of insoluble solids:

M_0 = fresh menstruum fed to the system, pounds
x_0 = composition of fresh menstruum, pounds extractant per pound menstruum
M_p = product menstruum leaving system, pounds
m_w = menstruum leaving the system adhering to the exhausted solids (i. e., the entrainment), pounds
x_p = composition of product menstruum, pounds extractant per pound menstruum
x_w = composition of menstruum leaving the system adhering to the exhausted solids, pounds extractant per pound menstruum
S_f = solvent, if any, present in untreated solids fed to system, pounds
E_f = extractant in untreated solids entering system as feed, pounds
x_f = composition of menstruum in untreated solids fed to system, pounds extractant per pound menstruum

Whence $x_f = \dfrac{E_f}{E_f + S_f}$

Referring to Figure 3, the following material balances may be written:

$$\text{Menstruum balance: } M_0 + E_f + S_f = M_p + m_w \quad (3)$$

$$\text{Extractant balance: } E_f + M_0x_0 = M_px_p + m_wx_w \quad (4)$$

In most extraction problems, E_f and S_f are known from the analysis of the untreated solids, and x_0 from the analysis of the fresh menstruum. The entrainment, m, of the sludge is known as a $f(x)$. The product m_wx_w is known from the value of E_f and the percentage of recovery desired; x_w and m_w may then be determined from the entrainment function. The three unknowns left—namely, x_p, M_0, and M_p may be calculated from Equations 3 and 4 for any assumed value of one of them. Often a definite composition of the final menstruum is desired—i. e., x_p is known; or again it may be desired to determine the results if a certain amount of fresh menstruum is used—i. e., M_0 is known; and finally it may be desired to produce a definite amount of product menstruum —i. e., m_p is known.

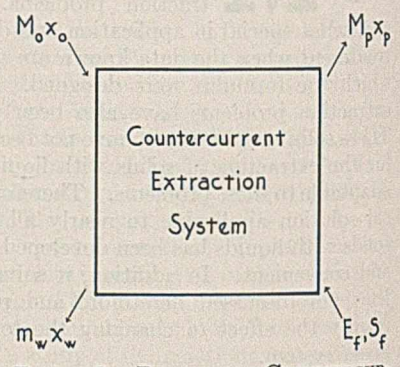

FIGURE 3. DIAGRAM OF COUNTERCURRENT EXTRACTION

Graphically these cases may be quickly solved as follows: On a set of x,y coördinates as in Figure 4, draw the curve $y = m = f(x)$ and $y = mx = x\,f(x)$. By laying off the distances S_f and E_f above the x axis on the vertical line $x = 1.0$, the line $y = (E_f + S_f)x$ is easily constructed. Draw the horizontal line $y = E_f$. The value of x_f may be read as shown, since by definition it is the value of x which makes $(E_f + S_f)x = E_f$. By definition the horizontal line $y = m_wx_w$ intersects the curve $y = mx$ at $x = x_w$. The vertical line $x = x_w$ intersects the curve $y = m$ at $y = m_w$.

Assuming the value of M_0 is known, lay it off down the line $x = 1.0$ as shown, thereby locating point A. The value of M_p may then be read directly since, from the relation of the line segments along $x = 1.0$, we may write:

$$M_0 - m_w = M_p - E_f - S_f$$

which is Equation 3 in transposed form.

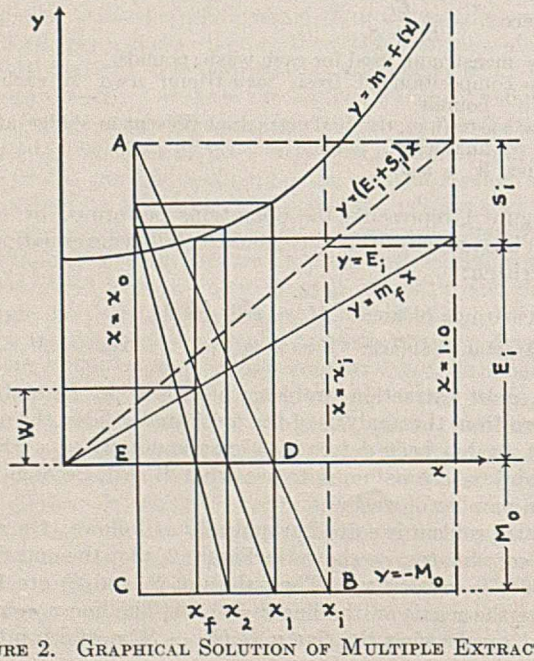

FIGURE 2. GRAPHICAL SOLUTION OF MULTIPLE EXTRACTION

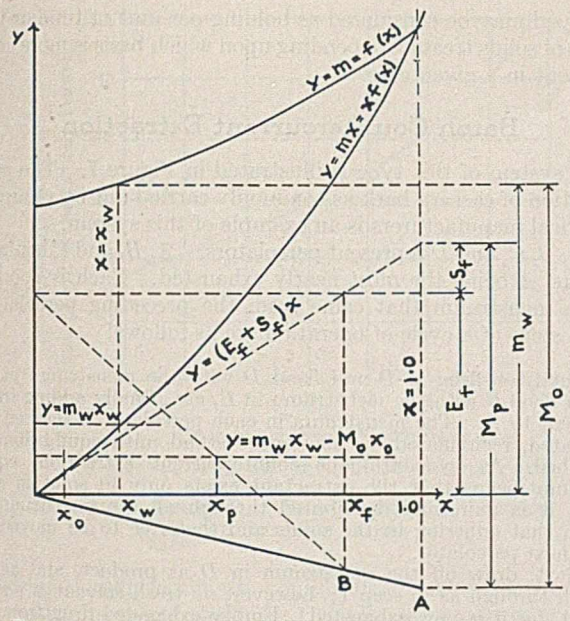

FIGURE 4. TERMINAL CONDITIONS IN COUNTERCURRENT EXTRACTIONS

Calculate the value of M_0x_0 from the known value of x_0 and the assumed value of M_0, and draw the horizontal line $y = m_wx_w - M_0x_0$.

Draw a line from A to the origin. Its slope is evidently $-(M_0 - m_w)$ and its equation is $y = -(M_0 - m_w)x$. This line will hereafter be referred to as the menstruum line. It intersects $x = x_f$ at point B where $y = -(M_0 - m_w)x_f$. Draw a line through B having a y intercept equal to E_f. From Figure 4 the slope of this line is evidently

$$-\frac{E_f + (M_0 - m_w)x_f}{x_f} = -\frac{E_f}{x_f} - (M_0 - m_w) = -(E_f + S_f) - (M_0 - m_w)$$

which from Equation 3 simplifies to $-M_p$; the equation of the line is therefore:

$$y = -M_px + E_f$$

Now, at $y = x_wm_w - M_0x_0$, this becomes

$$m_wx_w - M_0x_0 = -M_px + E_f$$

and from Equation 4,

$$M_px_p = -M_px$$
$$x = x_p$$

Thus the value of x_p may be read as shown.

From the geometry of Figure 4 it is evident that we could have started with an assumed value of M_p or x_p and solved for the other unknowns.

Since Equations 3 and 4 apply to all countercurrent extraction systems, the above construction will have a similar broad application. It will be used as the starting point in the following graphical solutions for the number of tanks required in continuous and batch countercurrent extractions.

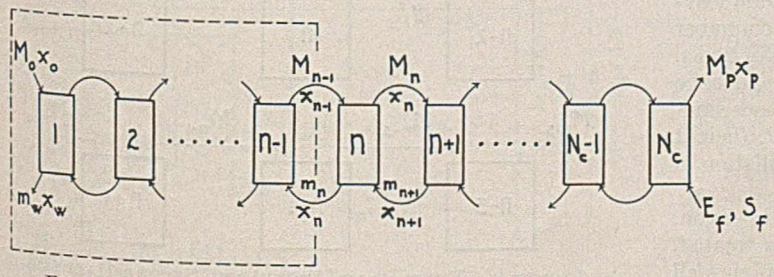

FIGURE 5. DETAILED DIAGRAM OF COUNTERCURRENT EXTRACTION

Continuous Countercurrent Extraction

Extraction systems of this type may be represented as in Figure 5. Dorr thickeners hooked up for countercurrent washing form such a system. The workings of such a system are well known. Examining the nth tank in detail, we find that sludge is entering this tank from the n + 1 tank carrying with it menstruum represented by m_{n+1}. The composition of this menstruum is represented by x_{n+1} expressed as pounds of extractant per pound of menstruum. We find also that wash menstruum is entering this tank from the n − 1 tank. The number of pounds of this menstruum is represented by M_{n-1} and its composition by x_{n-1}. These two flows of material mix and, after reaching equilibrium, the menstruum in the tank has composition x_n. The pounds of wash menstruum leaving this tank to go to the n − 1 tank are represented by M_n, and the menstruum carried into tank n − 1 with the sludge is represented by m_n.

Equations 3 and 4 apply and may be used to determine the terminal conditions graphically as described heretofore.

Referring again to Figure 5, we may write:

Menstruum balance around tanks 1 . . . . n − 1:

$$m_n + M_0 = M_{n-1} + m_w \quad (5)$$

Extractant balance: $M_{n-1}x_{n-1} = m_nx_n + M_0x_0 - m_wx_w$ (6)

Substituting the value of m_n from Equation 5:

$$M_{n-1}x_{n-1} = M_{n-1}x_n + (m_w - M_0)x_n - (m_wx_w - M_0x_0)$$

Whence: $M_{n-1}(x_n - x_{n-1}) = (M_0 - m_w)x_n + (m_wx_w - M_0x_0)$

From (6): $M_{n-1} = \dfrac{m_nx_n - (m_wx_w - M_0x_0)}{x_{n-1}}$

Substituting and rearranging:

$$\frac{x_n - x_{n-1}}{x_{n-1}} = \frac{(m_wx_w - M_0x_0) + (M_0 - m_w)x_n}{m_nx_n - (m_wx_w - M_0x_0)} \quad (7)$$

Equation 7 contains only the compositions x_n and x_{n-1} and is the basis of the construction used to determine the number of tanks required.

Figure 6 is a set of x, y coördinates on which have been drawn the curves $y = m$, $y = mx$, the vertical line $x = 1.0$, and the horizontal line $y = m_wx_w - M_0x_0$. The menstruum line is then constructed as described previously.

Starting with a given composition line, x_n, draw the horizontal line $y = m_nx_n$ having a y intercept at C. The menstruum line crosses the composition line $x = x_n$ at F. Draw the diagonal line CF, which intersects the horizontal line $y = m_wx_w - M_0x_0$ at D. Draw a vertical composition line through this point. From the similar triangles CBD and DEF we may write:

$$\frac{DE}{CB} = \frac{EF}{BD}$$

By the nature of the construction, $EF = (m_wx_w - M_0x_0) + (M_0 - m_w)x_n$ and $BD = m_nx_n - (m_wx_w - M_0x_0)$. Assuming $CB = x_{n-1}$, then $DE = x_n - x_{n-1}$, and by substituting all these values in the preceding equation we obtain Equation 7. Hence, $CB = x_{n-1}$. Therefore, to determine the number of tanks required in a given problem, this construction is repeated starting at $x = x_p$ until a value of x equal to or less than x_w is obtained. The number of such constructions will be one less than the number of tanks required for continuous countercurrent extraction.

This construction, when once mastered, does not take very long and is much shorter than a

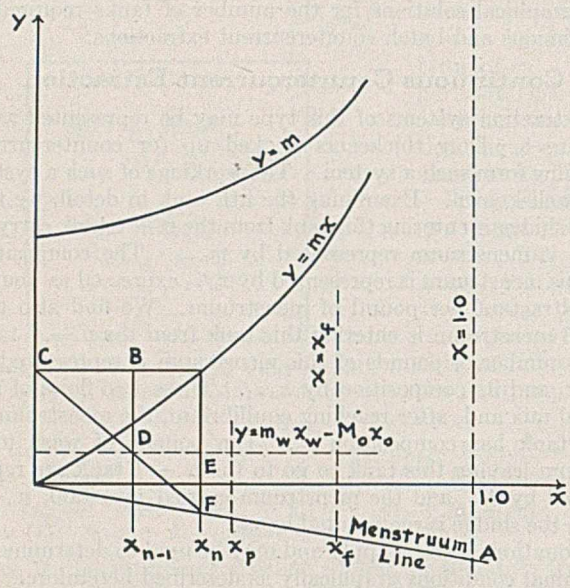

FIGURE 6. PARTIAL SOLUTION OF CONTINUOUS COUNTERCURRENT EXTRACTION

series of algebraic solutions to Equations 5 and 6. Since the entrainment is an empirical function of x, there can be no short cut to this rather tedious mathematical procedure.

In case the variation in entrainment is negligible from tank to tank, the curve $y = mx$ becomes a straight line and the triangulation just described is performed with equal ease.

In the case where the entering solids contain no solvent, the vertical line $x = x_f$ coincides with the line $x = 1.0$. In the case where the entering menstruum contains no extractant, $x_0 = 0$, and the entrainment line $y = m_w x_w - M_0 x_0$ coincides with the line $y = m_w x_w$; the triangulation is otherwise unaffected.

In some cases point A may be found to lie above the x axis ($M_0 < m_w$) but the construction is performed otherwise in identical manner and with equal facility.

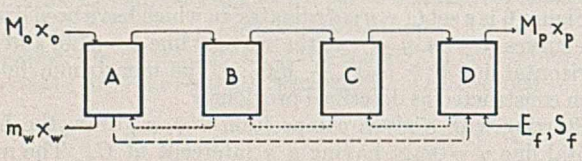

FIGURE 7. BATCH COUNTERCURRENT EXTRACTION

The use of cross-section paper greatly facilitates the construction of this type of graph since it makes the use of a T square, etc., unnecessary.

These ideas and graphical methods may be applied equally well to tubular extractors where the solid material is moved along by a screw conveyor by using the concept of the "equilibrium length." An equilibrium length is defined as a section of the extractor of length such that the wash menstruum leaving has the same concentration as the entrained menstruum leaving with the sludge. The graphical solution gives the number of equilibrium lengths required instead of the number of tanks. The actual value of the equilibrium length must, of course, be determined experimentally in any given case by methods similar to those employed to determine the H. E. T. P. (height equivalent to a theoretical plate) for fractional distillation in packed columns.

No mention of time has been made in this discussion. Since all equations were written per unit of solids treated, they could be rewritten per unit of time by multiplying all terms by the rate of feed of solids. Hence, all relation developed may be considered as holding per unit of time or per unit of solids treated, depending upon which basis is more convenient in a given case.

Batch Countercurrent Extraction

A system of this type is illustrated in Figure 7. The percolation of cascara bark as commonly carried out by pharmaceutical manufacturers is an example of this system.

A, B, C, and D represent percolators. A, B, and C contain drugs, A being the most nearly exhausted. Each is flooded with menstruum that came from the preceding percolator. The steps of a cycle of operation are as follows:

Put fresh drug in D and flood D with the menstruum in C; then flood C with the menstruum in B, etc., finally adding fresh solvent to A. The menstruum in each percolator is then either agitated, recirculated, or allowed to stand until equilibrium is reached. As in continuous countercurrent extraction, equilibrium means that the extractant exists only in solution and that it is uniformly distributed through all the menstruum—both that adhering to the solids and that free to be moved to the next percolator.

Next, draw off the menstruum in D as product, and again wash through as in step 1; however, no fresh solvent is added to A, for it is now exhausted. Empty exhausted drug from A, leaving it empty and ready to receive fresh drug for the next cycle. After all percolators have again reached equilibrium, we may consider that percolator A has now become percolator D, and percolators B, C, and D have become A, B, and C, respectively.

When this cycle has been repeated several times, the system reaches a steady state similar to that found in continuous systems; that is, the cycle consumes raw material, produces product, and returns all parts of the system to their original conditions.

Equations 3 and 4, of course, still apply. If we multiply all terms by the pounds of drugs treated per cycle, then the equations express the relationships per cycle. In the following discussion all equations will be considered as covering one cycle.

To show the relation between this system and the continuous system, let us examine the percolator containing the nth equilibrium at the start of a given cycle. There are two equilibriums in each cycle, after which each percolator may be considered to move one space to the left so that the one on the right may be moved into its place, as it now contains nth equilibrium. Hence, the percolators to the left contain the n − 2 equilibrium and the percolators to the right contain the n + 2 equilibrium. The upper part of Figure 8 shows the mechanism of the first half of the cycle. The n − 2 menstruum meets n solids which, according to the countercurrent principle, produces the n − 1 equilibrium; also the n menstruum meets the n + 2 solids, producing n + 1 equilibrium. The center percolator now contains the n − 1 equilibrium. The lower part of Figure 8 shows the mechanism of the last half of the cycle. Here the n − 1 menstruum meets n + 1

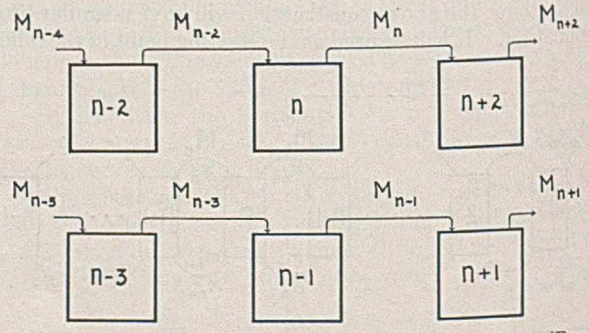

FIGURE 8. FIRST HALF (ABOVE) AND SECOND HALF (BELOW) OF BATCH COUNTERCURRENT EXTRACTION CYCLE

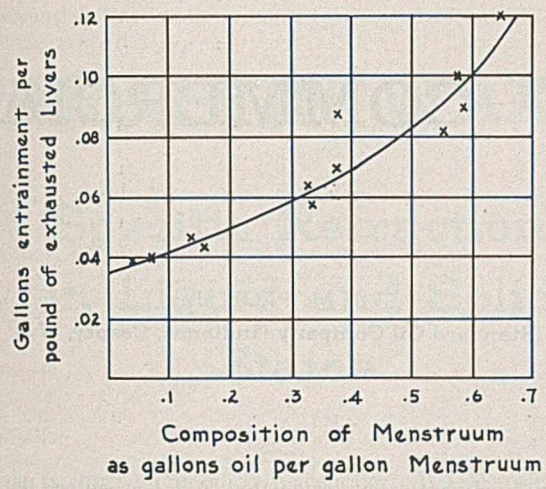

FIGURE 9. ETHER-OIL ENTRAINMENT IN GRANULATED HALIBUT LIVERS

solids and produces the nth equilibrium. Likewise, the n − 3 menstruum meets the n − 1 solids and produces n − 2 equilibrium. The center percolator now contains the n − 2 equilibrium, and, after the percolators are shifted one space to the left, we again have the conditions illustrated in the lower part of Figure 8 and are ready to proceed with another cycle.

From the discussion it is evident that the processes going on in this system are the same as those of the continuous system, except that the number of percolators required is about half (each cycle involves two equilibriums). At the end of the first half of the cycle as originally outlined, the first percolator contains the equilibrium of the first tank of the continuous system since its solids are considered exhausted and are thrown away after the menstruum is removed. Likewise, the last percolator contains the equilibrium found in the last tank of the continuous system since its menstruum is about to be withdrawn as product. If N_c represents the number of tanks required in the continuous system, the percolators above represent tanks numbered 1, 3, 5, 7 . . . . N_c, and N_c must naturally be an odd number. Let N_b represent the number of percolators required for the equivalent batch system. The exact relationship between N_c and N_b may now be written as:

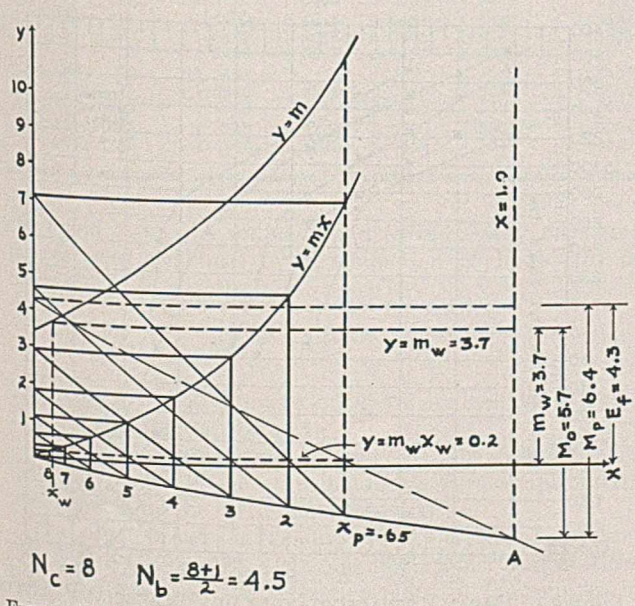

FIGURE 10. COUNTERCURRENT EXTRACTION OF HALIBUT LIVERS

$$N_b = \frac{N_c + 1}{2} \tag{8}$$

Thus, to calculate the number of percolators required in a given case of batch countercurrent extraction, calculate the number of tanks required for continuous extraction under the same conditions, add 1, and divide by 2.

Extraction of Halibut Livers

Early in 1932 the writer had occasion to make a practical application of this construction. The problem involved the batch countercurrent extraction of oil from halibut livers with ether as a solvent. The solution of this problem is presented here as an example of the complete graphical construction involved in a case where allowance must be made for the varying entrainment.

As a first step the entrainment of the ether-oil menstruum in the granulated liver mass was determined experimentally as a function of the composition of the menstruum. An agitated extractor of semi-commercial capacity was used for this purpose. Successive samples of the menstruum were withdrawn every 30 seconds to determine the time required to reach equilibrium. This period was found to be from 2 to 3 minutes of good agitation. To ensure consistent results, each mixture was agitated 10 minutes and then allowed to settle for 30 minutes before decanting the free menstruum for analysis. The entrainment found at various menstruum concentrations is plotted in Figure 9.

The menstruum figures are given on a volume instead of a weight basis. Separation of menstruums of over 70 per cent of oil by volume from the liver mass was found to be too slow for commercial practicability.

Figure 10 shows the graphical solution of the problem. The charge per extractor is taken as 100 pounds, and the data from Figure 10 are used to plot $y = m$ and $y = mx$.

Analysis of the unextracted livers showed $E_f = 0.043$ gallon oil per pound exhausted livers. A 90 per cent recovery was desired, whence $m_w x_w = 100 \times 0.05 \times 0.043 = 0.2$ gallon. It was also desired to build the concentration of the final menstruum as high as possible, and $x_p = 0.65$ was chosen as the practical limit at which separation of menstruum from livers would take place.

In solving the problem graphically, it was first noted that the vertical line $x = x_f$ coincides with $x = 1.0$ and that $x_0 = 0$ so that $y = m_w x_w - M_0 x_0$ becomes with $y = m_w x_w$, 0.2. First, the line $y = m_w = 3.7$ was constructed and then the point A located so that the values of $M_0 + M_p$ could be read directly. The ether required was found to be 5.7 gallons per charge, and the volume of final menstruum found 6.4 gallons per charge. The menstruum line was then drawn and by the triangulation previously described the number of tanks for continuous extraction was found to be 8. Whence the number of extractors to be used for the proposed batch process would be 4 or 5. Later in actual practice a series of five extractors were used to obtain better than 98 per cent recovery.

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COMMERCIAL

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The refractive indices for the D-line, and the densities, of the commercial-grade paraffin waxes were determined for the liquid and solid states. The commercial paraffins show both an ordinary and extraordinary refractive index in the solid state and therefore appear to be anisotropic, uniaxial crystalline solids. These paraffins are treated as individual hydrocarbons, using molecular weight data to fix the number of carbon atoms in each.

Specific refractions in the liquid state, calculated by the equation of Lorenz and Lorentz, are in good agreement with theoretical values derived from Eisenlohr's atomic refraction constants for carbon and hydrogen.

Refractive indices in the solid state, comparable in kind to refractive indices of isotropic substances, were calculated from the ordinary and extraordinary values by the method of Pope. Discrepancies between liquid and solid state specific refractions were then attributed to occluded air in the solidified waxes, the occluded air causing low observed values for density. True densities are calculated, and from the two values the volume per cent of occluded air is obtained.

ALTHOUGH considerable data are available on the refractive indices of the paraffin waxes in the liquid state (*1, 5, 7, 8, 19*) with corresponding densities in some cases (*1, 7, 8*), instances in which both density and index of refraction are given for the solid state appear to be lacking.

Commercial paraffin waxes are composed of several, but not many, individual hydrocarbons (*4*). Ferris, Cowles, and Henderson (*7*) give evidence in the form of molecular refraction to show that narrow fractions separated by physical means from commercial paraffin wax consist only of paraffinic and isoparaffinic hydrocarbons, with the normal type in predominance. The x-ray diffraction patterns obtained by Clark and Smith (*4*) on the same fractions confirm these conclusions and exclude the possible presence of cyclic or unsaturated hydrocarbons. Meyer and Stegeman (*12*) show that the amount of oil (usually regarded as naphthenes and aromatics) retained by wax at the final sweating temperature is scarcely detectable; this finding is confirmed by Diggs and Büchler (*5*) in their work on the determination of oil in fully refined paraffin waxes.

Description of Commercial Waxes

Samples of fully refined paraffin waxes were selected at random from commercial lots, care being taken only to space the melting points about equally apart. Table I lists the properties of these waxes. Melting points are by the A. S. T. M. method; the apparent oil content, accurate to 0.3 per cent, by the method of Diggs and Büchler (*5*); and molecular weights by the cryoscopic method, using *p*-dichlorobenzene as solvent. Although the molecular weights do not increase regularly with increase in melting point, the observed values agree closely with those calculated from Carpenter's data (*3*) on the aniline point–molecular weight relationship.

TABLE I. PROPERTIES OF WAXES

A. S. T. M. Melting Point °F.	°C.	Apparent Oil %	Obsvd. Mol. Wt.	Aniline Point °C.	Calcd. Mol. Wt.	Corresponding Hydrocarbon
121	49.4	0.5	332	116.7	330	$C_{23.55}H_{49.1}$
126	52.2	0.5	340	117.8	342	$C_{24.1}H_{50.2}$
131	55.0	0.3	355	119.0	359	$C_{25.2}H_{52.4}$
136	57.8	0.3	372	121.0	370	$C_{26.4}H_{54.8}$
141	60.6	0.3	376	122.2	375	$C_{26.7}H_{55.4}$

Determination of Refractive Index in the Solid State

The Abbé type refractometer was successfully employed with little difficulty, except on high-melting waxes. These waxes were applied to the prisms in the melted state and allowed to cool to the desired temperature with the prisms closed. Other samples of lower melting point were merely pressed into thin sheets and applied to the prisms cold. About 5 minutes were sufficient to allow for thermometric lag, both in the prisms and in the wax crystals, for readings taken at the end of 16 hours did not differ from those obtained after reheating, recooling, and allowing to stand at the same temperature for 4 or 5 minutes. The light and dark fields were not so sharply divided as is the case with wax in the molten state,

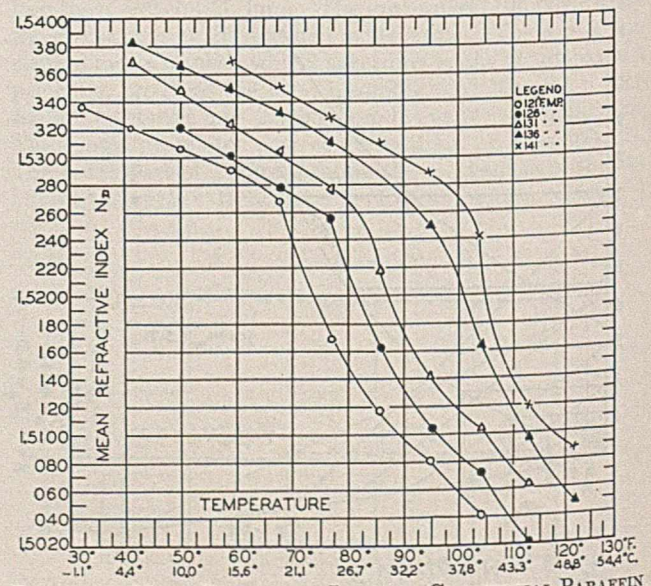

FIGURE 1. MEAN REFRACTIVE INDEX OF COMMERCIAL PARAFFIN WAXES IN THE SOLID STATE

PARAFFIN WAXES

Specific Refraction in Liquid and Solid States

yet the readings obtained were accurate to 0.0005 scale division. Probably because of crystal growth the fields became intensified on standing for 16 hours or more; that is, the light and dark fields were much lighter and much darker, respectively, than when rapid work was being done. A second line was observed—very faint, yet unmistakable—and was recognized as the extraordinary refractive index of the crystals. It therefore appears that paraffin wax is an anisotropic, uniaxial crystalline solid.

The D-line refractive indices of the solidified waxes, both ordinary (n_o) and extraordinary (n_e), are given in Table II. In order that a comparison of specific refractions in the solid state may be made with those obtained on the same waxes in the liquid state, the ordinary and extraordinary refractive indices were combined by the equation of Pope (*16*) as follows:

$$n_D = \frac{2n_o + n_e}{3} \qquad (1)$$

Values of the mean refractive index, n_D, are included in Table II and are plotted on Figure 1.

Beyond the temperature limits given, the field becomes quite hazy and indistinct, thus rendering more complete data unobtainable by the method employed.

The refractive index in the liquid state was shown by Wilson and Wilkin (*19*) to plot a straight line against temperature. Since this was true, the refractive index of the samples in question was taken at one temperature only as being sufficient for the purposes of this work. The liquid-state values, accurate to 0.0002 scale division, are given in Table V.

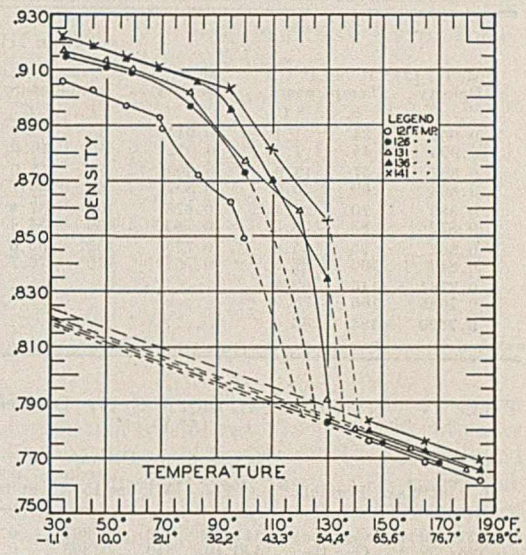

FIGURE 2. DENSITY OF COMMERCIAL PARAFFIN WAXES

Determination of Densities

Densities were determined in pycnometers at several temperatures in both the liquid and solid states. Morris and Adkins (*13*) showed that to seek an accuracy in the solid state greater than 0.001 in density is unjustified, since different samples cut from the same block of wax vary by that amount because of differences in quantity of occluded air. The average accuracy for the determinations in the liquid state is approximately 0.0002. Density data are given in Table III and presented graphically on Figure 2.

TABLE II. ORDINARY AND EXTRAORDINARY D-LINE REFRACTIVE INDICES OF SOLID COMMERCIAL PARAFFINS

Temperature		M. P., 121° F. (49.4° C.)				M. P., 126° F. (52.2° C.)				M. P., 131° F. (55.0° C.)			
° F.	° C.	n_o	n_e	$n_o - n_e$	n	n_o	n_e	$n_o - n_e$	n	n_o	n_e	$n_o - n_e$	n
32	0	1.5490	1.5030	0.0460	1.5337	....	....	....	....	....	....	....	....
41	5	1.5475	1.5015	0.0460	1.5321	....	....	....	....	1.5538	1.5033	0.0505	1.5369
50	10	1.5460	1.5000	0.0460	1.5306	1.5463	1.5038	0.0425	1.5321	1.5513	1.5020	0.0493	1.5348
59	15	1.5445	1.4985	0.0460	1.5291	1.5442	1.5020	0.0422	1.5301	1.5486	1.5000	0.0488	1.5324
68	20	1.5422	1.4960	0.0462	1.5268	1.5420	1.4995	0.0425	1.5278	1.5465	1.4985	0.0490	1.5305
77	25	1.5330	1.4848	0.0482	1.5169	1.5398	1.4972	0.0426	1.5256	1.5441	1.4950	0.0491	1.5277
86	30	1.5275	1.4802	0.0473	1.5117	1.5323	1.4840	0.0483	1.5162	1.5384	1.4888	0.0496	1.5218
95	35	1.5235	1.4770	0.0465	1.5080	1.5262	1.4790	0.0472	1.5104	1.5308	1.4810	0.0498	1.5142
104	40	1.5190	1.4740	0.0450	1.5040	1.5227	1.4760	0.0467	1.5071	1.5265	1.4780	0.0485	1.5103
113	45	....	....	....	....	1.5173	1.4715	0.0458	1.5020	1.5220	1.4743	0.0477	1.5061

		M. P., 136° F. (57.8° C.)				M. P., 141° F. (60.6° C.)			
		n_o	n_e	$n_o - n_e$	n	n_o	n_e	$n_o - n_e$	n
41	5	1.5538	1.5073	0.0465	1.5383	....	....	....	....
50	10	1.5520	1.5060	0.0460	1.5366	....	....	....	....
59	15	1.5503	1.5045	0.0458	1.5350	1.5523	1.5062	0.0461	1.5369
68	20	1.5487	1.5022	0.0465	1.5332	1.5505	1.5040	0.0465	1.5350
77	25	1.5465	1.5003	0.0462	1.5311	1.5482	1.5020	0.0462	1.5328
86	30	1.5442	....	....	....	1.5465	1.5002	0.0463	1.5310
95	35	1.5410	1.4930	0.0480	1.5250	1.5452	1.4960	0.0492	1.5288
104	40	1.5325	1.4840	0.0485	1.5163	1.5405	1.4915	0.0490	1.5241
113	45	1.5260	1.4770	0.0490	1.5096	1.5282	1.4795	0.0487	1.5119
122	50	1.5200	1.4748	0.0452	1.5049	1.5249	1.4763	0.0486	1.5087

Hypothetical Liquid State Densities at 15° C.

The density curves show an extrapolation from the liquid state values, which plot a straight line, through the temperature range in which the wax is normally solidified, and is taken as representing the density of the wax if it were liquid, or in solution in oil at those temperatures. At 15° C. (59° F.) the observed hypothetical values were found to be in good agreement with those calculated from the equation of Traube (*9*):

$$d = \frac{M}{\Sigma A_v + 25.9} \qquad (2)$$

Where d is the density at 15° C., M the molecular weight, ΣA_v the molecular volume (atomic volume of carbon = 9.9,

TABLE III. DENSITY OF COMMERCIAL PARAFFINS

M. P., 121° F. (49.4° C.)			M. P., 126° F. (52.2° C.)			M. P., 131° F. (55.0° C.)			M. P., 136° F. (57.8° C.)			M. P., 141° F. (60.6° C.)		
Density	Temperature		Density	Temperature		Density	Temperature		Density	Temperature		Density	Temperature	
	° F.	° C.		° F.	° C.		° F.	° C.		° F.	° C.		° F.	° C.
0.906	34	1.1	0.915	35	1.7	0.917	34	1.1	0.922	34	1.1	0.922	34	1.1
0.903	45	7.2	0.911	50	10.0	0.914	50	10.0	0.919	45	7.2	0.919	45	7.2
0.897	57	13.9	0.909	59	15.0	0.910	59	15.0	0.914	57	13.9	0.915	57	13.9
0.893	69	20.6	0.897	80	26.7	0.902	80	26.7	0.911	69	20.6	0.911	69	20.6
0.889	70	21.1	0.873	100	37.8	0.877	100	37.8	0.906	83	28.3	0.905	83	28.3
0.872	83	28.3	0.7830	130	54.4	0.859	120	48.9	0.896	95	35.0	0.903	95	35.0
0.862	95	35.0	0.7753	150	65.6	0.791	130	54.4	0.870	110	43.3	0.881	110	43.3
0.849	100	37.8	0.7682	170	76.7	0.7805	140	60.0	0.834	130	54.4	0.855	130	54.4
0.7761	145	62.8	....	...	....	0.7744	160	71.1	0.7795	145	62.8	0.7832	145	62.8
0.7688	165	73.9	....	...	....	0.7660	180	82.2	0.7724	165	73.9	0.7755	165	73.9
0.7620	185	85.0	....	...	....	....	...	....	0.7653	185	85.0	0.7690	185	85.0

TABLE IV. HYPOTHETICAL LIQUID STATE DENSITY OF WAXES AT 15° C.

M. P. of Wax		Formula	ΣA_v + Co − Vol.	Mol. Wt.	Extrapolated d at 15° C.	d liquid at 15° C.[a]	Calcd. $d_{15°}$
° F.	° C.						
121	49.4	$C_{23.55}H_{49.1}$	411.25	332	0.807	0.808	0.807
126	52.2	$C_{24.1}H_{50.2}$	420.10	340	0.808	0.809	0.809
131	55	$C_{25.2}H_{52.4}$	437.82	355	0.809	0.811	0.811
136	57.8	$C_{26.4}H_{54.8}$	457.14	372	0.810	0.812	0.814
141	60.6	$C_{26.7}H_{55.4}$	461.97	376	0.813	0.816	0.814

[a] By Bureau of Standards Petroleum Density Tables.

atomic volume hydrogen = 3.1), and 25.9 is a constant termed "co-volume." These hypothetical densities are given in Table IV.

Comparison of Curves for *n* and d in the Solid State

As would be expected, the curves for the mean refractive index and density in the solid state have much the same shape. Both show a certain irregularity until some temperature is reached below which the points plot a straight line against temperature.

Carpenter (*2*) whose density data for a commercial wax melting at 132.8° F. (56° C.) plot a curve similar to that for the wax given here which melts at 131° F. (55° C.) attributes the irregular portion of the curve to a transition occurring between different crystalline forms in the solid condition, and does not look upon this behavior as due to the co-existence of both molten and solid phases.

Other abnormalities at temperatures near, but below, the solidification point, were noted recently by Jackson (*11*) in connection with specific conductivity, and by Yannaquis (*20*), who finds a transition from orthorhombic to hexagonal crystals as the melting point is approached. Müller (*14*) also finds a transition from a state of lower symmetry to hexagonal symmetry near the melting point.

Specific Refraction of Commercial Paraffin Waxes

According to Lorenz and Lorentz the equation for specific refraction,

$$r_D = \left(\frac{n^2 - 1}{n^2 + 2}\right)\left(\frac{1}{d}\right) \qquad (3)$$

is independent of temperature. That the equation is likewise independent of state of aggregation is discussed in the work of Nernst (*15*). However, Hückel (*10*) points out that variations with temperature as great as 0.01 per cent may be expected. Vlugter, Waterman, and Van Westen (*18*) also find that the equation is not strictly independent of temperature when applied to petroleum lubricating oils of high cold test, and a correction of 0.0005 must be subtracted from the observed value of r_D for each 20° C. increase in temperature above 20° C. Application of this correction was found to be necessary in the present case, in comparing the specific refraction of the waxes in the molten state with the theoretical value. The theoretical value is derived from the summation of the D-line constants of Eisenlohr (*6*) for the atomic refraction of carbon (2.418) and hydrogen (1.100) by dividing the resulting molecular refraction by the molecular weight.

In Table V the specific refraction, uncorrected and corrected for temperature, is compared with the value as calculated from Eisenlohr's constants. The very good agreement between the corrected values for these mixtures of paraffins and the theoretical values for individual paraffins of a corresponding molecular weight appears not only to justify the treatment of such commercial fractions as individual hydrocarbons in the present case, but also to indicate that they possess a degree of purity perhaps not heretofore fully realized.

The specific refraction in the solid state is calculated from the refractive index derived from the ordinary and extraordinary observed values by the equation of Pope:

$$n = \sqrt[3]{n_o^2 \cdot n_e} \text{ or } n = \frac{2n_o + n_e}{3} \text{ (approx.)}$$

Refractive indices calculated in this manner are comparable to the refractive index of isotropic or liquid substances, and are therefore comparable to the specific refraction of the waxes in the liquid state.

In Table VI the specific refraction is shown to be reasonably constant in the solid state over that temperature range in which both density and refractive index are linear functions

TABLE V. SPECIFIC REFRACTION OF COMMERCIAL PARAFFINS IN THE LIQUID STATE

M. P. of Wax		n	d	Temp.	Mol. Wt.	Approx. Formula	r_D At t°	r_D At 20° C.	r_D Calcd.
° F.	° C.			t° C.					
121	49.4	1.4349	0.7780	60	332	$C_{23.55}H_{49.1}$	0.3353	0.3343	0.3341
126	52.2	1.4352	0.7788	60	340	$C_{24.1}H_{50.2}$	0.3352	0.3342	0.3338
131	55.0	1.4355	0.7800	60	355	$C_{25.2}H_{52.4}$	0.3349	0.3339	0.3340
136	57.8	1.4370	0.7815	60	372	$C_{26.4}H_{54.8}$	0.3351	0.3341	0.3337
141	60.6	1.4294	0.7690	85	376	$C_{26.7}H_{55.4}$	0.3353	0.3337	0.3337

TABLE VI. SPECIFIC REFRACTION OF COMMERCIAL PARAFFINS IN THE SOLID STATE[a]

Temperature		r_D of Wax Melting at: 121° F. (49.4° C.)	126° F. (52.2° C.)	131° F. (55.0° C.)	136° F. (57.8° C.)	141° F. (60.6° C.)
° F.	° C.					
30	−1.1	0.3434	0.3405	0.3413	0.3400	....
40	4.4	0.3429	0.3403	0.3410	0.3401	....
50	10.0	0.3430	0.3401	0.3412	0.3403	0.3415
60	15.6	0.3437	....	0.3410	0.3405	0.3414
70	21.1	....	....	0.3411	0.3405	0.3413
80	26.7	....	....	....	....	0.3414
100	37.8	....	....	....	....	0.3414

[a] Calculated from curves of n of Table II and d of the curves.

of temperature. Such is not the case, however, for the irregular portions of the density and index curves. It is assumed that the lack of agreement between the values of r_D calculated from liquid-state data (Table V) and those of Table VI is due solely to errors in density determinations in the solid state, these errors being caused by air occluded in the samples. The fact that the specific refraction of the solid waxes fails to diminish regularly with increase in molecular weight is likewise attributed to the variable quantity of occluded air affecting the densities.

Table VII. True Density of, and Volume Per Cent Air in, Solid Commercial Paraffin Waxes

M. P. of Wax ° F.	M. P. of Wax ° C.	r_D at 20° C.	Temp. ° F.	Temp. ° C.	n (Obsvd.)	d_1 (Obsvd.)	d_2 (Calcd.)	$d_2 - d_1$	Vol. % Air
121	49.4	0.3343	50	10.0	1.5306	0.900	0.925	0.025	2.7
			60	15.6	1.5289	0.897	0.922	0.025	2.8
126	52.2	0.3342	50	10.0	1.5321	0.911	0.927	0.016	1.8
			60	15.6	1.5297	0.909	0.924	0.015	1.7
131	55.0	0.3339	50	10.0	1.5348	0.912	0.932	0.020	2.2
			60	15.6	1.5323	0.909	0.928	0.019	2.1
136	57.8	0.3341	50	10.0	1.5366	0.917	0.934	0.017	1.9
			60	15.6	1.5347	0.914	0.931	0.017	1.9
141	60.6	0.3337	60	15.6	1.5366	0.914	0.935	0.011	2.3
			70	21.1	1.5344	0.911	0.932	0.011	2.3

Air in Paraffins in the Solid State

After the liquid-state values of r_D are corrected to 20° C. (Table V), it is apparent that the equation of Lorenz and Lorentz may now be employed for the purpose of calculating the true (air-free) density of the waxes at 20° C. (68° F.), using the observed refractive index at that temperature. However, since in some cases the wax is undergoing a transition at 20° C., densities are calculated at temperatures safely under the transition range. In Table VII, in addition to the true densities, the volume per cent occluded air is given, as calculated from the equation:

$$A = 1 - \frac{d_1}{d_2} \times 100 \qquad (4)$$

where d_1 represents the density of the air-containing wax and d_2 the density of the air-free wax, or true density. Equation 4 gives only occluded or mechanically enveloped air, since dissolved air would have a negligible effect upon d_1.

Carpenter (*2*) reports as high as 12 per cent air in an American refined wax of 132.8° F. (56° C.) melting point. The density of this wax in an air-free condition is given as 0.919 at 60° F. (15.6° C.). On the assumption that the entire 12 per cent air was occluded, the density before deaëration must have been 0.809 at 60° F. Since this low density is improbable and not in agreement with the values observed by the author or with the figure 0.9158 given by Seyer and Inouye (*17*) for Parawax of 129.6° F. (54.2° C.) melting point, a large portion of the air found by Carpenter must have been held in true solution or by other means having a negligible effect upon the volume occupied by a given weight of the wax. Morris and Adkins (*13*) give 0.920 as the specific gravity of an air-free paraffin of 127.2° F. (52.9° C.) melting point at 60°/60° F.; this figure is in good agreement with the density as found by Carpenter. However, in determining the density or specific gravity in the solid state, Carpenter and also Morris and Adkins use flotation methods. Such methods are amply accurate for many purposes, but a block of paraffin wax consists of many individual crystals with closed air spaces between (or evacuated pockets, if crystallization was carried out under vacuum), few of which spaces become filled with the liquid medium in which densities are being taken. Thus, although all occluded air was removed and measured, and the apparent density was increased somewhat by virtue of the surface penetration of the liquid medium, the density so determined is not the true density.

Acknowledgment

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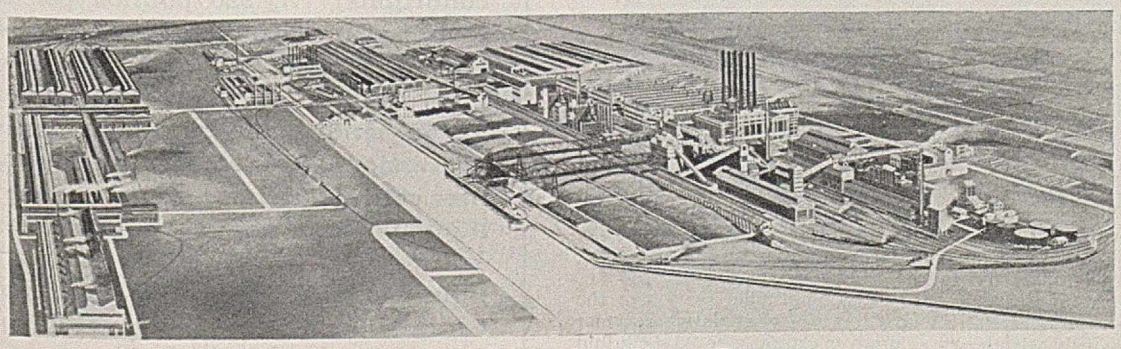

Fordson Plant of the Ford Motor Company

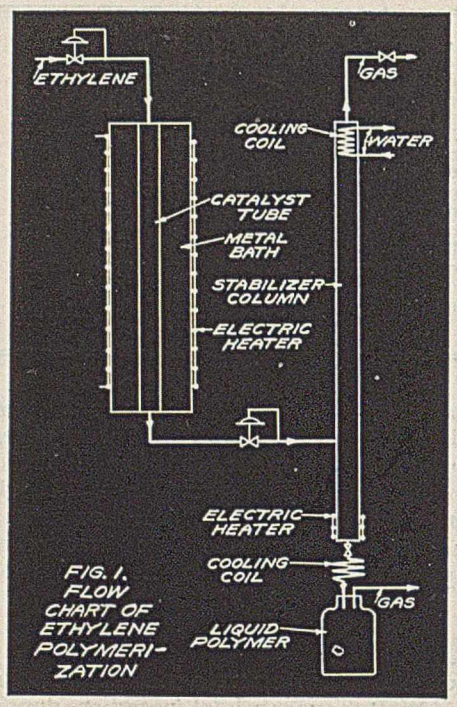

FIG. 1. FLOW CHART OF ETHYLENE POLYMERIZATION

GASOLINE FROM ETHYLENE BY CATALYTIC POLYMERIZATION

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THIS paper describes the properties of gasoline obtained by the catalytic polymerization of ethylene. Ethylene was polymerized in the presence of commercial "solid phosphoric acid" catalyst (*1*) in a small pilot plant with continuous flow.

This investigation was made under conditions approximating commercial operation for gasoline production, whereas the previous study of this reaction by Ipatieff and Pines (*3*), using liquid phosphoric acid as catalyst and long contact time, was concerned only with the chemical composition of the liquid product.

Under the conditions employed, polymerization was not the only reaction, as was evident from the nature of the product which contained not only polymeric olefins but also paraffins (aliphatic and cyclic) and aromatic hydrocarbons. Cyclization, dehydrogenation, hydrogenation, and isomerization also took place. Such polymerization the authors propose to call "conjunct polymerization" in order to differentiate from pure polymerization. It is assumed that a master reaction—in this case, polymerization—furnishes the energy necessary for other reactions.

Pilot Plant, Charging Stock, and Method of Calculation

The pilot plant (Figure 1) consisted of a vertical catalyst tower, charged with solid catalyst, followed by a stabilizer. The catalyst tube was welded inside a larger tube which was filled with a 50:50 mixture of lead and tin; this metal bath was incased in an electrical heater. Polymerization was carried out at 520 pounds per square inch gage pressure. The pressure of the incoming ethylene was controlled by an automatic valve, and the pressure on the exit gas from the polymerizer was lowered to the stabilizing pressure of 50 pounds by another automatic valve. The bottom temperature of the stabilizer was held at 150° F. (66° C.), the top at 70° F. (21° C.). The boiler section of the stabilizer was an electrically heated Jerguson gage glass. Polymer was continuously withdrawn so as to maintain a constant liquid level in the stabilizer.

The charging stock was ethylene of 98 per cent purity, the 2 per cent impurity being mainly ethane. The exit gas was mostly ethylene (about 70 per cent), together with ethane, butenes, isobutane, higher hydrocarbons, and a small amount of hydrogen (about 0.3 per cent by volume). The production of liquid polymer ranged from 0.01 to 0.03 gallon per hour per pound of catalyst, depending on the operating conditions. The theoretical yields are shown in Figure 2.

In calculating the contact times, the free space in the catalyst charge was taken as 63 per cent, the arithmetical mean of the inlet and outlet rates was used as the gas rate, and deviations from the perfect gas laws were neglected.

Catalytic polymerization of ethylene in the presence of commercial "solid phosphoric acid" catalyst yields 4.7 gallons of 82 octane number (C. F. R. motor method) gasoline per thousand cubic feet of ethylene charged (total liquid yield, 7 to 8 gallons). The operating pressure was 520 pounds per square inch gage pressure. Two temperatures were employed, 565° and 615° F. (296° and 324° C.). Weight balances were calculated for two sets of conditions: *A*, 520 pounds per square inch, 565° F. (296° C.), 1400 seconds contact time; and *B*, 520 pounds per square inch, 615° F. (324° C.), and 200 seconds. These conditions showed the following conversions: *A*, recovered ethylene 13.7 per cent, butene 0.7, isobutane 11.6, liquid polymer 73.7; *B*, recovered ethylene 18.0 per cent, butene 0.8, isobutane 6.4, liquid polymer 74.5. The liquid polymer contained paraffins, cycloparaffins, olefins, and aromatics.

Polymerization of Ethylene and Characteristics of Ethylene Polymer Gasoline

Table I presents run data obtained under three sets of operating conditions. Increasing the temperature 50° F. [from 565° to 615° F. (296° to 324° C.)] almost doubled the rate of polymer production. Polymer yields are reported on the basis of once-through operation. Recirculation would raise the liquid yield to 90 per cent and better since the only nonpolymerizable material in the exit gas was isobutane—6 to 12 per cent, depending on the operating conditions (Table IV).

TABLE I. RUN DATA ON ETHYLENE POLYMERIZATION AND PROPERTIES OF CRUDE LIQUID POLYMER

	A	B	C
Operating conditions:			
Hours on test	288	192	264
Gage pressure, lb./sq. in.	520	520	520
Temp., ° F.	565	615	615
Temp., ° C.	296	324	324
Inlet gas rate, cu. ft./hr./lb. of catalyst[a]	1.5	2.5	3.4
Contact time, sec.	790	420	320
Ethylene polymerization, conversion to liquid polymer, %	73	72	65
Gal./1000 cu. ft. of gas:			
Liquid polymer	8.0	7.9	7.1
Gasoline[b]	4.7	4.7	4.6
Properties of crude liquid polymer:			
Gr., ° A. P. I. at 60° F. (15.6° C.)	48.8	48.7	48.8
Reid vapor pressure at 100° F. (38° C.), lb.	8.8	8.3	8.1

100-Cc. A. S. T. M. Distillation

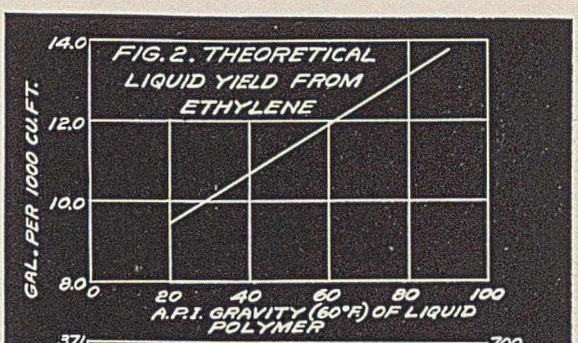
	A		B		C	
	° F.	° C.	° F.	° C.	° F.	° C.
Initial b. p.	99	37	108	42	111	44
Per cent distilled over:						
5	118	48	132	56	142	61
10	134	57	145	63	158	70
20	165	74	177	81	188	87
30	209	98	212	100	220	104
40	272	133	267	131	261	127
50	352	178	336	169	314	157
60	409	209	400	204	364	184
70	462	239	453	234	411	211
80	512	267	503	262	466	241
90	597	314	577	303	534	279
95	639	337	631	333	591	311
End point	644	340	635	335	625	329

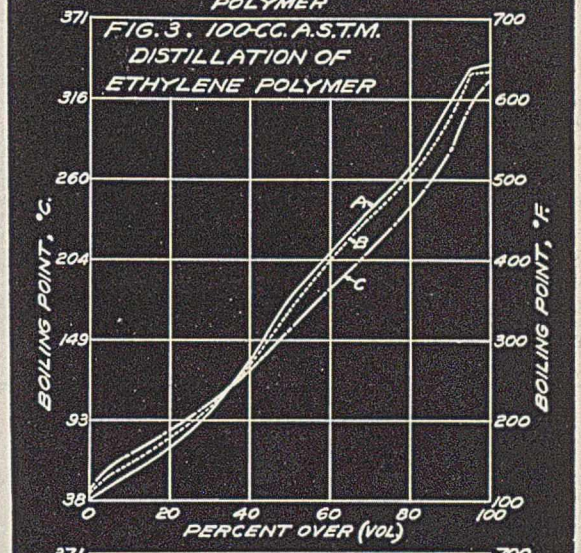
[a] Apparent density of catalyst, 0.9.
[b] Initial boiling point, ca. 106° F. (41° C.); end point 400° F. (204° C.); Reid vapor pressure at 100° F. (38° C.), ca. 6.5 pounds.

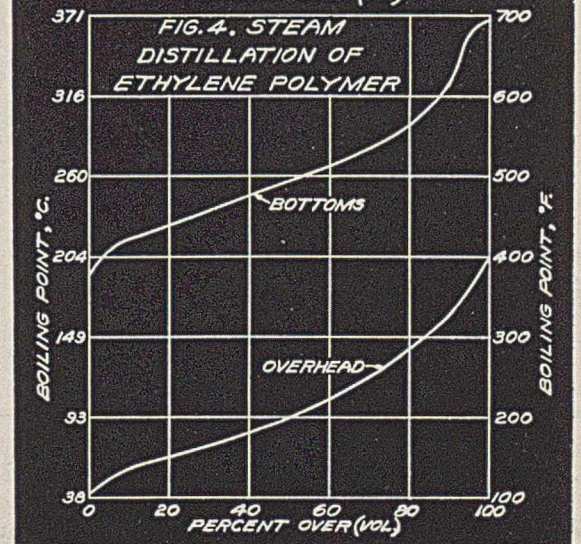
The effects of temperature and contact time are shown in Figure 3 which represents the A. S. T. M. distillation curves of crude liquid polymer obtained under different operating conditions. It is evident that increase in severity of the polymerizing conditions increased the amount of higher boiling material, and vice versa. Difference in degree of stabilization is probably responsible for the shape of the first portion of the distillation curves.

Table II presents characteristics of 400° F. (204° C.) end point, steam-distilled gasoline from a composite of the crude polymer produced under the various conditions described in this paper (Figure 4). Distillation data for the bottoms from steam distillation are included. Color and gum were satisfactory, and the octane number was 82 (same as crude polymer). The induction period of the uninhibited distillate was only 100 minutes, but 0.025 per cent of inhibitor raised it to 1600.

Distillation characteristics of the crude ethylene polymer are further illustrated by the Podbielniak distillation data (together with the operating conditions of pressure, temperature, and contact time) listed in Table III and presented graphically in Figure 5. The less severe polymerizing conditions favored the production of a simpler product as shown by the more pronounced plateaus in curve *E*. The same tendency had been previously observed in the polymerization of isobutene (*2*). The plateau at 150° F. (66° C.) corresponds







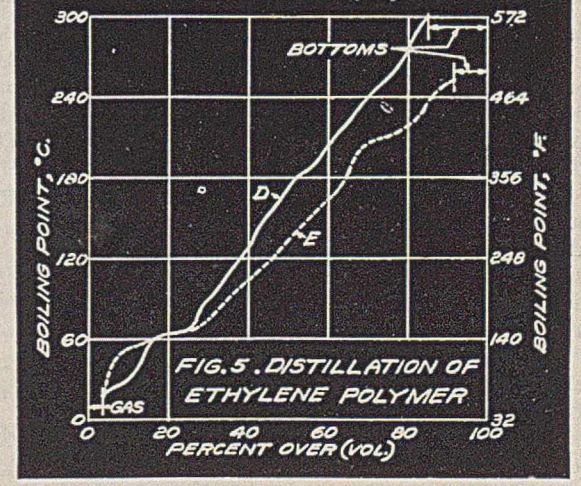


TABLE II. PROPERTIES OF STEAM-DISTILLED ETHYLENE POLYMER

	Steam-Distd. Polymer	Bottoms from Steam Distn.
Gr., ° A. P. I. at 60° F. (15.6° C.)	67.4	26.2
Sp. gr. at 60° F. (15.6° C.)	0.711	0.897
Color, ° Saybolt	30+	...
Color stability[a]	26	...
Gum (copper dish), mg./100 cc.	10	...
Gum (copper dish), mg./100 cc. + 0.025% wood dist. inhibitor	2	...
Induction period, min.	100	...
Induction period + 0.025% wood dist. inhibitor	1600	...
Octane No. (C. F. R. motor method)	82	...
Octane blending value[b] (25% in fuel A-3, C. F. R. motor method)	96	...
Reid vapor pressure at 100° F. (38° C.), lb.	6.5	...

100-Cc. A. S. T. M. Distillation

	° F.	° C.	° F.	° C.
Initial b. p.	106	41	378	192
Per cent distilled over:				
5	126	52	407	208
10	136	58	421	216
20	151	66	439	226
30	165	74	457	236
40	180	82	475	246
50	199	93	492	256
60	222	106	511	266
70	250	121	533	278
80	287	142	561	294
90	325	163	615	324
95	362	183	680	360
End point	398	203	696	369

[a] Equivalent to 2 hours of noon June sunlight.
[b] Octane number of fuel A-3, 44.

TABLE III. PODBIELNIAK DISTILLATION OF ETHYLENE POLYMER

	D	E
Polymerizing conditions:		
Gage pressure, lb./sq. in.	520	520
Temp., ° F.	565	615
Temp., ° C.	296	324
Contact time, sec.	810	170

Fraction No.	Boiling Point ° F.	Boiling Point ° C.	Per Cent Distilled Over	
1	Gas	Gas	3.8	4.0
2	64–86	18–30	6.2	0.5
3	86–108	30–42	3.1	1.5
4	108–129	42–54	1.9	5.0
5	129–151	54–66	10.0	14.0
6	151–183	66–84	3.2	7.9
7	183–194	84–90	1.8	1.8
8	194–248	90–120	8.0	11.3
9	248–270	120–132	3.2	4.0
10	270–302	132–150	3.5	5.1
11	302–356	150–180	7.7	9.1
12	356–378	180–192	5.1	2.0
13	378–410	192–210	4.1	8.1
14	410–432	210–222	3.6	7.7
15	432–464	222–240	4.8	3.7
16	464–486	240–252	4.0	6.3
17	486–518	252–270	5.1	0.0
18	518–540	270–282	1.7	0.0
19	540–572	282–300	4.2	0.0
20	Bottoms	Bottoms	15.0	8.0

o C_6, whereas that at 410° F. (210° C.) corresponds roughly o C_{12}.

Weight Balance of Ethylene Polymerization

Table IV presents weight balances for the polymerization of ethylene under two sets of operating conditions, 1400 seconds of contact time at 565° F. (296° C.) and 200 seconds at 615° F. (324° C.). The appearance of isobutane and of butene (mixture of *n*- with smaller amount of iso-) among the products confirms the work of Ipatieff and Pines (*3*). It is evident that the relative amount of isobutane production depends upon the operating conditions—11.6 per cent in *E* and 6.4 per cent in *F*.

Dissolved gas was removed from the crude liquid polymer by stabilization under a Podbielniak column, and the composition of this gas was combined with that of the exit gas proper in calculating the weight balances. Liquid polymer includes all components above isobutane. The absence of methane and hydrogen indicates that no cracking took place.

TABLE IV. WEIGHT BALANCE OF ETHYLENE POLYMERIZATION

	E	F
Polymerizing conditions:		
Gage pressure, lb./sq. in.	520	520
Temp., ° F.	565	615
Temp., ° C.	296	324
Contact time, sec.	1400	200
Liquid polymer (crude):		
Gal./1000 cu. ft. of inlet gas	7.9	7.6
Gr., ° A. P. I. at 60° F. (15.6° C.)	47.2	50.2
Conversion of ethylene into various products (% by weight):		
Ethylene (recovered)	13.7	18.0
Butenes	0.7	0.8
Isobutane	11.6	6.4
Liquid polymer	73.7	74.5

TABLE V. PROPERTIES OF ETHYLENE POLYMER

Fraction No.	Boiling Point ° F.	Boiling Point ° C.	Per Cent Distilled Over	n_D^{20}	d_4^{20}	Bromine No.
1	Below 64	Below 18	3.4	....	...	...
2	64–100	18–38	5.3	1.3605	0.640	31
3	100–160	38–71	11.0	1.3808	0.666	55
4	160–190	71–88	10.3	1.3938	0.686	78
5	190–253	88–123	11.0	1.4108	0.723	96
6	253–311	123–155	10.8	1.4295	0.761	114
7	311–390	155–199	15.4	1.4529	0.787	125
8	390–424	199–218	6.8	1.4690	0.837	113
9	424–527	218–275	19.3	1.4996	0.889	61
10	Above 527	Above 275	6.8	1.5506	0.962	...

TABLE VI. SOLUBILITY OF ETHYLENE POLYMER IN SULFURIC ACID AND PROPERTIES OF INSOLUBLE HYDROCARBON

Fraction No.	Boiling Point ° F.	Boiling Point ° C.	Soly. of Polymer in H_2SO_4 Sol., %	Soly. of Polymer in H_2SO_4 Insol., %	Insol. Hydrocarbon Reaction with: $KMnO_4$	Insol. Hydrocarbon Reaction with: Nitrating mixture	Insol. Hydrocarbon n_D^{20}
1	86–122	30–50	21	79	0	0	1.366
2	122–158	50–70	24	76	0	0	1.376
3	158–212	70–100	62	38	0	0	1.393
4	212–302	100–150	96	4	0	0	1.404
5	302–392	150–200	52	48	0	Weak	1.432
6	392–482	200–250	50	50	0	Vigorous	1.477
7	482–572	250–300	46	64	0	Vigorous	1.502

Chemical Composition of Ethylene Polymer

Table V presents refractive indices, densities, and bromine numbers of different fractions of the polymer.

Table VI shows the solubility of ethylene polymer in sulfuric acid and characteristics of the residual hydrocarbon. The polymer was shaken with two volumes of 96 per cent sulfuric acid at 32° F. (0° C.), and, after standing 15 to 30 minutes at this temperature, the residual hydrocarbon was separated and redistilled to the original temperature range. The diminution in volume corresponded approximately to the original olefin content. The residual hydrocarbon was olefin-free as shown by the permanganate test. Aromatics first appeared in the 302–392° F. (150–200° C.) fraction and were present in larger amounts in the higher fractions.

Table VII presents analytical data for several fractions of the hydrocarbon insoluble in sulfuric acid. The lower boiling fractions (1 and 2) were paraffinic (hexane and octane, respectively). The fraction boiling at 340–349° F. (171–176° C.) contained paraffins (cyclic and aliphatic), presumably a mixture of diethylcyclohexane and decane. The

TABLE VII. PROPERTIES OF HYDROCARBON INSOLUBLE IN SULFURIC ACID

Fraction No.	Boiling Point ° F.	Boiling Point ° C.	n_D^{20}	d_4^{20}	Analyses Found Mol. wt.[a]	Found % C	Found % H	Calcd. Formula	Calcd. Mol. wt.	Calcd. % C	Calcd. % H
1	135–149	57–65	1.3749	0.658	...	83.5	16.4	C_6H_{14}	86	83.6	16.4
2	194–198	90–92	1.3925	0.697	108	84.0	15.9	C_8H_{18}	114	84.1	15.9
3	340–349	171–176	1.4308	0.776	141	84.8	14.8	$C_{10}H_{20}$	140	85.6	14.4
								$C_{10}H_{22}$	142	84.4	15.6
4	480–487	249–253	1.4925	0.897	188	87.4	12.5	$C_{14}H_{22}$	190	88.3	11.7
								$C_{14}H_{28}$	196	85.6	14.4

[a] Determined by freezing point method in benzene.

TABLE VIII. PRODUCTS OF DESTRUCTIVE HYDROGENATION OF 220–280° C. FRACTION OF ETHYLENE POLYMER

Fraction No.	Boiling Point ° F.	Boiling Point ° C.	Aromatics, %[a]	n_D^{20}	Mol. Wt.	Analysis % C	Analysis % H	Products
1	338–401	170–205	50	1.4681	135	87.8	12.4	$(C_2H_5)_2C_6H_4$ (60%) + C_nH_{2n} (40%)
2	401–437	205–225	50	1.4862	149	88.2	12.0	$(C_2H_5)_3C_6H_3$ (70%) + C_nH_{2n} (30%)
3	437–464	225–240	75	1.4936	161	88.2	11.9	$(C_2H_5)_4C_6H_2$ (90%) + C_nH_{2n} (10%)

[a] Determined by solubility in fuming sulfuric acid (15% SO_3).

480–487° F. (249–253° C.) fraction was aromatic-cycloparaffinic, presumably a mixture of tetraethylbenzene and tetraethylcyclohexane.

The fraction boiling at 428–536° F. (220–280° C.) contained cyclic compounds, the evidence being that hydrogenation [nickel catalyst, 100 atmospheres initial hydrogen, 572° F. (300° C.)] converted this fraction (carbon 87.1, hydrogen 12.5) into cycloparaffins (carbon 85.9, hydrogen 14.4). The product did not react with nitrating mixture.

Information regarding the side chains in this high-boiling fraction was obtained by means of a method of destructive hydrogenation [molybdic oxide catalyst, 100 atmospheres initial hydrogen, 572–617° F. (300–325° C.)] (*4*). Under these conditions side chains are eliminated as paraffins.

Destructive hydrogenation of 24.5 grams of the 428–536° F. (220–280° C.) fraction yielded a residual gas containing 85.6 per cent of hydrogen and 14.4 per cent of ethane (6.1 grams). The liquid product was stable to the permanganate test but reacted vigorously with nitrating mixture. Table VIII presents constants and analyses (*4*) of different fractions of the liquid.

Acknowledgment

The authors express their thanks to Marvin Smith for assistance in constructing and operating the pilot plant, and to R. C. Wackher for the carbon-hydrogen analyses.

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OIL OXIDATION

The Reaction Which Is Unaffected by the Products

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The rate of oxygen absorption in a circulatory system is applied to a study of lubricating oils whose oxidation is unaffected by the nonvolatile oxidation products. All experimental results can be represented by a simple empirical rate law: The total oxygen absorbed is a linear function of the time at constant oxygen pressure and constant temperature. The rate of oxidation varies nearly linearly with the partial pressure of oxygen. The principle oxidation products are water and carbon dioxide; no peroxides are formed. Probably no chain mechanism is involved in this oxidation. The net heat of activation for oils of this type varies between 19,000 and 43,000 calories. The catalytic effect of copper, iron, tin, and lead is studied by the oxygen absorption procedure. The catalytic effect of these metals depends upon the oxygen partial pressure and the ratio of metal to oil. For copper the rate of oxidation increases rapidly with the copper-oil ratio; for the other metals this ratio has only a slight effect. The net heat of activation for the catalyzed reaction is determined for a fixed metal-oil ratio. These metals cause no significant change in the net activation heat, although the rate of oxidation is increased several fold. This is due to the rather large error inherent in the determination of the heat of activation. The method gives a sound empirical evaluation of catalytic effects on oil oxidation.

IN A GENERAL investigation of oils it is convenient to group together those oils whose oxidation reactions have the same empirical kinetics. Results of previous work[1] were reported on the autoxidation of white oils, and it was shown that oxygen absorption data could be interpreted unambiguously. The purpose of the present work is to extend this study to oils whose oxidation reaction is unaffected by the oxidation products, and to present preliminary results on catalysis of

[1] Dornte, R. W., IND. ENG. CHEM., 28, 26 (1936).

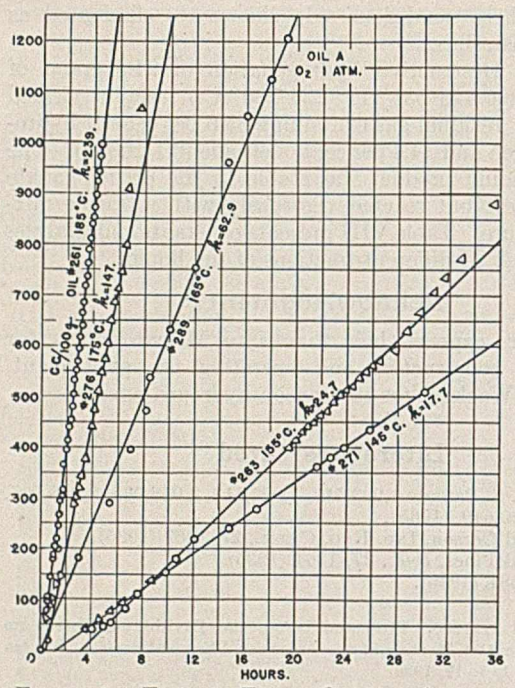

FIGURE 1. TYPICAL TOTAL OXYGEN ABSORPTION DATA

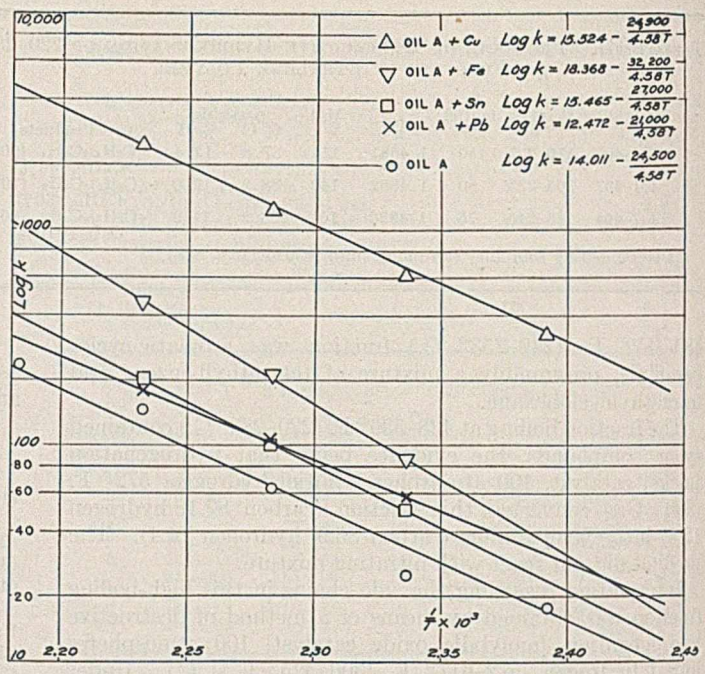

FIGURE 2. TEMPERATURE COEFFICIENTS OF REACTION RATES

this oxidation by various metals. The catalytic effect of metals on the oxidation of these oils is of considerable importance since most of the oils studied are used as lubricants. The authors also hope to aid in developing sound methods of evaluating the oxidation characteristics of oils.

The apparatus and experimental procedures described previously[1] were used in the present work. The problem was approached by a detailed study of a typical oil whose rate of oxidation is independent of the nonvolatile oxidation products. In this way some of the numerous factors which influence the kinetics of the oxidation of these oils have been evaluated. The oxygen absorption data on several other oils of this group are included.

The properties of the oils investigated are as follows:

Oil designation	A	B	C	D	E	F
Sp. gr. at 15.5° C.	0.910	0.922	0.891	0.904	0.876	0.892
Flash point, ° C.	177	154	205	235	263	276
Fire point, ° C.	199	177	249	274	324	338
Saybolt Universal viscosity, sec.:						
At 100° F. (38° C.)	300	100	389	790	962	1258
At 210° F. (99° C.)	48	62[a]	56	71	81	986
Acid No.	0.1	0.01	0.03	0.03	0.02	0.03
Pour test, ° C.	0	−30	−15	−15	−27	−15
Color (N. P. A.)	6	2	3	3	3	5

[a] At 130° F.

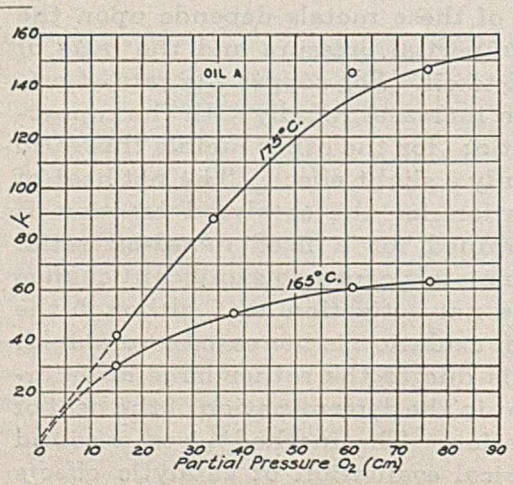

FIGURE 3. EFFECT OF OXYGEN PRESSURE IN REACTION RATES

These oils were selected to represent the probable variations in oxidation characteristics of oils whose rates of oxidation are independent of the oxidation products, other than water and carbon dioxide. Most of the oxidation data relate to oil A which is believed to be typical of this group.

Oxidation of Oil A

The outstanding characteristic of the oxidation of oil A is the constant rate of oxygen absorption which is independent of the extent of the oxidation within the absorption range 0–10 per cent by weight. Volatile oxidation products (water and carbon dioxide) which retard the reaction are continuously removed in all absorption runs. The data for run 261 at 185° C. and with a constant oxygen pressure of 76 cm. are as follows, where the total volume of oxygen absorbed is calculated to standard conditions (0° C. and 76 cm.) for 100 grams of oil:

Time Hours	O_2/100 Grams Cc.	Time Hours	O_2/100 Grams Cc.	Time Hours	O_2/100 Grams Cc.	Time Hours	O_2/100 Grams Cc.
0.50	108	2.2	441	3.6	763	5.0	1091
0.75	145	2.4	481	3.8	812	5.2	1149
1.00	187	2.6	531	4.0	851	5.4	1197
1.2	220	2.8	570	4.2	896	5.6	1247
1.4	267	3.0	619	4.4	943	5.8	1296
1.6	304	3.2	666	4.6	997	6.0	1348
1.8	341	3.4	720	4.8	1047	6.2	1404
2.0	396						

It is evident from these data that the total volume of oxygen absorbed is a linear function of the time as shown in Figure 1, which also shows results of several other runs. The data can be represented by the equation:

$$V = kt \tag{1}$$

where V = total vol. of oxygen absorbed (cc. at N. T. P. per 100 grams of oil)
t = time, hours
k = constant which characterizes the oxidation reaction

This equation satisfactorily represents all oxygen absorption data for oil A even in the presence of metals.

The experimental results of the absorption experiments with oil A are given in Table I. The Arrhenius equation

$$\log k = a - Q/4.58T \tag{2}$$

which best represents the several groups of experiments at various temperatures is also given in Table I.

TABLE I. RESULTS OF ABSORPTION EXPERIMENTS

Run No.	Temp. ° C.	k	Exptl. Conditions Cm. O_2	
271	145	17.7	76	
263	155	24.7	76	
296	155	25.0	76	
289	165	62.9	76	
276	175	147	76	
261	185	239	76	
278	175	131	76; glass beads	
		$\log k = 14.011 - \frac{24,500}{4.58T}$		
		Effect of Oxygen Pressure		
			Cm. O_2	Cm. N_2
279	175	145	60.9	15.1
277	175	87.9	34.2	41.8
275	175	41.9	15.2	60.8
285	165	61.5	61.5	14.5
282	165	50.2	38.0	38.0
280	165	30.1	15.2	60.8
		Effect of Copper		
		G. Cu/100 g. oil	Cm. O_2	Cm. N_2
297	175	1218	4.08	76 ..
308	175	2243	15.1	76 ..
306	175	2454	17.9	76 ..
309	175	2440	30.9	76 ..
298	175	2450	36.8	76 ..
310	175	2215	50.5	76 ..
305	175	2143	84.6	76 ..
301	145	329	31.2	76 ..
302	155	614	25.5	76 ..
300	165	1219	35.4	76 ..
298	175	2450	36.8	76 ..
		$\log k = 15.524 - \frac{24,900}{4.58T}$		
304	165	156	31.9	15.2 60.8
303	175	337	34.2	15.2 60.8
		Effect of Iron		
		G. Fe/100 g. oil	Cm. O_2	Cm. N_2
311	175	467	6.1	76 ..
316	175	467	11.4	76 ..
312	175	493	38.9	76 ..
313	175	658	52.5	76 ..
315	155	86.7	11.5	76 ..
314	165	214	12.6	76 ..
		$\log k = 18.368 - \frac{32,200}{4.58T}$		
319	165	156	16.6	15.2 60.8
318	175	220	11.5	15.2 60.8
		Effect of Tin		
		G. Sn/100 g. oil	Cm. O_2	Cm. N_2
320	175	202	10.9	76 ..
322	175	358	78.5	76 ..
323	155	50	11.1	76 ..
321	165	100	13.4	76 ..
		$\log k = 15.465 - \frac{27,000}{4.58T}$		
325	165	33.1	17.2	15.2 60.8
324	175	121	17.2	15.2 60.8
		Effect of Lead		
		G. Pb/100 g. oil	Cm. O_2	Cm. N_2
329	175	143	3.3	76 ..
330	175	166	56.2	76 ..
331	175	531	85.0	76 ..
328	155	57	13.5	76 ..
327	165	105	14.2	76 ..
326	175	172	14.0	76 ..
		$\log k = 12.472 - \frac{21,000}{4.58T}$		

TABLE II. PRODUCTS OF OXIDATION OF OIL A

Time Hours	Cc. O_2/100 Grams Oil H_2O	CO_2	Time Hours	Cc. O_2/100 Grams Oil Peroxide	Acid
0.75	19	..	1	0	16
1.75	42	..	2	0	25
2.50	77	..	3	0	27
3.75	83	44	4	0	43
4.75	154	48	5	0	73
5.75	254	57	6	0	159
6.50	283	63	7	0	166

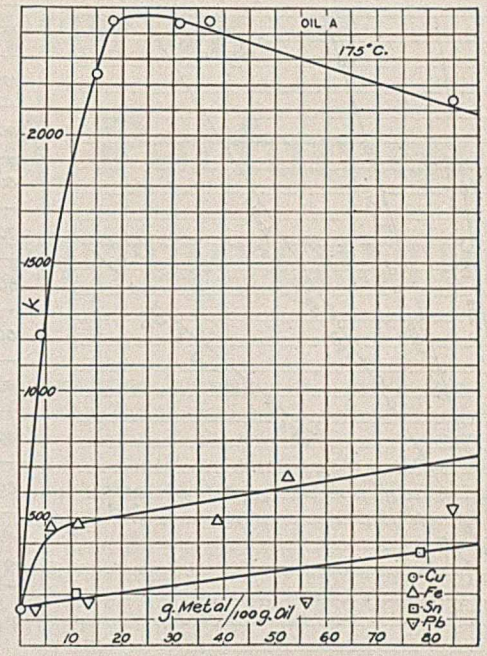

FIGURE 4. EFFECT OF CATALYST-OIL RATIO ON RATE OF OXIDATION

Determinations of the products of the oxidation of oil A at 175° C. and 1 atmosphere of oxygen are summarized in Table II, where the results are recorded in equivalent cubic centimeters of oxygen at N. T. P. per 100 grams of oil. The determinations of unsaturation and carbonyl groups showed no significant change during the oxidation.

The rates of oxygen absorption of five other commercial oils of various viscosities and types of refining were studied. The values for the constants of Equations 1 and 2 are as follows:

Oil	k for O_2 at 76 Cm. 135° C.	145° C.	155° C.	165° C.	175° C.	185° C.	a	Q
A	...	17.7	25.0	62.0	147	239	14.011	24,500
B	...	27.8	46.8	80.5	...	...	11.564	19,400
C	...	...	....	53.7	138	298	18.679	34,100
D	...	...	....	79.5	148	308	15.169	26,600
E	2,800	5,860	11,170	...	...	...	16.315	24,000
F	...	...	28.6	113	...	864	23.621	43,400

Discussion of Results

The oxygen absorption results at a constant oxygen pressure of 76 cm. as shown in Figure 1 reveal no significant deviations from Equation 1. In general the values of k are reproducible within ±5 per cent. It must be concluded from run 278 that there is a small surface reaction involved in the absorption experiments. This small surface effect is quite reproducible and can be neglected in the interpretation of the results without introducing any error. The values of k for an oxygen pressure of 76 cm. conform to the Arrhenius equation,

$$\log k = 14.011 - \frac{24,500}{4.58T}$$

as shown in Figure 2. The probable error in the value of the net activation heat, Q, is estimated at 2000–3000 calories for the uncatalyzed oxidation.

The effect of the oxygen partial pressure upon the rate of the reaction was studied by adding nitrogen. In Figure 3 the values of k at 165° and 175° C. are plotted against the oxygen partial pressure. The present results do not justify a detailed discussion of the effect of nitrogen on the oxidation rates of

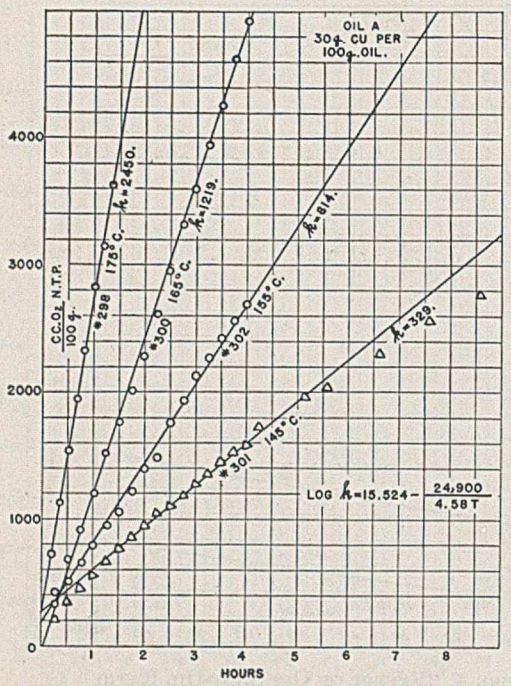

FIGURE 5. TOTAL OXYGEN ABSORPTION IN PRESENCE OF COPPER

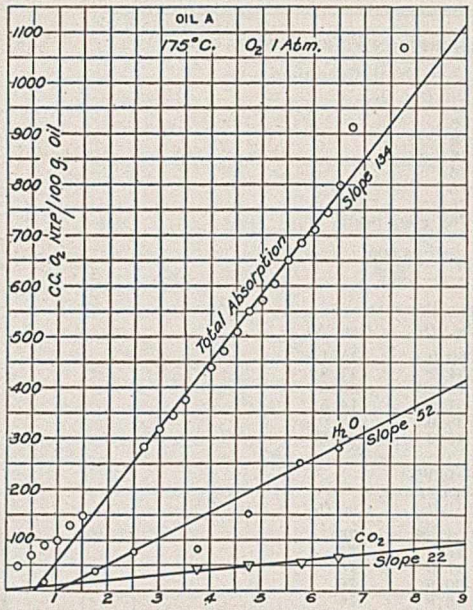

FIGURE 6. DISTRIBUTION OF OXYGEN AFTER ABSORPTION

oil A. The oxygen absorption rates decrease with decreasing oxygen partial pressure.

The addition of an inhibitor such as phenyl-α-naphthylamine at various concentrations had only a slight retarding effect on the oxidation of oil A; viz., 0.1 per cent phenyl-α-naphthylamine reduced the rate of oxygen absorption only 15 per cent at 165° C. Several other inhibitors were equally ineffective. This behavior may indicate the absence of chains in the oxidation mechanism. The addition of inhibitors to white oils,[1] on the other hand, prevented the absorption of oxygen for a definite time, depending upon the concentration of the inhibitor and the temperature.

The catalytic effect of metals on the oxidation of oil A was investigated by adding 1-inch lengths of 10-mil copper wire and 7-mil iron wire to the absorption cell. For the experiments with tin and lead the granular metal was used (1–2 mm. particles). An extremely active catalyst was not desired for these experiments, but rather the effect of the massive metals which are usually in contact with lubricating oils. For this reason the metals were cleaned with solvents and dilute acids only. Two types of experiments were used to show the catalytic effect of metals on the oxidation: The first involved a constant weight (or surface) ratio of metal to oil at various temperatures, and the second involved various metal-oil ratios at constant temperatures. The effect of the oxygen partial pressure also was investigated.

The oxidation experiments with various ratios of copper surface to oil at constant temperature and constant oxygen pressure show the pronounced catalytic effect of copper on the rates of the oxidation. Figure 4 shows the effect of the copper-oil ratio upon the values of k. The variation of k with temperature for a constant copper-oil ratio is shown in Figures 5 and 2; in Figure 2 the logarithms of k are plotted against the reciprocals of the absolute temperature. From these experiments it is evident that the catalyst increases the rate of oxidation twenty fold but does not decrease the net activation heat beyond the error involved in its determination. The rate of the oxidation is increased only eightfold by the copper when the oxygen pressure is reduced by circulating air; the net activation heat under these conditions, however, is increased about 5000 calories. It is evident that copper functions as a heterogeneous catalyst in the oxidation of this oil and is less effective at lower oxygen pressures.

The catalytic effect of copper on the oxidation of oil A could not be successfully inhibited by the addition of phenyl-α-naphthylamine or thio-β-naphthol. The latter inhibitor might be expected to inhibit the catalysis by copper by being strongly adsorbed on the copper surface. These materials at a concentration of 0.1 per cent at 175° C. reduced the values of k about 50 per cent. This effect is comparable to the effect of an inhibitor upon the uncatalyzed oxidation of oil A.

The catalytic effects of iron, tin, and lead on the oxidation of oil A are much smaller than that of copper. It is also interesting to note that the values of k do not increase much by increasing the ratio of metal surface to oil. These effects are illustrated in Figures 2 and 4. With iron there is a threefold increase in values of k although the net activation heat is increased about 7000 calories, which just exceeds the experimental errors in the net activation heats. Tin and lead each double the rate of the reaction, but with tin the net activation heat is increased 2500 calories; with lead it is decreased 3500 calories. In the cases of iron and tin the catalytic effect of the metal decreases with the partial pressure of oxygen in the gas phase. These results indicate the magnitude of the catalytic effect of metals on the oxidation of this oil.

The main products of the oxidation of oil A are water, acid, and carbon dioxide, which together represent over one-half of the total oxygen absorbed. The rates of formation of water and carbon dioxide follow the empirical rate law (Equation 1) and are shown in Figure 6. Small amounts of carbon monoxide were found in the gas from the absorption cell. The concentrations of aldehydes and ketones were too low to permit determination. The absence of peroxides is believed to be characteristic of this type of oxidation.

Acknowledgment

The authors wish to acknowledge the assistance of Earl T. Marx in the experimental work.

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Correction

The captions with the illustrations used on page 640 (June, 1936, issue) of the article by D. H. Killeffer on "Chlorinated Solvents in Dry Cleaning" were inadvertently reversed. The equipment with which an operator is shown was manufactured by the United States Hoffman Machinery Corporation. The totally enclosed unit of the Prosperity Company, Inc., is the lower picture.

CHANGE IN SPECIFIC GRAVITY OF Essential Oils and Perfumes WITH TEMPERATURE

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Determinations of the specific gravities of a large number of perfumes were made and recorded. A table shows the correction to be made per degree of temperature for each of these perfumes. The perfumes may be tested for specific gravity at the room temperature, and by applying the correction, the specific gravity at 15° C., based on water at 15° C., is obtained.

GENERALLY the specific gravities of essential oils and other liquid perfumes are obtained at 15° C. based on water at 15° C., with a plummet balance. This offers some difficulty, especially in hot summer weather when the room temperature is frequently as high as 35° C. or even higher. Obviously if we had a factor that could be applied for the variation of the specific gravity of perfumes with the temperature, we could make the tests at the temperature prevailing at the time and correct to 15° C. If the perfumes all had the same coefficient of expansion, this would be a simple matter since the same correction per 1° C. could be made in each instance. But since this is not the case, it becomes necessary to determine the coefficient of expansion of each separate perfume and apply the correction.

This work was therefore undertaken to find the proper correction for each of the more commonly used perfumes.

Literature

In 1885 Lyons (*3*) made determinations on the coefficient of expansion of various liquids, among them a few essential oils. Since these are not in very close agreement with the values found in the course of this work, they are not given here. Schimmel & Company (*4*) in 1887 made determinations on about forty essential oils at 10°, 15°, and 20° C. and gave the change per degree between 10° and 15°, 15° and 20°, and 10° and 20°. These, likewise, are not considered to be in sufficiently close agreement and are not given here. The changes per degree were for a range between 10° and 20°, which would not be very useful in any case.

Schreiner and Downer (*7*) made determinations of the change per degree on thirty-two essential oils at 15°, 20°, and 25° C., in most cases on two different samples. Their specific gravity determinations are based on water at the same temperature, and therefore the changes per degree have to be recalculated to bring them to the same basis as those here obtained. The variations per degree agree in some cases with the author's or with those obtained in 1906 by Schimmel & Company (*6*) when the latter have been calculated from the specific gravities found, but many of the results are so widely different that they are omitted here. Schreiner and Downer found a mean variation in the specific gravity of 0.00064 per degree, which they considered satisfactory to use in calculating results from 25° to 15° C. to meet the requirements of the U. S. Pharmacopeia then in force. Considering that their maximum temperature was 25°, this was no doubt satisfactory for this particular purpose since they estimated the maximum error in specific gravity would be 0.0018. Their value of 0.00064 when calculated for 15°/15° to 25°/15° C. becomes 0.00084. The average found in this work for 15°/15° to 35°/15° on the same oils is 0.00081. The agreement is only moderately close.

Schimmel & Company (*5*) state that they found differences of 0.0007 to 0.0008 per degree based on water at 15° C., but their published work points to greater differences. Later (*6*) they published specific gravity tests on about forty perfume oils at 15°/15° and 25°/25° C., and gave a table showing their results. From these results the variations per degree based on water at 15° may be calculated. This calculation has been made by the author, and the results are recorded in Table I together with the values here determined for the same oils in so far as determinations on these oils have been made. The present results are in fairly close agreement. For the sake of simplicity only the variations per degree are given in this

TABLE I. VARIATIONS IN SPECIFIC GRAVITY PER 1° C.

	Variation per 1° C. Based on Water at 15°	
	Calcd. by author from Schimmel's tests	Detd. by author
Anise oil	0.00080	0.00082
Benzaldehyde	0.00091	0.00089
Bitter almond oil	0.00090	0.00089
Cajeput oil	0.00083	.....
Caraway oil	0.00076	0.00078
Cassia oil	0.00084	0.00081
Chenopodium oil	0.00083	.....
Cinnamic aldehyde	0.00078	0.00080
Clove oil	0.00086	0.00085
Copaiba oil	0.00073	.....
Coriander oil	0.00085	.....
Cubeb oil	0.00074	.....
Erigeron oil	0.00080	.....
Eucalyptol	0.00086	.....
Eucalyptus oil	0.00082	0.00084
Eugenol	0.00088	0.00087
Fennel oil	0.00082	.....
Hedeoma oil (Am. pennyroyal)	0.00079	0.00078
Juniper-berry oil	0.00080	.....
Lavender oil	0.00085	0.00082
Lemon oil	0.00075	0.00077
Mustard oil	0.00101	.....
Nutmeg oil	0.00083	0.00082
Peppermint oil	0.00073	0.00076
Pimenta oil	0.00089	.....
Rosemary oil	0.00084	0.00081
Safrol	0.00092	0.00089
Sandalwood oil	0.00067	0.00070
Sassafras oil	0.00089	0.00087
Savin oil	0.00077	.....
Spearmint oil	0.00081	0.00079
Sweet-orange oil	0.00074	0.00078
Thyme oil	0.00079	0.00079
Turpentine oil	0.00084	.....
Turpentine oil, rectified	0.00083	.....
Wintergreen oil:		
From *Betula lenta* L.	0.00100	.....
From *Gaultheria procumbens* L.	0.00100	0.00099
Artificial	0.00103	0.00098

TABLE II. SPECIFIC GRAVITIES AND VARIATIONS IN SPECIFIC GRAVITY PER 1° C.

	Specific Gravity			Variation per 1° C.			
	15°/15° C.	25°/15° C.	35°/15° C.	15–25° C.	25–35° C.	15–35° C.	Value to use
Acetophenone	.....	1.02464	1.01604	.....	0.000865	.....	0.00087
α-Amyl cinnamic aldehyde	0.97102	.....	0.95581	.....	.....	0.0007605	0.00076
Amyl salicylate	1.05714	1.04861	1.04023	0.000853	0.000838	0.0008455	0.00085
Anisaldehyde (aubepine)	1.12751	.....	1.11049	.....	.....	0.0008510	0.00085
Benzaldehyde	1.05008	.....	1.03224	.....	.....	0.00892	0.00089
Benzyl acetate	1.06119	1.05191	1.04272	0.000928	0.000919	0.0009235	0.00092
Bornyl acetate	0.99014	.....	0.97294	.....	.....	0.000860	0.00086
Bromostyrene	1.40984	1.39837	1.38699	0.001147	0.001138	0.0011425	0.00114
Carvacrol	0.98351	0.97592	0.96837	0.000759	0.000755	0.0007565	0.00076
Cinnamic aldehyde	1.05638	.....	1.04033	.....	.....	0.0008025	0.00080
Citral	0.89355	.....	0.87764	.....	.....	0.0007955	0.00080
Citronellal	0.86788	.....	0.85154	.....	.....	0.000817	0.00082
Citronellol	0.86925	.....	0.85534	.....	.....	0.0006955	0.00070
p-Cresyl acetate:							
No. 1	1.05429	.....	1.03573	.....	.....	0.000928	.....
No. 2	1.05343	.....	1.03494	.....	.....	0.0009245	.....
Average	.....	.....	.....	.....	.....	.....	0.00093
p-Cymene	0.86715	.....	0.85127	.....	.....	0.000794	0.00079
Diethyl phthalate	1.12366	.....	1.10680	.....	.....	0.0008430	0.00084
Diphenyl oxide	.....	1.07142	1.06289	.....	0.000853	.....	0.00085
Eugenol	1.07173	.....	1.05434	.....	.....	0.0008695	0.00087
Geraniol, pure	0.87497	.....	0.86081	.....	.....	0.000708	0.00071
Geraniol, technical	0.88575	.....	0.87110	.....	.....	0.0007325	0.00073
Geranyl acetate	0.91905	0.91051	0.90210	0.000854	0.000841	0.0008475	0.00085
Hydroxycitronellal	0.92597	.....	0.91065	.....	.....	0.000766	0.00077
Ionone	0.93517	.....	0.92002	.....	.....	0.0007575	0.00076
Isoeugenol	1.09134	.....	1.07394	.....	.....	0.000870	0.00087
Limonene	0.85393	.....	0.83828	.....	.....	0.000783	0.00078
Linaloöl from bois de rose	0.87355	.....	0.85707	.....	.....	0.000824	0.00082
Linalyl acetate:							
92%, No. 1	0.93322	0.92478	0.91646	0.000844	0.000831	0.0008375	.....
92%, No. 2	0.91239	.....	0.89559	.....	.....	0.000840	.....
Extra	0.95574	.....	0.93893	.....	.....	0.0008405	.....
Average	.....	.....	.....	.....	.....	.....	0.00084
Methyl anthranilate	1.17293	1.16406	1.15534	0.000887	0.000872	0.0008795	0.00088
Methyl benzoate:							
No. 1	1.09487	.....	1.07581	.....	.....	0.000953	.....
No. 2	1.09384	.....	1.07485	.....	.....	0.0009495	.....
Average	.....	.....	.....	.....	.....	.....	0.00095
Methyl phenyl acetate:							
No. 1	1.07218	.....	1.05366	.....	.....	0.000926	.....
No. 2	1.07238	.....	1.05384	.....	.....	0.000927	.....
Average	.....	.....	.....	.....	.....	.....	0.00093
Methyl salicylate	1.18957	.....	1.16988	.....	.....	0.0009845	0.00098
Oils:							
Almond, bitter, genuine, free from prussic acid	1.05064	.....	1.03284	.....	.....	0.0008905	0.00089
Anise, star, U. S. P.	0.98925	.....	0.97276	.....	.....	0.0008245	0.00082
Bay	0.97198	.....	0.95489	.....	.....	0.0008545	0.00085
Bergamot, extra fine	0.88414	.....	0.86788	.....	.....	0.000813	0.00081
Bois de rose, Brazilian	0.89651	0.88835	0.88014	0.000816	0.000821	0.0008135	0.00081
Cade from *Juniperus oxycedrus*	0.98733	.....	0.97248	.....	.....	0.0007425	0.00074
Camphor:							
Brown	1.00146	.....	0.98592	.....	.....	0.000777	.....
Light-colored	1.01919	.....	1.00240	.....	.....	0.0008395	.....
Sp. gr. 0.95 to 0.97	0.97369	.....	0.95767	.....	.....	0.000801	.....
Average	.....	.....	.....	.....	.....	.....	0.00081
Cananga	0.94074	.....	0.92596	.....	.....	0.000739	0.00074
Caraway, U. S. P.	0.91156	.....	0.89604	.....	.....	0.000776	0.00078
Cassia:							
No. 1	1.06120	.....	1.04514	.....	.....	0.000803	.....
No. 2	1.06440	.....	1.04802	.....	.....	0.000819	.....
Average	.....	.....	.....	.....	.....	.....	0.00081
Cedarwood	0.95206	.....	0.93791	.....	.....	0.000707	0.00071

table and not the specific gravities. Schimmel & Company's work was not done for the purpose of finding the variation per degree but to show the relationship between the specific gravities at 15°/15° and 25°/25° because the then new U. S. Pharmacopeia used the temperature 25°/25°. They were not interested in the variations per degree and did not trouble to calculate them.

Gildermeister and Hoffmann (*1*), taking into account that Schimmel & Company (*5*) found a variation of 0.0007 to 0.0008 per degree based on water at 15° C., state that the mean variation for essential oils is 0.00075. This figure is probably too low since the average variation for the essential oils here tested is 0.00078, and for the essential oils, synthetics, and isolates taken together is 0.00081. Schreiner and Downer's figure of 0.00084 (recalculated), on the other hand, is too high. In any case it would be unsatisfactory to take an average figure obtained from a variety of oils and apply it to any particular oil, all the more so when there is a difference of opinion as to what that figure should be.

Irk (*2*) gives a table showing results on a number of oils tested at 15°/15° and 20°/15° C. by several observers. Results for such a narrow temperature range would be of little value except for the fact, as shown later, that the variation is the same for each degree, at least up to a temperature of 35° C. However, some of the values given agree so poorly with those recorded in this paper that they are not given here.

Experimental Procedure

An attempt was made to select the most commonly used perfumes, fully realizing that many perfumers may make considerable use of some not given here and that a few of those given may not necessarily be widely used.

Specific gravity was first determined at 15° based on water at 15° C. as unity, then at 35° likewise based on water at 15° as unity. On a number of perfumes the specific gravity was also determined at 25°/15° to discover whether there was any appreciable difference in the rate of expansion from 15° to 25° as compared with 15° to 35°. In no case was any appreciable difference noted (Table II). The variation per degree is so uniform that the same correction may be safely used even if the temperature exceeds 35°, as it may occasionally on very warm days.

In Table II the various perfumes tested are recorded together with their specific gravities and the variation in specific gravity per 1° C. The last column, taken in conjunction with Table III, gives the data for practical use. Table III gives the variation per 1° C. on some additional perfumes tested by

TABLE II. SPECIFIC GRAVITIES AND VARIATIONS IN SPECIFIC GRAVITY PER 1° C. (*Continued*)

	Specific Gravity			Variation per 1° C.			
	15°/15° C.	25°/15° C.	35°/15° C.	15–25° C.	25–35° C.	15–35° C.	Value to use
Citronella, Ceylon:							
No. 1	0.89924	.....	0.88292	.....	.....	0.000816	.....
No. 2	0.89742	.....	0.88150	.....	.....	0.000796	.....
No. 3	0.89750	.....	0.88115	.....	.....	0.0008175	.....
No. 4	0.90060	.....	0.88428	.....	.....	0.000816	.....
Average	.....	.....	.....	.....	.....	.....	0.00081
Citronella, Java:							
No. 1	0.89840	.....	0.87992	.....	.....	0.000924	.....
No. 2	0.89355	.....	0.87468	.....	.....	0.0009435	.....
No. 3	0.89664	.....	0.87815	.....	.....	0.0009245	.....
No. 4	0.89752	.....	0.87915	.....	.....	0.0009185	.....
Average	.....	.....	.....	.....	.....	.....	0.00093
Clove	1.04991	.....	1.03285	.....	.....	0.000853	0.00085
Eucalyptus globulus, 70 to 80%	0.91442	.....	0.89763	.....	.....	0.0008395	0.00084
Geranium African, extra fine	0.90082	.....	0.88561	.....	.....	0.0007605	0.00076
Geranium Bourbon	0.89182	.....	0.87654	.....	.....	0.000764	0.00076
Ho	0.88770	.....	0.87119	.....	.....	0.0008255	0.00083
Lavender:							
38/42% Barreme, No. 1	0.88906	.....	0.87259	.....	.....	0.0008235	.....
No. 2	0.90164	.....	0.88529	.....	.....	0.000818	.....
Average	.....	.....	.....	.....	.....	.....	0.00082
Lemon	0.85684	.....	0.84145	.....	.....	0.0007695	0.00077
Lemongrass	0.90822	0.90020	0.89234	0.000802	0.000785	0.00079	0.00079
Linaloe	0.88143	.....	0.86489	.....	.....	0.000827	0.00083
Mace	0.91112	.....	0.89479	.....	.....	0.0008165	0.00082
Mirbane (nitrobenzene)	1.20940	.....	1.18974	.....	.....	0.000983	0.00098
Orange, sweet	0.84993	.....	0.83438	.....	.....	0.0007775	0.00078
Origanum	0.96526	.....	0.95002	.....	.....	0.0007620	0.00076
Palmarosa	0.88751	.....	0.87282	.....	.....	0.0007345	0.00073
Patchouli	0.96749	.....	0.95288	.....	.....	0.0007305	0.00073
Pennyroyal	0.93969	.....	0.92415	.....	.....	0.000777	0.00078
Peppermint:							
No. 1	0.93020	.....	0.91499	.....	.....	0.0007605	.....
No. 2	0.91343	.....	0.89813	.....	.....	0.000765	.....
Average	.....	.....	.....	.....	.....	.....	0.00076
Petitgrain	0.89317	.....	0.87690	.....	.....	0.0008135	0.00081
Pine	0.93704	.....	0.92124	.....	.....	0.000790	0.00079
Rosemary	0.90170	.....	0.88545	.....	.....	0.008125	0.00081
Sandalwood, East Indian	0.97759	.....	0.96366	.....	.....	0.0006965	0.00070
Sassafras, artificial	1.07263	.....	1.05519	.....	.....	0.000872	0.00087
Spearmint	0.92760	.....	0.91180	.....	.....	0.000790	0.00079
Spike (oil lavender aspic)	0.90944	.....	0.89301	.....	.....	0.0008215	0.00082
Tansy	0.92375	.....	0.90770	.....	.....	0.0008025	0.00080
Thyme	0.93140	.....	0.91569	.....	.....	0.0007855	0.00079
Vetivert:							
Bourbon, No. 1	0.99156	.....	0.97722	.....	.....	0.0007165	.....
Bourbon, No. 2	1.00917	.....	0.99503	.....	.....	0.000707	.....
Average	.....	.....	.....	.....	.....	.....	0.00071
Wintergreen, southern, from *Gaultheria procumbens*	1.18813	.....	1.16837	.....	.....	0.000988	0.00099
Ylang-ylang	0.92637	.....	0.91183	.....	.....	0.000727	0.00073
Orange terpenes	0.84750	.....	0.83199	.....	.....	0.0007755	0.00078
Phenyl ethyl acetate:							
No. 1	1.03867	.....	1.02072	.....	.....	0.0008925	.....
No. 2	1.03879	.....	1.02072	.....	.....	0.0009035	.....
Average	.....	.....	.....	.....	.....	.....	0.00090
Phenyl ethyl alcohol	1.02450	.....	1.00962	.....	.....	0.000744	0.00074
Phenyl methyl carbinyl acetate (styrallyl acetate)	1.03196	.....	1.01362	.....	.....	0.000917	0.00092
Phenyl propyl alcohol	1.00590	.....	0.99132	.....	.....	0.000729	0.00073
Rhodinol	0.87836	.....	0.86417	.....	.....	0.0007095	0.00071
Safrol	1.10644	.....	1.08861	.....	.....	0.0008915	0.00089
Terpineol	0.93840	.....	0.92279	.....	.....	0.0007805	0.00078
Terpinyl acetate	0.96604	.....	0.94963	.....	.....	0.0008205	0.00082

Schimmel & Company in 1906 at 15°/15° and 25°/25° C. From these determinations the author has calculated the variation from 15°/15° to 25°/15° C. and considers the results satisfactory for use, considering that the agreement of their results with his as shown in Table I is close.

TABLE III. VARIATION PER 1° C. ON SOME PERFUMES TESTED BY SCHIMMEL & COMPANY

Perfume	Calcd. Variation per 1° C. Based on Water at 15°	Perfume	Calcd. Variation per 1° C. Based on Water at 15°
Eucalyptol	0.00086	Oil fennel	0.00082
Oil cajeput	0.00083	Oil mustard	0.00101
Oil copaiba	0.00073	Oil pimenta	0.00089
Oil coriander	0.00085	Oil savin	0.00077
Oil cubeb	0.00074	Oil sweet birch	0.00100
Oil erigeron	0.00080	Oil turpentine	0.00084

Notes

The most surprising result was in the difference between Ceylon and Java citronella oil. Four different samples of each of these oils were therefore tested.

Tests were made on three samples of linalyl acetate. There was a wide variation in the specific gravities of these samples, no doubt indicating difference in purity, but the change per 1° C. was the same in every case.

When practicable, fresh perfumes and perfumes of high purity were used.

Acetophenone could not be determined readily at 15° C. on account of its rather high solidifying point. It was therefore tested at 25°/15° and 35°/15°, and the variation calculated from these results. Diphenyl oxide was handled in the same manner.

Pycnometers of about 50 cc. capacity were used for the determinations of the specific gravities, instead of a plummet balance, for the sake of both accuracy and speed. The pycnometers filled with the perfumes were immersed in a water bath kept at the desired temperature ± 0.1° C. for at least 30 minutes.

All tests made before 1906 may be classed as unsatisfactory. Schimmel & Company's results reported in 1906 were not published for the purpose of establishing the variation per degree of temperature, but their specific gravity determinations at 15°/15° and 25°/25° C. are considered satisfactory, and the author therefore calculated the variations for the difference from 15°/15° and 25°/15° from their results and gives them as acceptable values. These variations do not differ from those found here by more than 0.00003 on the

twenty-three perfumes tested in both laboratories except in the case of sweet-orange where the difference is 0.00004 and artificial wintergreen where the difference is 0.00005.

No allowance was made for the coefficient of expansion of the glass in the pycnometers. This should make a difference of about 0.0005 in the specific gravity at the maximum temperature of 35°. In determining the specific gravity with a plummet balance at the same temperature, however, this error would be exactly compensated, assuming that the glass of the plummet and that of the pycnometer have the same coefficient of expansion.

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Compressibility of BUTANE-AIR MIXTURES below One Atmosphere

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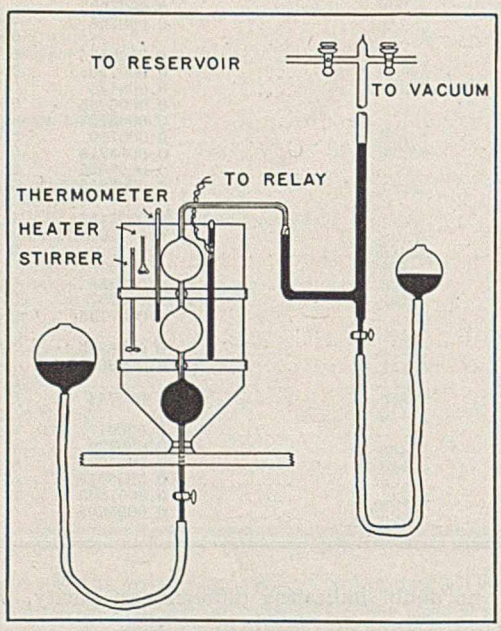


FIGURE 1. DIAGRAM OF APPARATUS

THE use of readily liquefiable gases for fuel, light, and domestic purposes has led to an ever-increasing demand for commercial butane and propane. Recently a number of municipal gas systems which use a mixture of butane and air have been installed. A knowledge of the compressibility of such a gas mixture is of importance in the design and operation of plants that use this type of fuel supply. The purpose of this investigation was to determine the pressure-volume-temperature relations of gaseous mixtures of air and butane at pressures below one atmosphere.

The literature records no compressibility measurements for butane-air mixtures. For air $(1 + \lambda) = 1.00061$ at 0° C. and one atmosphere (*6*). Lebeau (*7*) and Oudinoff (*8*) report a value of $(1 + \lambda) = 1.0437$ for *n*-butane at 0° C. and one atmosphere. Beckers (*2*) found that for *n*-butane $(pv)_{760} = 0.997013$; Felsing and Jessen (*4*) obtained a value of $(1 + \lambda) = 1.04212$ at 0° C. and one atmosphere. Batuecas (*1*) has calculated $(1 + \lambda) = 1.0419$ from the data of Seibert and Burrell (*9*).

The method employed in this investigation was essentially that of Guye and Batuecas (*5*). Since the apparatus and method have been fully described elsewhere (*5*), only a brief outline is presented here. Figure 1 illustrates the apparatus.

The gas chamber consisted of three glass bulbs of approximately 220-cc. capacity each, connected with 1-mm. capillary tubing. The volume of the gas chamber was varied by filling the lower and middle bulb, respectively, with mercury. The gas under consideration was admitted to volume I until the pressure was approximately one-third atmosphere. The mercury in the manometer was brought to the reference point and the mercury column height read. The data were completed by reading the mercury column height with the gas subsequently occupying volume II and then volume III.

The volume of the separate bulbs and "nuisance" volume (the volume of the capillary tubing and small volume to the reference point) were obtained by calibration with triple-distilled mercury. The results (in cc.) are as follows:

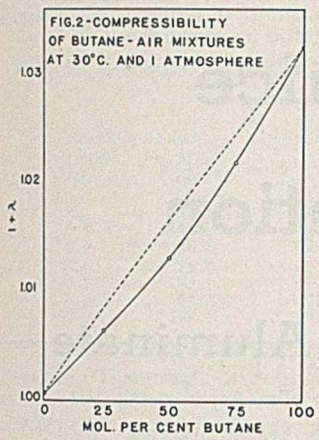
Bulb 1	220.1372	Bulbs 1, 2, and 3	655.8070
Bulbs 1 and 2	438.8484	"Nuisance" volume	1.9694

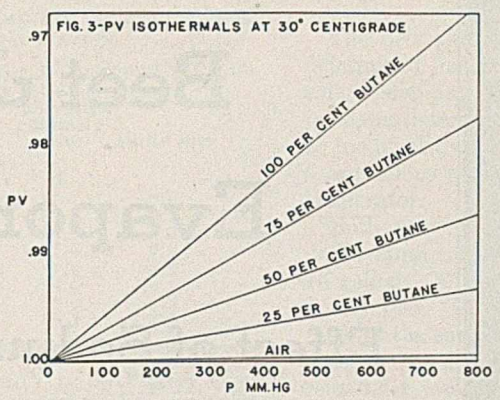
The temperature of the water bath surrounding the gas chamber was maintained at 30° C. ± 0.01° by means of supersensitive thermoregulator and relay. A temperature correction of the "nuisance" volume was made for any variation in room temperature compared to that of the bath.

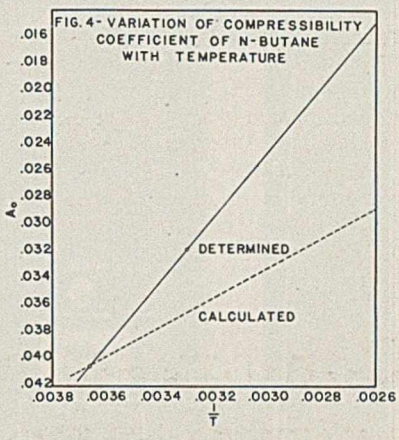
All pressure measurements were observed by means of an absolute manometer, the mercury column heights being read to 0.03 mm. with a sensitive cathetometer. Proper correction for the meniscus was made.

A 3-liter, round-bottom flask served as a mixing chamber and reservoir for the gases under consideration. The flask was first evacuated and then filled with one gaseous component until the partial pressure was that required for a definite mole per cent mixture. The other gaseous component was then allowed to fill the flask until the pressure reached atmospheric. To test the method of obtaining mixtures of definite mole percentages,

The compressibility of *n*-butane-air mixtures and of *n*-butane was determined at 30° C. It is shown that the additive rule for determining the compressibility of gas mixtures at low pressure does not hold for butane and air, the maximum deviation being 23 per cent. The variation of the compressibility coefficient of *n*-butane with temperature is presented.







equal known volumes of butane and air at atmospheric pressure were mixed and allowed to reach equilibrium. No measurable change in volume occurred. Density determinations showed that the composition of the mixture was identical with that resulting when the composition was obtained by using partial pressures. Before making any compressibility determination, the apparatus was evacuated for several hours. Gas was admitted to the system from the reservoir (3-liter flask), and the system thoroughly flushed several times. It was then filled with the gas for subsequent measurements. *n*-Butane of 99.5 per cent purity was obtained from the Ohio Chemical and Manufacturing Company. Carbon-dioxide-free and moisture-free air was used in all experiments.

Results

The results of this investigation are presented in Table I. Values for $(1 + \lambda)$ were calculated, using the expression

$$(1 + \lambda) = \frac{(pv)_0}{(pv)_{760}} \qquad (1)$$

where $(pv)_0$ = pressure × volume at 0 pressure
$(pv)_{760}$ = pressure × volume at 760-mm. mercury

The product of pressure × volume was obtained by means of the expression

$$pv = a + bp + cp^2$$

where a, b, and c are constants which were found from the experimental data. The pressure (p) and volume (v) are expressed in mm. of mercury and cc., respectively.

Table I. Values of $(1 + \lambda)$ for Butane-Air Mixtures at 30° C.

Mole % Butane	p_1	v_1	p_2	v_2	p_3	v_3	$1 + \lambda$
0	....	.....	....	.....	....	.....	1.00055[a]
25	213.34	657.8076	318.09	440.8490	629.65	222.1378	1.00597
	213.36	657.8039	318.04	440.8453	629.62	222.1341	1.00644
	213.44	657.7961	318.15	440.8361	629.84	222.1359	1.00672
	194.60	657.7764	290.10	440.8178	574.45	222.1066	1.00654
	217.09	657.7961	323.50	440.8375	640.75	222.1263	1.00683
						Average	1.00650
50	252.99	657.7965	376.64	440.8379	743.76	222.1249	1.01311
	253.04	657.7965	376.69	440.8379	743.89	222.1256	1.01338
	253.16	657.7961	376.87	440.8375	744.36	222.1263	1.01328
	230.20	657.7888	342.79	440.8302	677.02	222.1191	1.01290
	230.39	657.7888	343.04	440.8302	677.43	222.1191	1.01340
						Average	1.01321
75	236.76	657.7879	352.05	440.8293	692.68	222.1181	1.02186
	236.69	657.7897	351.98	440.8311	692.55	222.1199	1.02145
	243.13	657.7879	361.53	440.8311	711.24	222.1181	1.02144
	243.18	657.7940	361.48	440.8361	711.13	222.1249	1.02293
	260.94	657.7961	387.83	440.8435	762.74	222.1343	1.02261
						Average	1.02206
100	246.94	657.7928	366.51	440.8361	717.14	222.1249	1.03345
	241.30	657.7961	358.29	440.8375	701.19	222.1263	1.03213
	258.93	657.8039	384.22	440.8416	751.62	222.1304	1.03332
	246.86	657.7940	366.43	440.8556	716.93	222.1444	1.03281
	258.98	657.7961	384.39	440.8416	751.83	222.1263	1.03216
						Average	1.03278

[a] Calculated from Equation 3.

The separate $(1 + \lambda)$ values listed are average values of three determinations. The maximum deviation between any two isolated values is 13×10^{-4}; the largest variation from the mean is 7×10^{-4}. Any error occurring in obtaining definite compositions of the gas mixture is well within the limit of experimental error, a one per cent error in composition resulting in a difference of ±0.0005 in the compressibility value. Figure 2 shows the deviation of the compressibility from the additive rule. In Figure 3 are plotted the pv isothermals at 30° C. It has been shown (*3*, *5*) that at pressures not exceeding one atmosphere the compressibility coefficient thus obtained varies only slightly from that which results when the p^2 term is used in calculating pv and is generally within the limit of experimental error. This point is substantiated by the results of this investigation, although some curvature of the isothermals is indicated.

From theoretical considerations Cawood and Patterson (*3*) have derived the following relation between the compressibility coefficient A_0 and temperature:

$$A_0 = cT^n \qquad (2)$$

where $A_0 = \dfrac{-d(pv)}{dp}$
c, n = constants

In order to determine the compressibility of *n*-butane at 30° C. from that at 0° C., A_0 is plotted against $1/T$ as in Figure 4; the resulting value of A_0 is 0.03642. Since $(1 + \lambda)$ is related (*3*) to A_0 by the equation

$$(1 + \lambda) = \frac{1}{(1 - A_0)} \qquad (3)$$

$$(1 + \lambda) = 1.03779$$

The experimentally determined value for $(1 + \lambda) = 1.03278$.

The discrepancy between the calculated and observed value of $(1 + \lambda)$ at 30° C. is beyond the limit of experimental error and may be due to the variation of the "constants" a and b of the van der Waal equation from which the equation relating the compressibility coefficient and the temperature was deduced.

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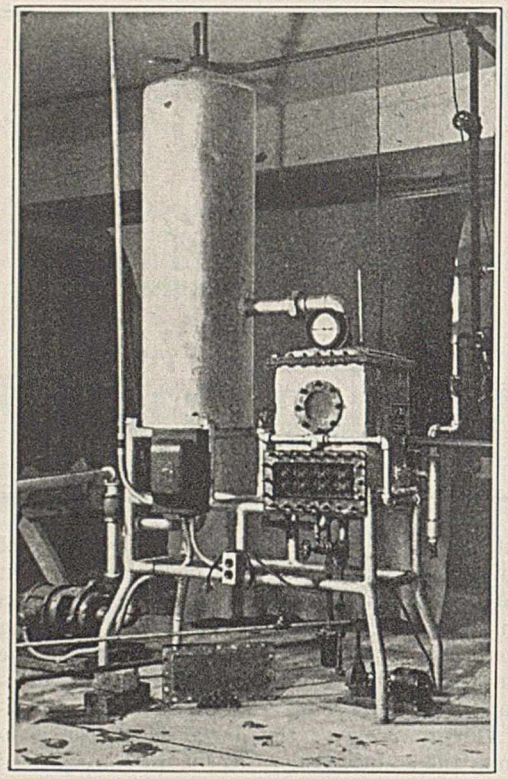

FIGURE 1. EXPERIMENTAL EVAPORATOR

Beet Juice Evaporation

Effect of Sodium Aluminate

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ONE of the most recent developments in the beet sugar industry has been the increasing use of sodium aluminate in the processing of the thin beet juice. This use has been the logical consequence of sodium aluminate utilization in the lime-soda water-softening process and in the prevention of silica scale in steam boilers. It has been reported (*3, 6, 7*) that the value of sodium aluminate in water softening is due to the formation of a flocculent precipitate with relatively high adsorptive power for both organic and inorganic colloids. The prevention of silica scale in boilers has been laid to the formation of insoluble alumino-silicates which do not adhere to the heating surfaces (*4*).

Since colloidal material and silicates are also detrimental constituents of beet juice, sodium aluminate may be expected to aid both in juice clarification and in prevention of evaporator scale. However, only two published articles have presented quantitative data pertinent to this subject; one deals with cane juice and the other with corn sirup. Wayne (*8*) reports that the addition of small amounts of dry sodium aluminate with lime in cane juice defecation increases the purity of the juice and eliminates phosphates, magnesia, and silicates without resorting to overliming. Badollet and Paine (*1*) report that sodium aluminate removes from 3 to 20 per cent more colloids from converter liquor for corn sugar manufacture than other materials tried.

The purpose of the present study was to determine the effect of the addition of small amounts of sodium aluminate to thin beet juice, particularly in regard to purity rise, colloid elimination, and scale formation in the evaporators. Obviously, determination of such effects in a commercial mill would be both slow and expensive. Therefore it was thought that a preliminary study might well be limited to a comparatively small apparatus, duplicating plant conditions as nearly as possible. To avoid further complications, a single point in the process—i. e., the evaporation of the thin juice—was chosen for this study. Although sodium aluminate is not ordinarily added just before evaporation, it is believed that results obtained by such addition would at least indicate those which might be expected if the aluminate were added at other stations.

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An experimental vacuum evaporator has been designed in which scale formation can be easily determined under conditions approaching those of commercial evaporation.

Data obtained indicate that the addition of small amounts of sodium aluminate to thin beet juice just before evaporation results in an increase in purity rise during evaporation of the juice. In the case of addition of sodium aluminate to juice from the Steffen's house run only (where hard water was used), the results indicate a decrease in scale formation and a decrease in colloid content of the juice during evaporation.

Based upon the reactions of sodium aluminate in water softeners and steam boilers, these results may be accounted for by (*a*) adsorption and neutralization of colloids by the aluminate floc and (*b*) reaction of sodium aluminate with silicates and other inorganic constituents of the juice to form a precipitate which does not adhere to the evaporator heating surfaces.

TABLE I. INFLUENCE OF SODIUM ALUMINATE ON PURITY RISE OF BEET JUICE DURING EVAPORATION

(Thin juice: specific gravity, 13.8° Brix; purity, 87.7 per cent; pH, 8.16)

$Na_2Al_2O_4$ Added		Thick Juice		
		Sp. gr.	Purity sugar in total solids	Purity Rise
Lb./1000 gal.	*Mg./liter*	*° Brix*	*%*	
0.0	0.0	58.2	87.7	0.0
0.3	35.9	60.0	87.8	0.1
0.4	47.9	60.0	88.0	0.3
0.5	59.9	62.0	87.9	0.2
0.6	71.9	60.0	87.9	0.2
0.7	83.9	62.0	88.0	0.3
0.8	95.8	60.0	88.0	0.3
0.9	107.8	63.0	88.1	0.4

TABLE II. INFLUENCE OF SODIUM ALUMINATE ON PURITY RISE AND COLLOID ELIMINATION OF BEET JUICE DURING EVAPORATION

(Thin juice: specific gravity, 12.3° Brix; purity, 87.6 per cent; pH, 8.38; dye value,[a] 645)

$Na_2Al_2O_4$ Added		Thick Juice				Decrease in Dye Value
		Sp. gr.	Purity	Dye value[a]	Purity Rise	
Lb./1000 gal.	*Mg./liter*	*° Brix*	*%*	*Grams*		
0.0	0.0	62.0	88.0	625	0.4	20
0.2	24.0	64.0	88.4	675	0.8	+30
0.4	47.9	64.0	88.6	585	1.0	68
0.6	71.9	64.0	88.6	673	1.0	+28
0.8	95.8	64.0	89.0	577	1.4	68
1.0	119.8	55.0	88.7	585	1.1	60

[a] Grams night blue dye required to neutralize colloids per 100,000 grams solids in solution.

Source of Beet Juice

The thin juice was obtained from the plant of the Garden City Company where it was taken from the Danek filters just before it reached the evaporators. The juice was run into clean 50-gallon (190-liter) drums to which 50 grams of toluene were added to prevent fermentation during shipment.

Prior to the Danek filtration, the juice from the diffusion battery was measured, heated by passing through the raw juice heaters, and pumped to the first carbonation tanks for defecation. The resulting carbonated juice was then twice filtered in hot presses and pumped into the second carbonation tanks. After this carbonation, the juice was again filtered in hot presses and sulfited at the thin juice sulfur station. After heating, a small amount of activated charcoal was added and the juice was pumped to the Danek filters.

Experimental Evaporator

The evaporator used in this work (Figure 1) was designed particularly to determine the amount of scale resulting from the evaporation of comparatively small volumes of juice under conditions approaching those used in the plant:

The evaporator body is of welded steel construction and holds twenty-four 0.75-inch (19.3-mm) horizontal brass tubes. The tubes are held in the tube sheet by rubber gaskets and conventional six-tube packing plates. Steam condensate is removed by means of a steam trap; a vent at the rear of the steam chest allows noncondensed gases to escape. Thin liquor is fed into the evaporator through a connection in the side of the body, and thick liquor is removed through an outlet in the center of the evaporator bottom. A sampling tube on the side of the body allows the operator to determine the gravity of the juice from time to time. Vacuum is maintained by a dry vacuum pump. Cooling water and condensate are removed from the jet condenser by means of a centrifugal pump. The condenser shown in Figure 1 was constructed from a discarded fire extinguisher and hence is larger than necessary.

Although multiple-effect evaporation is universal practice in sugar mills, the use of more than one effect in experimental work would add little to the value of results obtained. By using a single-effect experimental evaporator, all scale is deposited on a comparatively small surface, thus facilitating the determination of the amount of scale formed. The maintenance of steam pressure above atmospheric and a vacuum of about 26 inches (660 mm.) over the boiling juice approximates the over-all conditions attained in the multiple-effect evaporators in commercial mills.

Experimental Method

The Brix, purity, and pH of each drum of thin juice were determined just prior to evaporation. In the runs in which colloid elimination was of interest, the dye value of the thin juice was determined by the method of Badollet and Paine (*2*) as modified by Dawson, Keane, and Paine (*5*). Similar determinations were made on the thick juice removed from the evaporator.

Both the treated and untreated juice were evaporated under approximately the same conditions. Between 15 and 16 gallons (57 and 61 liters) of thin juice were evaporated in each test. The volume of thin juice remaining in the evaporator at the end of each run was about 2.5 gallons (9.5 liters). A sample of thick juice was then withdrawn for testing; the remainder was discarded. The density of this juice varied from about 55° to 64° Brix, as shown in the tables. From time to time the tubes were removed from the evaporator, dried, and weighed to determine the amount of scale formed, if any.

Results

Tables I and II show results using thin juice obtained when both the diffusion battery and Steffen's house were in operation. Table III shows results using thin juice obtained during the Steffen's house run at the end of the campaign.

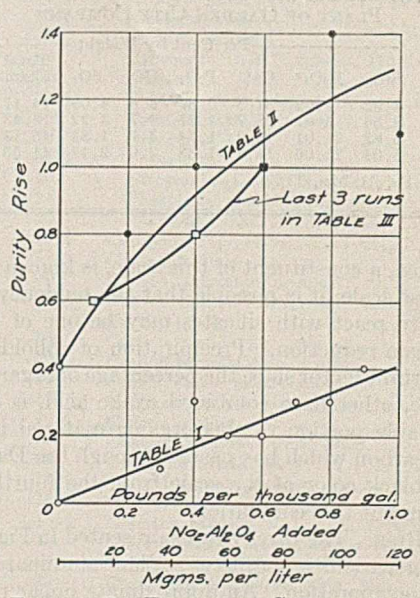

FIGURE 2. EFFECT OF SODIUM ALUMINATE ON PURITY RISE OF BEET JUICE DURING EVAPORATION

SCALE FORMATION. The tables do not show any data on scale formed by evaporation of the juice obtained during the normal operation of the mill. In fact, the evaporator tubes actually lost weight during these runs, probably because of corrosion by the ammonia liberated from the boiling juice. However, during the evaporation of 75.6 gallons (286 liters) of juice from the Steffen's house run, 2.1 grams of scale were deposited. These data correspond very well with observations made in the plant, where very little scale was noticed until the last week of the campaign when the slicers were shut down and Steffen's house juice only was run through the evaporators. During this latter period a heavy incrustation was deposited on the heating surfaces. A large percentage of this heavy scale formation during Steffen's house run was undoubtedly due to the use of hard water (hardness, 348 p. p. m. calcium carbonate) in the Steffen's house as compared to the use of treated water (hardness, 3 p. p. m. calcium carbonate) in the diffusion battery.

TABLE III. EFFECT OF SODIUM ALUMINATE ON BEET JUICE FROM STEFFEN'S HOUSE ONLY

Run No.	Thin Juice Sp. gr.	Thin Juice Purity	Thin Juice Dye value[a]	$Na_2Al_2O_4$ Added		Vol. Evapd.		Thick Juice Sp. gr.	Thick Juice Purity	Thick Juice Dye value[a]	Purity Rise	Decrease in Dye Value
	° *Brix*	%	*Grams*	*Lb./1000 gal.*	*Mg./liter*	*Gal.*	*Liters*	° *Brix*	%	*Grams*		
1–4[b]	11.5	90.7	780	0.0	0.0	75.6	286.0	56.2	91.1	705	0.4	75
5–6[c]	11.5	91.5	669	0.4	47.9	26.8	101.5	59.5	92.7	528	1.2	141
7	11.5	89.9	605	0.6	71.9	16.4	62.0	54.3	90.0	577	0.1	28
8	11.5	89.9	605	0.8	95.8	17.3	65.5	58.2	90.3	480	0.4	125
9[d]	11.5	89.9	605	1.0	119.8	15.6	59.0	56.2	90.5	480	0.6	125

[a] Grams of night blue dye required to neutralize colloids per 100,000 grams solids in solution.
[b] Average of four runs; scale formed, 2.1 grams.
[c] Average of two runs to which 0.4 lb./1000 gal. $Na_2Al_2O_4$ (47.9 mg. per liter) was added.
[d] Total evaporation in runs 5 to 9, 76.1 gal. (288 liters); scale formed, 0.2 gram.

Even so, when the Steffen's house juice was treated with an average of 0.6 pound sodium aluminate per 1000 gallons (71.9 mg. per liter) of thin juice, scale formation from the concentration of 76.1 gallons (288 liters) of thin juice was reduced 90 per cent to 0.2 gram of scale (Table III). The scale deposited in either case in the experimental evaporator was insufficient for analysis. However, an analysis was made of the scale obtained from the several bodies of the evaporator station in the mill (Table IV).

TABLE IV. INCOMPLETE ANALYSIS OF EVAPORATOR SCALE FROM PLANT OF GARDEN CITY COMPANY

Evaporator Body No.	Per Cent by Weight SiO_2	R_2O_3[a]	CaO	P_2O_5	CO_2	SO_3	Total organic	Oxalate (C_2O_4)
1	4.92	1.92	31.5	0.87	6.6	4.09	14.17	1.29
2 and 3	8.56	4.07	28.7	1.27	9.7	3.22	13.43	6.52
4	5.82	21.01	13.0	1.54	3.7	1.84	48.13	22.80
5	5.04	21.06	11.4	1.38	2.0	2.11	41.53	30.58

[a] Oxides of Fe, Al, Mn, Ti.

Since silica, a constituent of this scale, is known to produce a hard dense scale, it is possible that the tendency of sodium aluminate to react with silicates may be one of the factors favoring scale reduction. Precipitation of colloids may also be an important factor since the percentage of organic material in the scale, other than combined oxalic acid, is quite high. A considerable portion of this organic material is probably elemental carbon which has passed through the Danek filters. The deep black color of the scale from the fourth and fifth bodies bears out this contention.

PURITY RISE. The three curves presented in Figure 2 show the effect of various amounts of sodium aluminate on purity rise during evaporation. An approximate linear relationship is indicated. Variations in purity rise between different samples to which the same amount of sodium aluminate was added may be traced to variations in the juice itself. It is possible that variations in gravity, pH, and the type and quantity of colloids, lime salts, and other nonsugars present are important factors governing the increase in purity due to sodium aluminate addition. The exact relationship between these several factors offers an interesting field for further research.

COLLOID ELIMINATION. Tables II and III show data relative to the effect of sodium aluminate on colloid elimination. A definite relationship is not shown, although the data do indicate that sodium aluminate aids in precipitating some of the colloidal material present, particularly in the Steffen's house run. Here again, the type of colloids present may be an important factor. Some variation might also be accounted for by slight differences in the time of contact between the juice and sodium aluminate before evaporation, and the temperature at which the aluminate was added. Two runs are shown in Table II in which the colloidal content apparently increased during evaporation. This apparent increase could result from the precipitation of noncolloidal solids. The evaporation of the juice to a higher gravity than usual may have been the cause of such results. Lack of sufficient thin juice prevented the duplication of these particular runs. It should be mentioned, however, that in those cases where duplicate runs were made, results checked closely.

Acknowledgment

The authors are deeply indebted to the Garden City Company, Garden City, Kans., for furnishing the thin juice used in this work, and to the National Aluminate Corporation, Chicago, Ill., for supplying a generous quantity of sodium aluminate.

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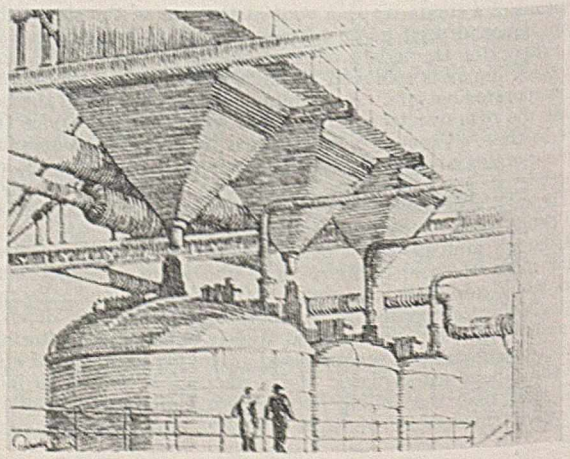
RECEIVED May 1, 1936. Presented before the Division of Sugar Chemistry at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936. Part of these data was taken from a thesis submitted by C. H. Sartorius in partial fulfillment of the requirements for the degree of master of science at Kansas State College. Contribution No. 210, Department of Chemistry.



MARKET REPORT—JUNE, 1936

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, JUNE 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Acetaldehyde, drums, lc-l., wks	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetamide, drums	lb.	.38
Acetanilide, U. S. P., powd., bbls	lb.	.26
Acetic anhydride, drums, frt. allowed	lb.	.15
Acetone, drums, wks., c/l., frt. allowed	lb.	.09
Acetphenetidin, bbls	lb.	1.30
Acid, abietic	lb.	.07
Acetic, 28%, c/l., bbls	100 lbs.	2.45
56%, c/l., bbls	100 lbs.	4.75
Glacial, c/l., drums	100 lbs.	8.43
Glacial, U. S. P., c/l., carboys	100 lbs.	11.00
Acetylsalicylic, bbls	lb.	.58
Adipic	lb.	.72
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls	lb.	.40
Boric, tech., bbls	ton	95.00
Butyric (99%), drums, wks	lb.	.22
Chloroacetic, mono-, bbls., wks	lb.	.18
Di-, cbys	lb.	1.00
Tri-, bbls	lb.	2.50
Chlorosulfonic, drums, wks	lb.	.03½
Chromic, 99%, drums	lb.	.14¾
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls	lb.	.27
Cresylic, pale, drums	gal.	.73
Formic, 90%, cbys., N. Y	lb.	.11
Furoic, tech., drums	lb.	.35
Gallic, U. S. P., bbls	lb.	.77
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.40
H, bbls., wks	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.67
Hydrobromic, 48%, cbys., wks	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks	lb.	.07
60%, bbls., wks	lb.	.15
Hydrofluosilic, 35%, bbls., wks	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls	lb.	.04
48%, light, bbls., wks	lb.	.11½
Linoleic, drums	lb.	.16
Maleic, kegs	lb.	.29
Mixed, tanks, wks	N unit	.07
	S unit	.008
Molybdic, 85%, kegs	lb.	1.25
Naphthenic, drums	lb.	.14
Naphthionic, tech., bbls	lb.	nom.
Nitric, C. P., cbys	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11⅞
Phosphoric, 50%, U. S. P	lb.	.14
Picramic, bbls	lb.	.65
Picric, bbls., c/l	lb.	.30
Pyrogallic	lb.	1.60
Salicylic, tech., bbls	lb.	.33
Sebacic, tech., drums	lb.	.58
Stearic, d. p., bbls., c/l	lb.	.09
Sulfanilic, 250-lb. bbls	lb.	.18
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks	ton	15.00
60°, tanks, wks	ton	10.50
Oleum, 20%, tanks, wks	ton	18.50
40%, tanks, wks	ton	42.00
Tannic, tech., bbls	lb.	.23
Tartaric, U. S. P., cryst., bbls	lb.	.25
Tungstic, kegs	lb.	1.35
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls	gal.	4.485
Amyl, from pentane, tanks	lb.	.143
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks., frt. allowed	lb.	.09½
Capryl, pure, for perfume	lb.	24.00
Cinnamic	lb.	3.50
Denatured, No. 5, comp. denat., c/l., drums	gal.	.40
Furfuryl, tech., 500-lb. drums	lb.	.35
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.09½
Isopropyl, ref., drums, frt. allowed	gal.	.55
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Aldol, 95%, drums, c/l	lb.	.21
Alpha-naphthol, bbls	lb.	.65
Alpha-naphthylamine, bbls	lb.	.33
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks	100 lbs.	7.00
Potash, lump, bbls., wks	100 lbs.	3.00
Soda, bbls., wks	100 lbs.	4.00
Aluminum, metal, N. Y	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l	lb.	.05
Aluminum stearate, 100-lb. bbl	lb.	.18
Aluminum sulfate, comm'l, bags, wks	100 lbs.	1.35
Iron-free, bags, wks	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks	lb.	.15½
50,000-lb. tanks, wks	lb.	.04½
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls	lb.	.15¼
Bromide, bbls	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	3.40
Linoleate, drums	lb.	.12
Nitrate, tech., cryst., bbls	lb.	.08½
Oleate, drums	lb.	.10
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls	lb.	.08½
Stearate, anhyd., drums	lb.	.21
Sulfate, bulk, wks	ton	24.00
Amylene, tanks, wks	lb.	.09
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Amyl chloride, normal, drums, wks	lb.	.56
Amyl chlorides, mixed, tanks, wks	lb.	.06
Amyl mercaptan, drums, wks	lb.	1.10
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks	lb.	.75
Anthraquinone, subl., bbls	lb.	.50
Antimony, metal	lb.	.12⅛
Antimony chloride, drums	lb.	.13
Oxide, bbls	lb.	.13½
Salt, dom., bbls	lb.	.22
Sulfide, crimson, bbls	lb.	.25
Golden, bbls	lb.	.22
Argols, red powder, bbls	lb.	.07
Arsenic, metal, kegs	lb.	.44
Red, kegs, cases	lb.	.15¾
White, c/l., kegs	lb.	.04½
Asbestine, bulk, c/l	ton	15.00
Barium carbonate, bbls., bags, wks	ton	45.00
Chloride, bbls., wks	ton	74.00
Dioxide, drs., wks	lb.	.12
Hydroxide, bbls	lb.	.05
Nitrate, casks	lb.	.08½
Barium thiocyanate, 400-lb. bbls	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzidine base, bbls	lb.	.72
Benzol, tanks, wks	gal.	.18
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.60
Alcohol, drums	lb.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls	lb.	.24
Beta-naphthylamine, bbls	lb.	.58
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, 25-lb. jars	lb.	1.10
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.30
Blanc fixe, dry, bbls	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, bags	ton	40.00
Bordeaux mixture, bbls	lb.	.10½
Bromine, bot	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.75
Butyl acetyl ricinoleate, drums	lb.	.24
Acetate, drums, c/l., frt. allowed	lb.	.09½
Aldehyde, drums	lb.	.18
Carbinol, norm., drums, wks	lb.	.60
Carbinol, sec., wks	lb.	.60
Lactate, drums	lb.	.22½
Oleate, drums	lb.	.25
Stearate, drums	lb.	.25
Butyraldehyde, drums, wks	lb.	.35½
Cadmium, metal, cases	lb.	1.05
Cadmium bromide, 50-lb. jars	lb.	1.54
Cadmium sulfide, boxes	lb.	1.00
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	2.10
Arsenate, bbls	lb.	.06½
Carbide, drums	lb.	.05½
Carbonate, U. S. P., precip., 175-lb. bbls	lb.	.06½
Chloride, bags, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Gluconate, U. S. P	lb.	.57
Tech	lb.	.28
Nitrate, bags, 15% N	ton	25.50
Phosphate, monobas., bbls	lb.	.07½
Tribas., bbls	lb.	.11
Camphor, Jap., slabs	lb.	.55
Carbazole, bbls	lb.	.80
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.04†
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls	lb.	.15
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.25
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq. c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	2.15
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls	lb.	.05
Coal tar, bbls., wks	bbl.	8.50
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.41
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	9.50
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls	lb.	.17
Cyanide, drums	lb.	.37
Oxide, red, bbls	lb.	.15
Sulfate, c/l., bbls	100 lbs.	4.00
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.16¾
Crotonaldehyde, drums, c/l	lb.	.26
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
Diaminophenol, kegs	lb.	3.80
Diamylamine, drums, wks	lb.	1.00
Diamylene, tanks, wks	lb.	.08½
Diamyl ether, drums, wks	lb.	.09
Diamyl sulfide, drums, wks	lb.	1.10
Diamyl phthalate, tanks	lb.	.18

† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

* F. O. B. destination.

Dianisidine, bbls.	lb.	2.35
Dibutoxyethyl phthalate, wks., drums	lb.	.42
Dibutyl ether, drums, wks.	lb.	.22
Dibutylphthalate, drums, wks., frt. allowed	lb.	.18
Dibutyl tartrate, drums	lb.	.35
Dichlorethyl ether, drums, c/l., wks.	lb.	.16
Dichloropentanes, tanks, wks.	lb.	.02½
Diethanolamine, drums, wks.	lb.	.31
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums, wks.	lb.	.16½
Monobutyl ether, drums, wks.	lb.	.26
Monoethyl ether, drums, wks.	lb.	.16
Diethylene oxide, drums, wks.	lb.	.20
Diethyl carbinol, drums, wks.	lb.	.60
Diethyl phthalate, drums	lb.	.18½
Diethyl sulfate, tech., drums, wks.	lb.	.20
Diglycol oleate, drums	lb.	.24
Dimethylamine, pure 25.40% sol.—100% basis, drums	lb.	.95
Dimethylaniline, drums	lb.	.29
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
Dimethylsulfate, drums	lb.	.45
Dimethyl phthalate, drums, wks., frt. allowed	lb.	.19½
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls.	lb.	.14½
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenyl	lb.	.15
Diphenylamine, bbls.	lb.	.31
Diphenylguanidine, bbls.	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.80
Ether, conc., drums	lb.	.09
Ether, nitrous, bot.	lb.	.75
Ethyl acetate, tanks, c/l. wks., frt. allowed	lb.	.06
Acetoacetate, 110-gal. drums, wks., frt. allowed	lb.	.37
Bromide, drums	lb.	.50
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorcarbonate, carboys	lb.	.30
Chloride, drums	lb.	.22
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Methyl ketone, drums	lb.	.07½
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride, drums, wks., frt. allowed	lb.	.0545
Ethylenechlorohydrin, anhyd., drums, wks	lb.	.75
Glycol, c/l., wks.	lb.	.17
Monobutyl ether, drums, wks.	lb.	.20
Monoethyl ether, drums, wks	lb.	.16
Monoethyl ether acetate, drums, wks.	lb.	.14
Monomethyl ether, drums, wks.	lb.	.19
Oxide, cylinders, wks.	lb.	.50
Feldspar, bulk	ton	10.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls.	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	6.50
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.28
Glycerine, C. P., drums	lb.	.14½
Glyceryl phthalate, drums	lb.	.30
Glycol phthalate, drums	lb.	.29
Stearate, drums	lb.	.23
G salt, bbls.	lb.	.45
Hexamethylenetetramine, tech., drums	lb.	.37
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20% paste, bbls.	lb.	.12
Iodine, resubl., jars	lb.	1.50
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03
Isobutyl carbinol (128–132° C.), tanks	lb.	.32
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.65
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.08
Oxide, litharge, bbls., 20-ton lots	lb.	.0610
Peroxide, drums	lb.	.20
Red, bbls., 20-ton lots	lb.	.0635
Sulfate, bbls.	lb.	.06
White, basic carb., bbls.	lb.	.06½
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	280 lbs.	1.70
Limestone, ground, bags, wks.	ton	4.50
Lithopone, bbls.	lb.	.04½
Magnesite, calcined, 500-lb. bbls., wks.	ton	60.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.06½
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 100 lbs.	lb.	.81
Mercury flasks, 76 lbs.	flask	75.50
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.82
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, wks., frt. allowed, c/l.	gal.	.40
Tanks, wks., frt. allowed	gal.	.35½
Methyl acetone, tanks, wks., frt. allowed	gal.	.48
Methyl chloride, cylinders	lb.	.40
Hexyl ketone, pure	lb.	1.20
Methyl propyl carbinol, drums, wks.	lb.	.60
Methyl salicylate, cases	lb.	.42
Michler's ketone, bbls.	lb.	2.50
Monoamylamine, drums, wks.	lb.	1.00
Monoethanolamine, drums, wks.	lb.	.31
Monomethylamine, drums	lb.	.75
Naphthalene, flake, bbls.	lb.	.06¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.13
Double, bbls.	lb.	.13
Niter cake, bulk	ton	16.00
Nitrobenzene, drums	lb.	.09
Octyl acetate, tanks, wks.	lb.	.15
Oil, castor, No. 1	lb.	.10¾
China wood, bbls.	lb.	.18¾
Coconut, tanks	lb.	.03⅞
Cod, N. F., bbls.	gal.	.40
Corn, crude, tanks, mills	lb.	.08
Cottonseed, oil refined, bbls.	lb.	.11
Linseed, boiled, bbls.	lb.	.098
Menhaden, crude, tanks	gal.	.32
Neat's-foot, pure, bbls.	lb.	.11½
Oleo, No. 1, bbls.	lb.	.09¼
Olive oil, denat., bbls.	gal.	.74
Foots, bbls.	lb.	.08
Peanut, crude, tanks	lb.	.08¼
Perilla, bbls.	lb.	.08
Rapeseed, bbls.	gal.	.52
Red, bbls.	lb.	.08⅝
Soy bean, crude, tanks	lb.	.07
Sperm, 38°, bbls.	lb.	.094
Whale, bbls., natural, refined	lb.	.076
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.06½
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.07
Ortho-toluidine, bbls.	lb.	.14
Paraldehyde, 110–50-gal. drums	lb.	.16
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.16
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.47
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.35
Para-phenylenediamine, bbls.	lb.	1.15
Para-tertiary amyl phenol, drums, wks.	lb.	.50
Para-toluidine, bbls.	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.60
Phenylethyl alcohol, 1-lb. bot.	lb.	3.75
Phloroglucinol, tech., drums	lb.	15.00
C. P., drums	lb.	20.00
Phosphorus, red, cases	lb.	.45
Oxychloride, 175-lb. cylinders	lb.	.20
Trichloride, cyl.	lb.	.18
Phthalic anhydride, bbls.	lb.	.14½
Platinum, metal, solid	oz.	36.00
Potash, caustic, drums	lb.	.06¼
Potassium abietate	lb.	.06
Acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08½
Binoxalate, bbls.	lb.	.14
Bromide	lb.	.31
Carbonate, 80–85%, calc., casks	lb.	.06
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls.	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.13½
Muriate, fert., bulk, per K_2O unit		.40
Permanganate, drums	lb.	.18½
Prussiate, red, casks	lb.	.35
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.32
Pyridine, drums	gal.	1.30
Pyrocatechin, C. P., drums	lb.	2.40
Resorcinol, tech., kegs	lb.	.75
Rochelle salt, bbls., U. S. P.	lb.	.14
R salt, bbls.	lb.	.52
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.32⅞
Soda, ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Sodium abietate, drums	lb.	.06
Acetate, bbls.	lb.	.05
Alginate, drums	lb.	.64
Benzoate, bbls.	lb.	.46
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.06½
Bisulfite, bbls.	lb.	.03
Bromide, bbls., U. S. P.	lb.	.31
Chlorate, kegs	lb.	.05
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07½
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	3.25
Metasilicate, gran., bbls.	100 lbs.	2.65
Naphthenate, drums	lb.	.13
Naphthionate, bbls.	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	ton	25.80
Nitrite, bbls.	lb.	.07¼
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, disodium, bags	100 lbs.	2.10
Phosphate, trisodium, bbls.	100 lbs.	2.30
Picramate, kegs	lb.	.67
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.06¾
Stannate, drums	lb.	.29
Sulfate, anhyd., bbls.	100 lbs.	1.30
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.30
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.85
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.08¾
Peroxide, 100-lb. drums	lb.	1.25
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Tetrachlorethane, 50-gal. drums	lb.	.08½
Thiocarbanilid, bbls.	lb.	.25
Tin	lb.	.46¾
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.23¾
Oxide, bbls.	lb.	.51
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Triamylamine, drums, wks.	lb.	1.25
Tribromophenol, cases	lb.	1.10
Trichloroethylene, drums, wks., frt. allowed	lb.	.0891
Triethanolamine, drums, wks., frt. allowed	lb.	.26
Trihydroxyethylamine oleate, drums	lb.	.40
Stearate	lb.	.35
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.37
Tungsten, powder	lb.	1.65
Urea, crystals	lb.	.0475
Vinyl chloride, 16-lb. cylinders	lb.	1.00
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks.	gal.	.30
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.90
Zinc ammonium chloride, bbls.	lb.	.0465
Chloride, granulated, drums	lb.	.05
Oxide, Amer., bbls.	lb.	.05
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25
Stearate, bbls.	lb.	.20
Zinc dust, bbls., c/l.	lb.	.065

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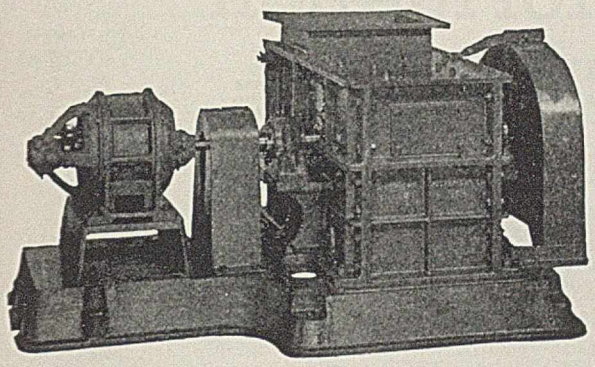

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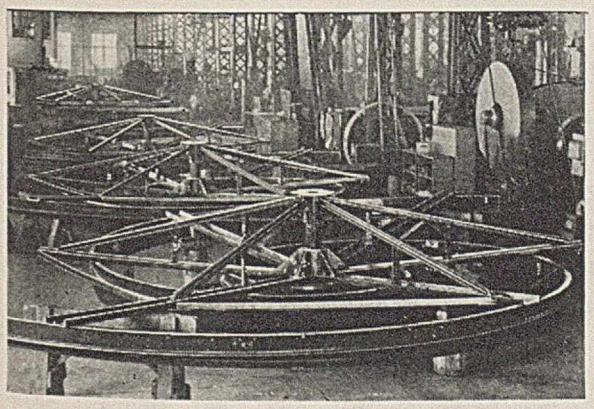

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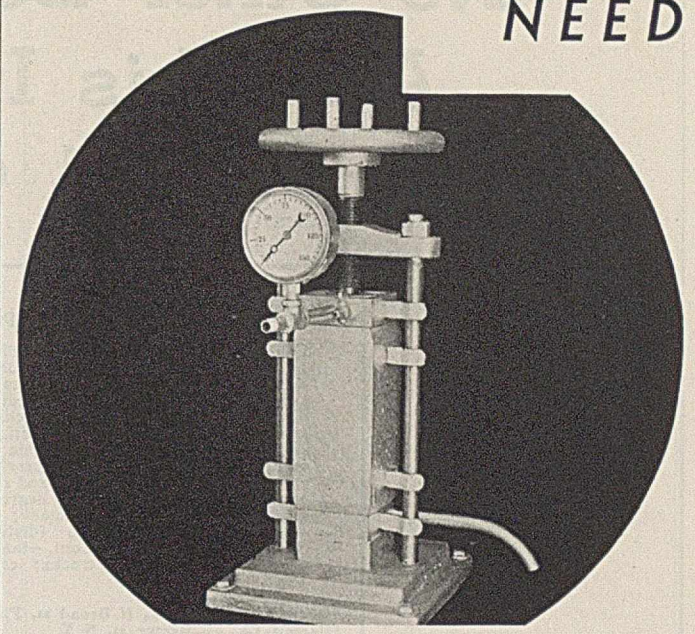

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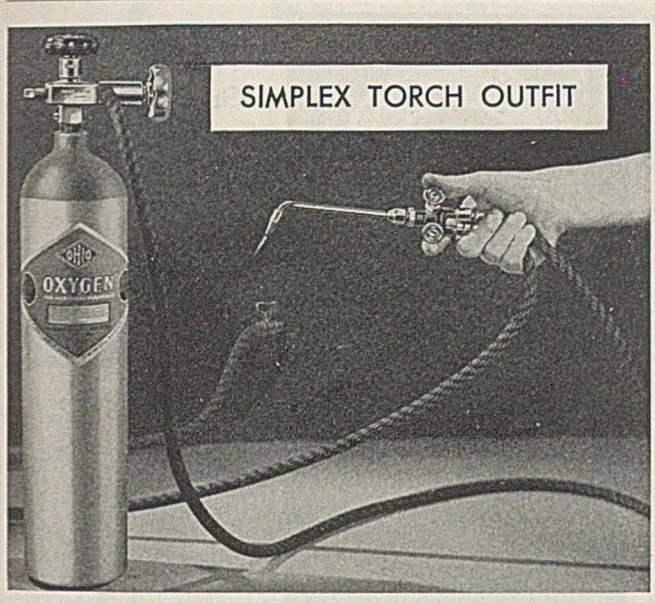

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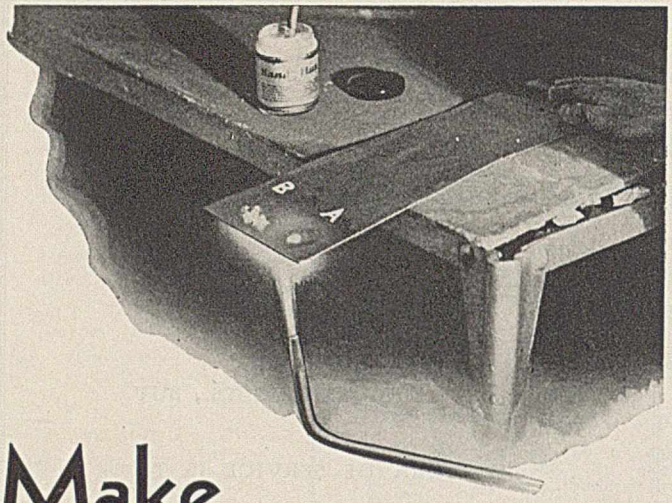

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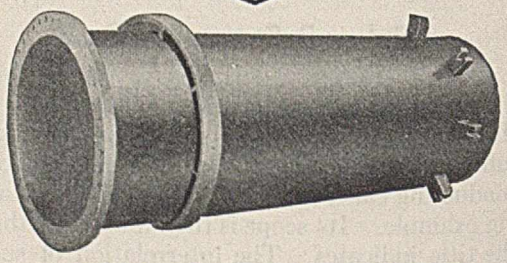

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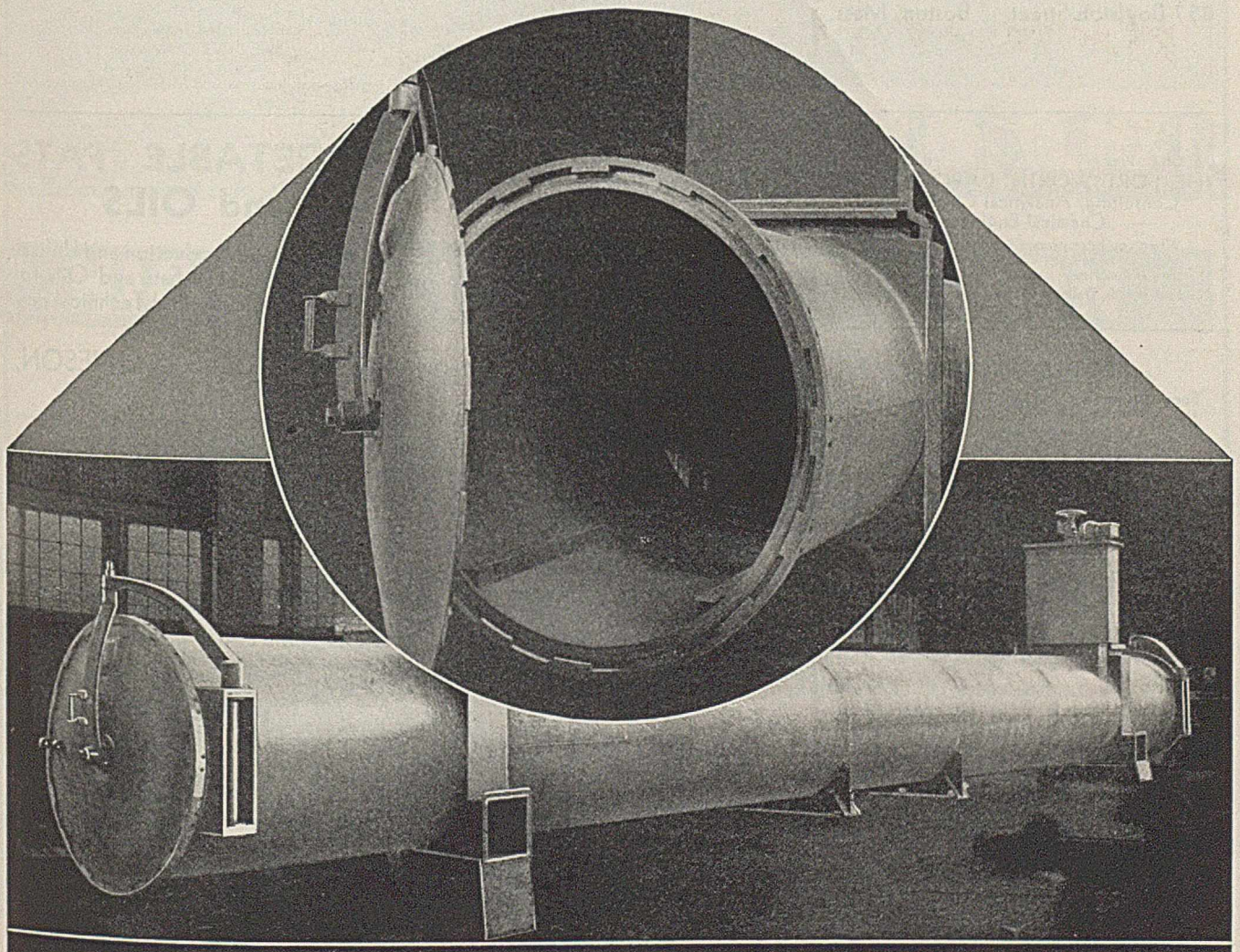

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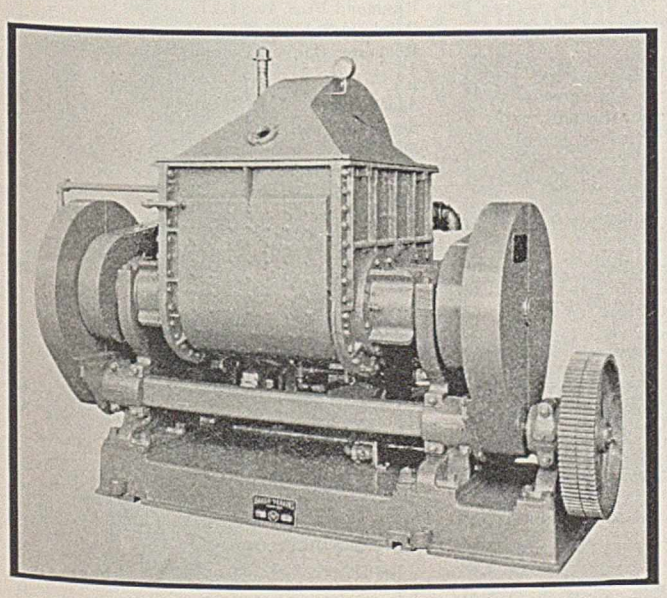

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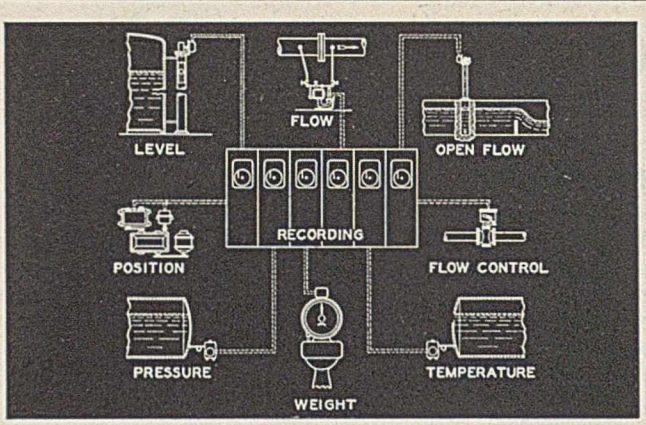

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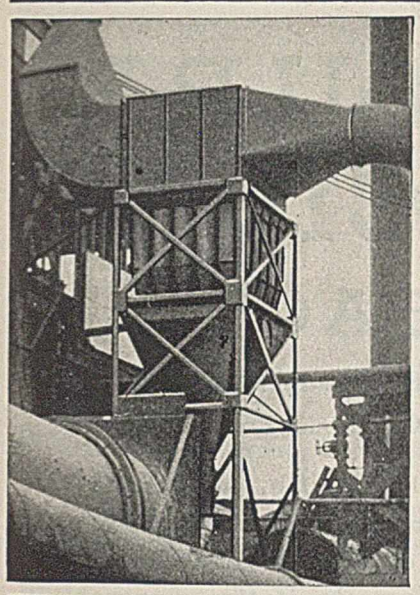

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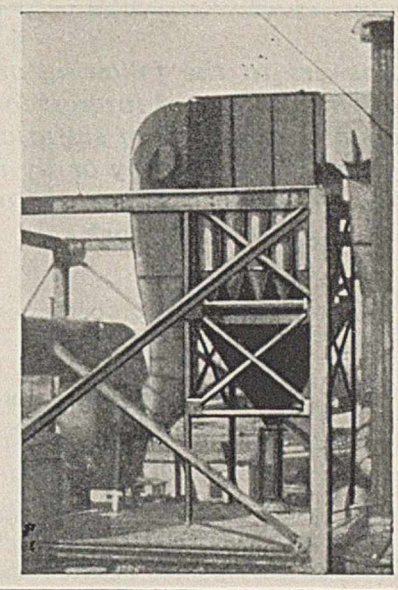

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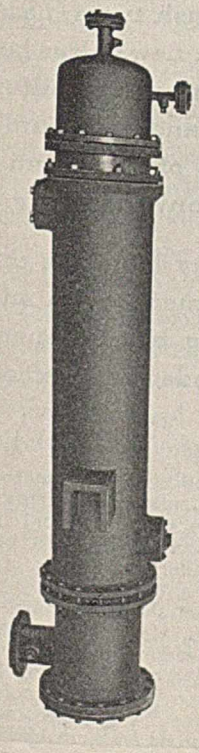

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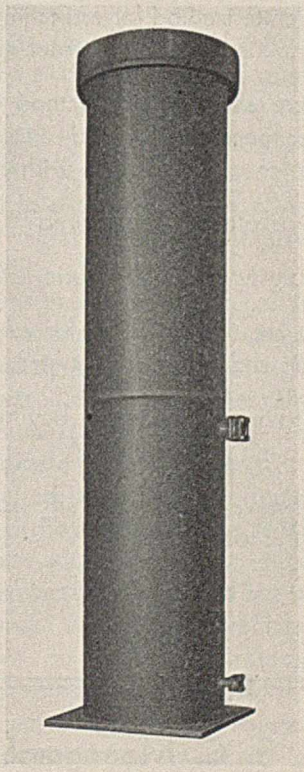

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