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An Antidumping Episode

THE demand for butyl acetate having developed to impressive proportions, thanks largely to the activities of those American workers engaged in the development of protective coatings, certain foreign producers apparently decided they should have a piece of the pie. Consequently, in due course increasing volumes of butyl acetate were imported by Kuttroff, Pickhardt & Company, Inc., who chose as an effective way to obtain the business a cut in prices. At the time there were some fifteen producers of butyl acetate obtaining their butyl alcohol from the Commercial Solvents Corporation, who were pleased to have their butanol so used and refrained from manufacturing the acetate. These manufacturers became growingly suspicious of dumping, and evoked the antidumping provisions of the tariff act. After thorough investigation and hearings, an order was issued.

Before the antidumping provisions can be exercised, two things must be shown. First, it must be proved beyond a doubt that the prices at which the product is offered in this country are lower than home prices. Next, it must also be established that injury is being done domestic producers. It was not difficult to show that the prices in America were lower than in Germany, but the attorney for the defense held that the importation of butyl acetate was not responsible for the low prices in this country, but that they had resulted from the entrance of the Commercial Solvents Corporation itself upon the production of butyl acetate. However, the facts were that it was not until eight or ten manufacturers of butyl acetate had discontinued operations because of the competition resulting from the dumped butyl acetate that Commercial Solvents, as a manufacturer of one of the basic raw materials, found it necessary to enter the field to save the situation. Therefore in the end the case was completely proved, the order issued, and the primary purpose of the antidumping legislation achieved—dumping was stopped.

The next part of the episode is secondary to the main purpose of the legislation. We refer to the assessment of duties and fines based upon an appraisal of the butyl acetate that had been imported. After due investigation Kuttroff, Pickhardt & Company, Inc., were called upon to pay in round numbers three million dollars. Instead, approximately one hundred and fifty thousand were offered in compromise, have been declined, and the defendants have appealed from the assessments. This appeal has been taken but lately, and it should be clearly understood that the Government does not have an enforceable claim against the defendants until the courts have sustained the appraisal. Meanwhile it is a matter of litigation which may be prolonged for some years. In other words, regardless of the decision that will be handed down in New York, either side might then appeal to the Court of Customs Appeals in Washington. If, after two or three years, a decision is handed down, it is barely possible that the case could then go to the Supreme Court.

In the meantime Kuttroff-Pickhardt have undertaken a dissolution of their business, distributing their assets to the

stockholders. It would appear fortunate that the collection of fines and duties is a consideration secondary to the effective stopping of dumping.

This interesting case is typical of the effectiveness of our antidumping legislation. The investigation required not only meticulous care in ascertaining the status of the American industry, but extensive investigations abroad, which were made by an expert of the Bureau of Customs who journeyed to Germany for the purpose. The case is not an exception, but is typical of the work quietly going forward in the Treasury Department under the present laws which, when final action is taken, effectively protect our industry. Such instances may at least serve fully to convince any who may have entertained doubts as to the wisdom and efficacy of the steps which the law provides.

Blow Your Horn

THERE are many men who have attended every exposition of the chemical industries, and they easily remember when the most interesting and instructive booths were those in which the products of the industry were displayed. To be sure, the equipment being developed in the early days of the exposition was just as important, and it was one of the objects of the project to let it be known that here in America were to be found those special devices and pieces of machinery essential to chemical production. No one passed these booths by, but after all it was an exposition of the chemical industries. In those days we were inordinately proud, perhaps, of the chemical compounds which first came into the exposition in small numbers, then showed rapid increase, only practically to disappear from the later expositions. This change in the character of the shows has called forth comment in the technical press and elsewhere critical of those industries which, though definitely identified with chemistry and chemical products, have latterly been conspicuous by their absence.

Just why should all this occur? For our part, we see no sound reason for it. It is true that a small handful of dyc-stuffs has grown to a large tonnage of great variety, accounting for some 95 per cent by weight of our domestic requirements. No longer are we dependent on other than our own resources for a long list of coal-tar synthetics, nor for a number of other products which our industry has developed. Even this progress and any strength it may indicate afford no adequate reason why the products of the chemical industry should not be continuously displayed at these biennial exhibits. Every progressive chemical industry has added some distinct product to its line during the past five years. Even since the last exposition some ten or twelve—perhaps fifteen—thousands of young men have been graduated into chemical careers. They should be effectively reached through the medium of the exhibit. The public has become more interested in chemical products, and the exhibit offers the opportunity to reach large numbers of the laity. Today the layman is the purchaser of chemical stocks,

and his interest must be obtained and held. An important by-product is the attention of the technical, trade, and daily press to the exhibits. They are news, and comment upon them is valuable publicity for our industries. We are never so strong but that strong public confidence is of the greatest benefit.

The returns on a well-planned exhibit of chemical products and the raw materials from which they are made are often immediate, but even though they are indirect, the general effect upon the whole industry is good and the ultimate return satisfactory. It is not the extent of the exhibit that matters so much. It is its quality—the story it tells and how well it is told. The small exhibit with human interest at its center will always attract more buyers than the elaborate display which is nothing more than just that. Plan your booth along the right lines and the buyers will congregate there.

Let the chemical industry see to it that after the thirteenth exposition, the week of May 4, no one can say that we have lost either our leadership in the production of chemical products or pride in our accomplishments, or that the showing of chemical products was disappointing.

Get into the exposition. Blow your own horn, and remember "He that bloweth not his own horn, verily his horn shall not be blown."

Naval Stores

THE older an industry the more reluctant it seems to be to avail itself of what science offers for its aid. Facts learned through the costly trial-and-error method of experience are not to be lightly discarded and may never be replaced by what science does. Yet when these old industries eventually turn to the research laboratory, they are often benefited immediately and quite out of proportion to the time and effort spent on their behalf.

The naval stores industry is perhaps the second oldest American industry, first place going to tobacco, thanks to the introduction of that famous weed into England by Sir Walter Raleigh and Sir Francis Drake. The English settlers who arrived in Jamestown in 1607 established the naval stores industry, which went on a business basis in 1622 as Neill's Virginia Company of London. The establishment was founded upon a commission from Queen Elizabeth to the English settlement and its primary purpose was to secure in the new colonies a suitable supply of tar, pitch, rosin, tar oils, turpentine, etc.—all of which were urgently required in the construction of wooden ships for the English navy and the merchant marine. From that day to this naval stores have been among the prominent industries of our Southern States, but until recent years the character of the industry changed but little from those earlier times. Relatively little has been done by the producers to improve their product, to eliminate their wastes, to conserve their raw materials, or to expand their markets. With the passing of wooden ships a change in consumption took place and new markets were more or less permitted to develop themselves.

Notwithstanding this well-known apathy, there have always been individuals keenly interested in the improvement of naval stores. Our own Doctor Herty is one of those who, beginning with marked improvements in methods for the collection of turpentine, has continued efforts to have the industry make progress and today is keenly concerned with the problem. A few years ago the Pine Institute of America was incorporated and this institute has begun a modest program of research. The Forest Products Laboratory has given special attention to the problems of the industry. For years the Bureau of Chemistry and Soils, repre-

sented by F. P. Veitch and his associates, has been prominent in the field. Those individuals and organizations making the distribution of naval stores their principal occupation have developed an efficient machine for their purpose and through their numerous contacts have come to realize that if the naval stores industry is to continue as an important industrial factor some energy must be put into educational campaigns as well as into research.

In October, at the eighth annual meeting of naval stores representatives, it was unanimously decided to set up a standing committee on turpentine advertising to plan a coöperative program for all naval stores interests. The public at large is to be told something of the merits of turpentine, not only in the manufacture of paint and varnishes, but as a thinner and for many other important manufacturing and household uses. An effort is to be made to overcome the apathy of producer and consumer, to make more firm the essential place of turpentine in industry, and to stress the fact that as yet no complete equivalent has arisen to replace it. Its position being continually challenged by competitive materials, these representatives feel that the time has come to say more of its merits and to have them recognized.

The group also went on record in favor of certain reforms designed to assist the industry. Strangely enough, rosin is still sold by the antiquated unit of 280 pounds gross, this being equivalent to the old 20 stones of English weight. There should be a simplification of the number of grades and the elimination of unnecessary grades. Uniform and improved packages are to be adopted. The need for more intensive research for the improvement and development of new uses of naval stores products is to be stressed, and efforts are to be made to get a full coöperation of all units involved in the naval stores industry.

The active interest of the naval stores consumers—identified with the National Paint, Oil, and Varnish Association—should give further stimulation to the work in hand and be potent in initiating further effort.

Radium's Competitor

IN DECEMBER at Los Angeles R. A. Millikan and his associates displayed a new tube which may become of the greatest importance. Utilizing 650,000 volts, it emits rays quite comparable to those given off by radium, and one specialist calculated that with such a tube one might accomplish results that would be equivalent to those obtained with \$5,000,000,000 worth of radium. There is no reason to believe that 650,000 volts is the uppermost limit, if there is any advantage in going higher, and we have confidence that the physicist can produce a tube with which results characteristic of radium can be obtained. One of these days radium, which has been listed as one of the wonders of the modern world, will find itself reduced by the new competition to a place where it will be glad to be on speaking terms with a larger proportion of our population.

There are many cases where a special technic has been developed in radium therapy. The insertion of tubes containing radium emanation into abnormal tissues affords an example. We do not expect these new types of electric tubes to compete in this field, but it seems fair to assume that in many instances where radium therapy has already proved its worth this newer form of energy will be found equally efficient, more susceptible to control, and of course available at but a fraction of the expense. Radium may retain its industrial applications, as for dial illumination, but the significance of the new 650,000-volt tube for industry is far-reaching and difficult to imagine. It is indeed intriguing.

Progress in Education

ANNOUNCED plans and others in progress seem to us hopeful signs in the field of higher education. For some time there has been put forward the idea that students should be graduated from colleges whenever a suitable comprehensive examination can be passed, thereby enabling the brilliant student to waste less time and to be of less expense to the institution than is the case where he is held back by the procession, which according to precedent must take four years to reach a given point.

The University of Chicago through its trustees and faculty has sanctioned the initiation of the experiment. In place of the present four-year undergraduate course, with its specified number of credits and the bachelor's degree at its conclusion, a new type of college is to be created in which the student can proceed directly in proportion to his capability and energy. A veritable genius might conclude the course in a few months; a few bright boys might save a year or two; and those who enjoy the social, athletic, and political aspects of student life may still be expected to put in their four years. In doing so, however, they will not impede the progress of the others. The plan has developed gradually at Chicago. A reorganization of the graduate school was involved, as well as a division into new groups of undergraduate courses. The announced departments of study include the humanities, social sciences, physical sciences, and biological sciences. There is also to be a college division. Without doubt this experiment will command wide attention.

At the Massachusetts Institute of Technology a new scheme has been adopted which at present operates to eliminate unqualified freshmen. It is to be expected that ere long the system will extend to the sophomores, the juniors, and ultimately to the seniors. No one has ever seen any reason why the incapable or the lazy student should be allowed to get in the way, especially in these days of crowded academic halls. The problem has been how to eliminate such students and at the same time practice extreme fairness and helpfulness. After three years of study and experiment the Institute has developed a system which affords a measure of a student's scholastic accomplishments and shows how they compare with minimum standards that have been established. It also indicates the grade of work which he must perform to maintain good academic standing. This is not the place to discuss this rating system. It is the result that is of interest. A student becomes disqualified, and thereby automatically dismissed, if he fails to meet minimum scholastic standards two terms in succession or in a total of three terms. Roughly stated, these minimum requirements are that he shall satisfactorily pass not less than half his work. Consideration is given to any student who is prevented from performing his work by some such unusual non-academic cause as continued illness. Great care has been exercised in establishing the minima, and it seems evident that when a student cannot or will not creditably discharge half his work he should make way for those who can.

In many educational institutions so much is being done for students that even remaining in classes, notwithstanding unsatisfactory records, has also been made easy. The success of the Institute in eliminating the unfit will be another experiment worth the watching.

And then, what do you think? Some one has suggested that it might be just as well to eliminate the leisure-loving professor! In some faculties appointments have been made quite out of proportion either to the work to be done or the students to be taught. The men in industry and in business,

if they thoroughly understood just what a five- or a ten-hour teaching schedule means, would be sure to lose patience with their academic brothers and perhaps withhold support. By the new plan salaries are to be arranged on a basis of the number of hours taught or devoted to laboratory work. To be sure, the idea of lessening the teaching hours carried with it the assumption that the rest of the time might be used for constructive research or investigation. In many places this has worked; in others it has meant added leisure. If a minimum wage for a minimum service could be established and the opportunity given to energetic professors to increase their income by increasing their hours of labor at their academic job, several things might be accomplished. By concentrating upon the work in hand the teacher might greatly improve, for if he was able to earn an adequate income at his chosen profession, outside activities to increase that income would be less appealing and less diverting. The friction that comes from the competition of professor with the graduate might also be lessened, and under such an arrangement also the unenergetic professor might see fit to take up another occupation, thereby enabling improvement in staff and consequently in students.

These various developments are of interest to the industry, for it is the academic institution that supplies raw material for the most important posts. You may have small patience with the academic profession, yet you must depend upon it for the type of man who comes into your business. The fundamental interests of industry cannot be separated from those of education.

Believe It or Not

IN a recent issue of *Mining and Metallurgy* under the above heading there was quoted a report of an analyst which is sufficiently unique to warrant reprinting here:

I received two samples of ferric-aluminic, conglomerate ore marked No. 1 and No. 2 of which samples, special attention is to be given No. 1 for specific rare metals.

The ore consists of aluminum chemically combined with silica and chromium, cobalt, nickel, manganese, and iron.

Percentages of Organic Elements

	Per cent
Aluminum	0.9
Chromium	0.6
Cobalt	0.5
Iron	0.39
Nickel	0.9
Manganese	Trace
Silica	0.32
Glucine	Trace

We seldom comment on the value of mineralized ore unless there is some special characteristic to which the analysis has drawn our attention.

In this instance the footings of the analysis show that pressure and volcanic heat have a cement and alloy welded to the content of the rock which render the ore a transitory vehicle for the elements already selected and proportioned for a valuable hardener for copper, aluminum, manganese, and iron in the making of the hardeners of steel.

Upon inquiry we learn, as was to be expected, that the "analyst" has no professional standing in his community, and it is hard to understand why anyone would utilize his services. Perhaps it goes to show that our campaign to obtain a better appreciation and understanding on the part of the public of what chemistry is and can do is worth stimulation. We cannot expect ever to bring all men to display discrimination when choosing scientific advice, but there should be some way of making it difficult for the sort of workman whose results are reported here to do mischief. Licensing does not do it, since some of the professions where the greatest care is exercised harbor the best examples of harmful impostors. Another way must be found.

Electric-Furnace Production of High-Heat-Duty Refractories¹

Fred W. Schroeder

CORHART REFRACTORIES COMPANY, 16TH AND LEE STS., LOUISVILLE, KY.

FOR many years the production of a high-heat-duty refractory with a vitreous body was believed to be impossible. However, approximately two and a half years ago the successful commercial production of such a refractory was commenced at Louisville, Ky., by the Corhart Refractories Company, a subsidiary of the Corning Glass Works and of the Hartford-Empire Company. The refractory had been used for several years at the Corning Glass Works.

The process consists in its essentials of the introduction of a mixture of several clays of high-alumina content into

During casting the sand mold is disintegrated and the sand mixes to some extent with the insulating powder. The two materials are separated in a series of three gravity air separators, sand being recovered from the first and insulating powder from the last, while the mixture from the second unit is returned to the feed of the first separator. The exit air from the third unit is passed through a bag filter to recover the fine particles which would otherwise be lost.

Preparation of Batch

The raw materials for Corhart refractories are obtained from Missouri and Kentucky. Diaspores containing from 9 to 18 per cent SiO_2 are procured from several sources in order to even out irregularities in composition, and kaolin is used to adjust the alumina-silica ratio to the value desired.

Shipments of clay are first unloaded to bins in a shed, where storage capacity for from 6000 to 8000 tons is necessary in order to carry the plant through the period of late winter and spring when ground conditions prohibit the digging of clay. The raw clay is first run through a crusher, then is calcined in a gas-fired rotary kiln, from which it is sent to storage in one of eight uniformizer bins, each bin containing a carload shipment. The material is handled on a monorail conveyor system throughout. Part of this system at the uniformizer is shown in Figure 1.

As required by the plant, clay is withdrawn from the uniformizer bins, being fed from five or six bins at a time in order to minimize

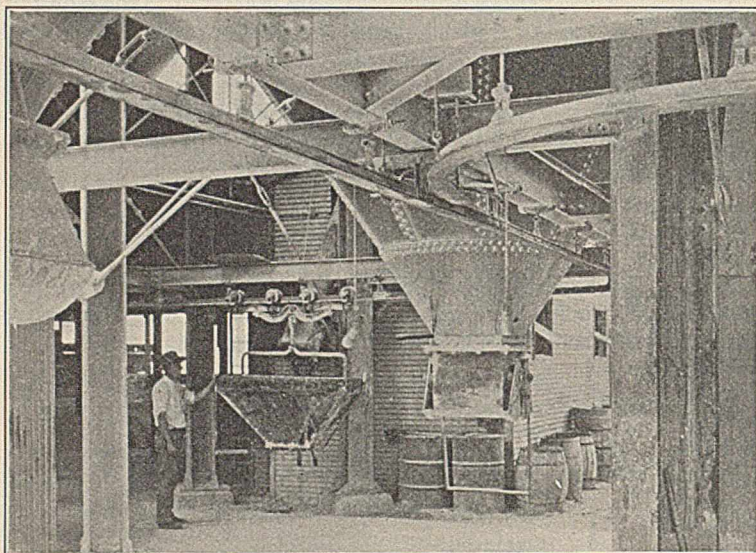


Figure 1—Part of Monorail Conveying System at Uniformizer Bins

the top of an electric furnace, from which molten aluminum silicate is tapped at intervals into molds built from sand slabs. The molds containing the cast blocks are sent to storage where they anneal for from 6 to 10 days before the blocks are removed to final storage or shipment. Behind this sequence of apparently simple operations lies the customary long period of developmental difficulties and a present system of accurate control.

Making Molds

High-silica sand is mixed with linseed oil, the slabs are formed on the slab tables, placed on racks, and baked in an oven. They are then trimmed to size with a cutting wheel and are built into molds of the desired shapes and sizes, using a graphite-gum binder. The molds are allowed to dry for from 24 to 36 hours. As required, they are set up in cans with an insulating material packed around them. The molds are then ready for the casting of the refractory blocks.

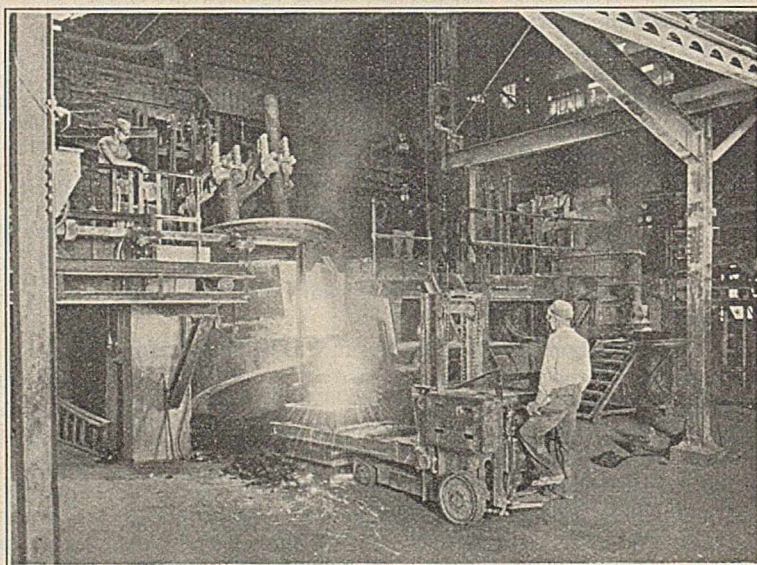


Figure 2—Casting Refractories from Electric Furnace

¹ Received December 10, 1930.

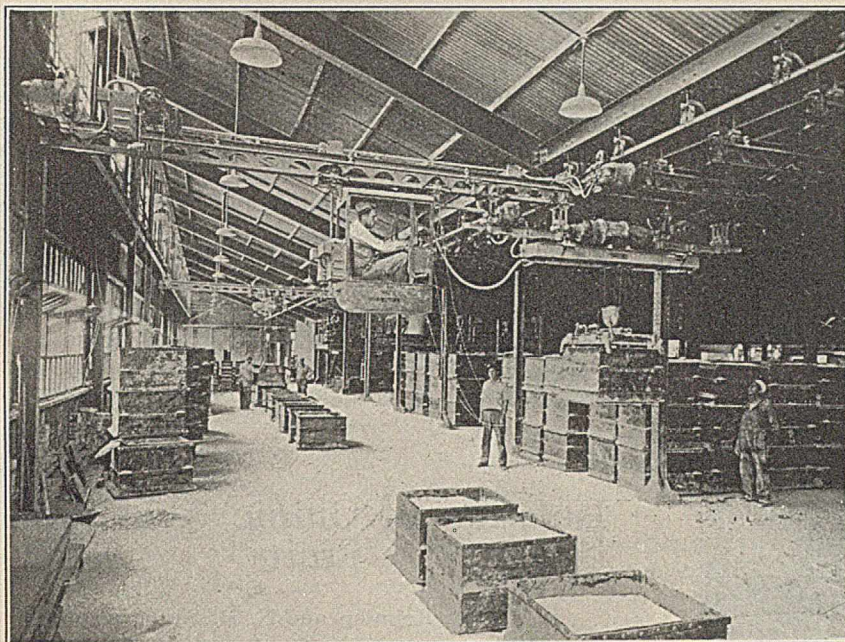


Figure 3—Annealing Storage for Refractory Blocks after Casting

variations in composition. A feed-discharge control on each bin feeds clay to a belt conveyor running beneath all the bins, and this conveyor delivers the combined feed to a bucket elevator discharging into any one of three storage bins of 300 tons capacity each. During the filling of each storage bin samples of material are withdrawn periodically from the belt conveyor, quartered, and analyzed to check the composition.

Uniformized clay is withdrawn from the storage bins as needed and is conveyed by monorail to service bins at the two furnaces. Other service bins contain the kaolin used in adjusting the alumina-silica ratio of the batch. The relative amounts of the materials are calculated from their analyses, and these amounts are posted for the furnace operator, who weighs out a furnace charge into a car by means of scales mounted on a weighing section of the monorail. This charge is dumped to the furnace deck, where the operator mixes it by shoveling and feeds it to the furnace at a rate of about 750 pounds per hour for the smaller furnace and proportionally more for the larger furnace.

Melting, Casting, and Annealing

The electric furnaces used for the manufacture of these refractories are of the dipping-electrode resistance type. The first furnace installed was a 500-kilovolt-ampere unit with a capacity of 600 pounds of refractory per hour. A second furnace was put in operation in June, 1930, using 750 kilovolt-amperes. The

electrodes are 8-inch graphite and the load is balanced manually between the three phases.

The furnace forms its own refractory lining by the natural cooling of the melt adjacent to the steel walls. The liquid between the electrodes is probably in the neighborhood of 4000° F. (2200° C.), since the stream of tapped liquid gives a reading of approximately 3400° F. (1870° C.) with an optical pyrometer.

At 2-hour intervals the furnace is tapped and the melted refractory is poured into the molds. The cans containing the molds are handled to and from the furnace by an electric truck, as shown in Figure 2. After casting, the cans are allowed to stand for a while, the fonts are knocked off, and the cans are then carried on the monorail system to storage (Figure 3), where the cast blocks anneal for from 6 to 10 days. After the annealing period the castings are dumped, cleaned, and sent to the shipping room or to

storage, while the mixture of sand and insulating powder in the cans is reclaimed in the air separator system to which previous reference was made.

There is at present a 1500-ton cullet pile composed of fonts from castings, which represents a loss of about 20 per cent of the material melted in the furnace. Work is in progress on the utilization of this material, which may possibly be ground up and used for the production of a bonded refractory. It has not been found advantageous to return the cullet to the furnace for remelting.

Properties and Uses of Refractories

The refractory obtained from the electric-furnace casting process has a pyrometric cone equivalent of cone 37. It has a close temperature range from solid to liquid, and does not deform gradually under combined load and temperatures below its melting range. It has a vitreous, non-porous body

and shows a linear coefficient of expansion approximately one-half that of first-class fire brick. The finished blocks cannot be chipped, cut, worked, or shaped, although it is possible to grind them on alundum wheels. Silicon carbide should not be used for grinding refractories for use in glass tanks because of the deleterious effect of small amounts of this material on the quality of glass.

Difficulty has been experienced in the past in casting large blocks, owing to the formation of pipes

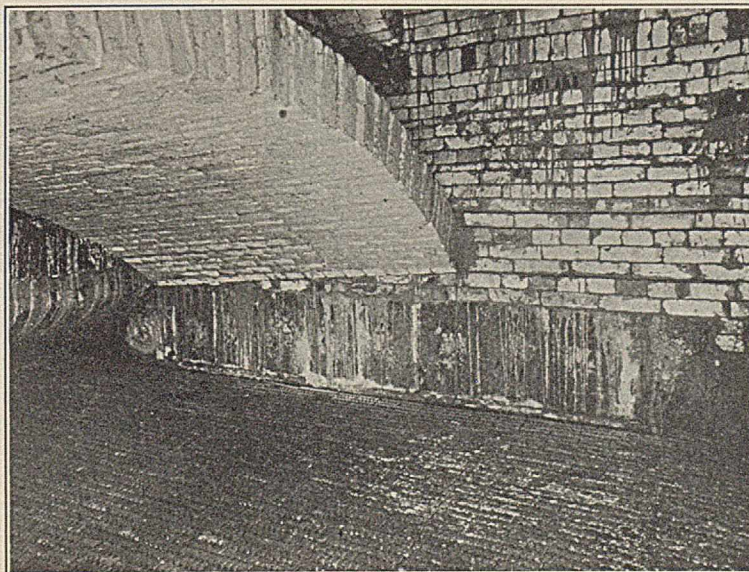


Figure 4—Corhart Blocks Used in Boiler Furnace at Clinker Line



Figure 5—Comparison of Corhart Blocks with Ordinary High-Grade Refractory in Glass-Tank Service

as the result of the 15 per cent shrinkage during solidification. This difficulty has now been largely overcome, and blocks as large as 18 by 18 by 48 inches weighing about 1625 pounds are cast satisfactorily. As mentioned previously, all blocks must be cast to exact dimensions because of the high cost of grinding finished pieces.

Developed first for use solely in glass tanks, Corhart refractories have a number of other indicated uses, as in the lining of the hot zones of rotary kilns, in the portion of modern boiler furnaces exposed to particularly severe duty, and in metallurgical equipment such as forging furnaces. The refractories have the advantage of long life and the minimum of repairs, which must be balanced against the greater first cost as compared with less durable materials. Figure

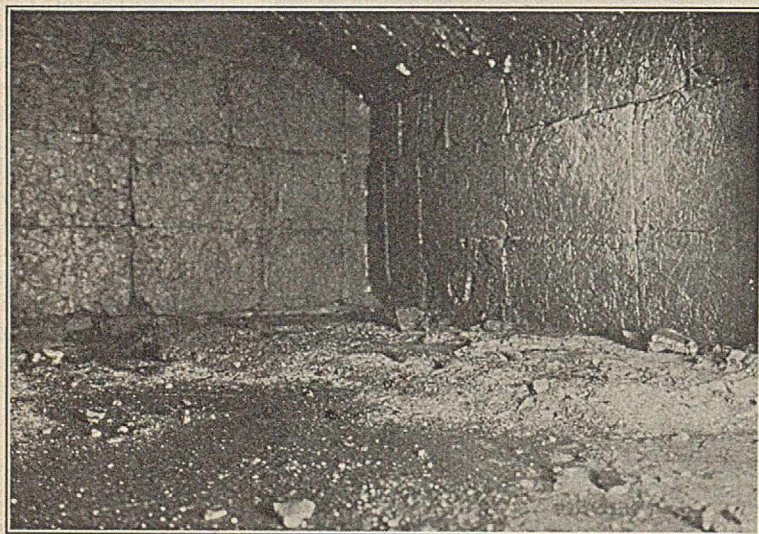


Figure 6—Appearance of Corhart Blocks after Three Months' Service in High-Heat-Duty Forge Furnace

4 pictures an installation of blocks at the clinker line of a boiler furnace.

Examples of the durability of these refractory blocks under extremely severe service conditions are shown in Figures 5 and 6. Figure 5 indicates the durability of Corhart refractory in glass-tank service, the purpose for which it was originally developed. The lighter-colored test blocks of Corhart were built into a wall of ordinary high-grade glass-tank refractory. When the tank was taken out of service, the Corhart blocks were practically untouched, while the other refractory had been eaten back as shown in the picture. Figure 6 pictures the interior of a high-duty forge furnace built of Corhart blocks as it looked after three months of service, the walls showing the durability of the refractory under the severe conditions imposed by this type of work.

Isolation of Quinic Acid from Fruits¹

E. F. Kohman and N. H. Sanborn

NATIONAL CANNERS ASSOCIATION, WASHINGTON, D. C.

IT HAS been known that certain fruits, noticeably prunes and cranberries, tend to create an acid condition in the system when eaten, even though their mineral content or ash after burning may be basic. In the case of these two fruits it has been shown that the hippuric acid to which they give rise is responsible. These fruits contain only traces of benzoic acid, however. It has recently been shown that grape juice may likewise have an acid reaction in the system, although the mineral residue is strongly basic. The cause of the acid reaction created by grape juice has not been demonstrated.

The writers have recently isolated quinic acid from prunes and cranberries. The basis for the method of isolation is the solubility of the lead and calcium salts of quinic acid compared with the relative insolubility of the same salts of other organic acids, and the low solubility of the double calcium salt of quinic and acetic acids. The solubility of the lead and calcium salts is being made the basis of a quantitative chemical method for determining quinic acid with a view to making a survey of the occurrence of quinic acid in other fruits. This is particularly desirable with those more or less closely related to prunes and cranberries. Some evidence has been obtained that indicates a considerable variation in its occurrence in different members of the plum family. Although this isolation is not quantitative, there are indications that there is approximately 1 per cent of quinic acid in cranberries and prunes on the fresh basis. Inconclusive evidence also suggests that grapes may contain some quinic acid. This is to be determined conclusively, if possible, by its isolation from grapes.

The presence of this interesting acid in these fruits merits consideration from the standpoint of plant physiology. It is possible that it is an intermediary in the synthesis of more complex structures. The form in which quinic acid exists in these fruits is of interest and may throw light on the above question.

¹ Received January 5, 1931.

Compatibility of Resins with Nitrocellulose Solutions¹

Harry E. Hofmann

VALENTINE & COMPANY, NEW YORK, N. Y.

IT WAS perhaps fortunate for the lacquer technologist that, when the industry commenced its present period of rapid growth a few years ago, butyl and amyl acetates were the principal nitrocellulose solvents and rosin ester was the most popular resin. These will mix with nitrocellulose in any proportions and give clear films, free from the white or turbid appearance often obtained with other resins and other solvents and commonly called a "gum blush."

When experimenters in the laboratories of the lacquer manufacturers began to try other resins than ester gum, or products closely related thereto, they experienced difficulties, as they also did when they substituted certain newly developed synthetic solvents for the butyl acetate in their usual formulas. It would be found, for example, that a certain resin gave a satisfactory solution in a given solvent, as did nitrocellulose, but that when these two solutions were mixed a cloudy lacquer was obtained, which was entirely unsatisfactory. Then it was found that the addition of certain liquids, themselves non-solvents of nitrocellulose, caused this cloudy solution to become clear, and in a number of instances the dried film deposited from the solution was clear also; but in some cases it was not. Butyl and amyl alcohols and toluene, as well as some other compounds, were heartily recommended by their makers for the elimination of this troublesome "gum blush," which was said to result from the precipitation of the resin, or gum; hence the name. However, most of the information obtained with regard to the use of certain resins, and certain solvents, in nitrocellulose lacquers has been largely empirical in nature, and is applied to new products only with difficulty, and rarely with success.

In this paper the author calls attention to the possibility of arriving at definite rules for handling solvents, resins, etc., by means of a systematic study of their properties, and presents some experimental data in support of this contention. The ideal will probably never be realized, since there are so many variables to consider, but if only a few general laws may be established, it will greatly lessen the uncertainty of lacquer formulation.

The usual dictionary definition of the word "compatibility" is "the ability to exist together in harmony or agreement" etc., and in its ordinary usage generally refers to the co-existence in harmony or agreement of two entities. But in view of the nature of the phenomenon under examination here—namely, the behavior of nitrocellulose and a resin in a

Resins and solvents are divided into two groups, the alcohol-soluble type and the hydrocarbon-soluble type. The alcohol-type resins are most readily soluble in the alcohol-type solvents, and the hydrocarbon-type resins in the hydrocarbon-type solvents.

A few resins appear to be solvents for nitrocellulose, but most ordinary resins are not miscible with nitrocellulose under all conditions and in all solvents. This immiscibility is known as incompatibility, or "gum blush."

Compatibility is most readily obtained by the use of a resin and a solvent belonging to the same class. Incompatibility can often be relieved by the addition of a solvent complementary to that originally present in the lacquer, and in some cases by the addition of a resin complementary to that already used.

Plasticizers, which may be considered as solvents, affect compatibility in different degrees. Changing the solvent composition during the drying of the film may cause incompatibility to develop.

solvent—it is necessary to think of this word as referring to the state of affairs existing in a system of three components. Thus, we will speak of the compatibility of ester gum with nitrocellulose in the presence of amyl acetate, and not simply of the compatibility of ester gum with nitrocellulose.

Experimental Procedure

Two parts by weight of dried $\frac{1}{2}$ -second R. S. nitrocellulose and 2 parts of resin were placed together in a glass tube with 15 parts of the solvent being examined. The tubes were corked and fastened on a slowly rotating

wheel until both nitrocellulose and resin had dissolved. The solutions were then examined visually. Those exhibiting a cloudy solution were marked "X." Those which were clear were tested by flowing a small portion on a glass plate and allowing to dry, then those clear solutions which gave clear films were marked "OK" and those which dried to dull or cloudy films were marked "F."

After these preliminary tests the cloudy solutions, which were in the majority, were examined further to ascertain what type of substance improves the compatibility to the greatest extent. Since a plasticizer is almost always used in lacquers, dibutyl phthalate, chosen as representative of this class of substances, was added in the ratio of 50 per cent of the nitrocellulose present. In the cases of kauri, manila, shellac, and pontianac, tricresyl phosphate was used, as it is a better solvent for these resins than dibutyl phthalate. This caused some of the clear solutions which formerly produced cloudy films to produce clear films, but did not clear up any of the cloudy solutions.

The solutions, now containing 2 parts nitrocellulose, 2 parts resin, and 1 part plasticizer, were then divided into four portions and to each portion was added an equal volume of diluent, as follows: 95 per cent denatured ethyl alcohol, toluene, 50 per cent denatured alcohol and 50 per cent toluene, and 20 per cent butyl alcohol and 80 per cent toluene.

In one or more of these instances a clear solution was obtained for practically all resins and all solvents, but all of these clear solutions did not produce clear films. The behavior with the mixture of toluene and butyl alcohol was the same in nearly all cases as with the ethyl alcohol-toluene mixture, so the former is taken as being more nearly representative of the diluents used in actual manufacture:

Those mixtures which originally gave cloudy solutions, but which were clear and gave clear films with the addition of an equal volume of alcohol, are marked "A." Those marked "H" gave similar results when diluted with an equal volume of toluene, and those marked "M" when diluted with a mixture of 80 per cent toluene and 20 per

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cent butyl alcohol (by weight). In no case did a solution fall both into the "A" group and the "H" group, but a few in the "M" group also fell into either the "A" or the "H" group.

Results

Table I shows the behavior of each of the common resins with nitrocellulose in each of the ordinary nitrocellulose solvents. These solvents are also solvents for the resins, except in a few cases, where the incompatibility is caused chiefly by the insolubility or partial solubility of the resin.

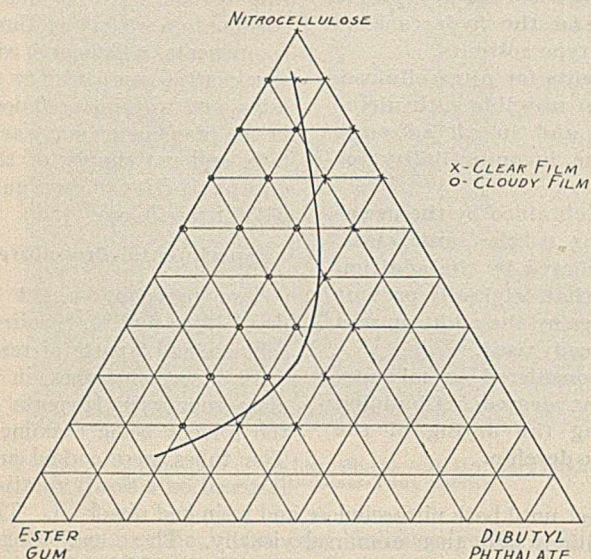


Figure 1—System Nitrocellulose-Ester Gum-Dibutyl Phthalate in the Single Solvent Cellosolve

A study of the results of these tests brings out at least two interesting points: (1) Some resins are compatible with nitrocellulose in any solvent, but the majority behave differently in different solvents; and (2) certain resins are compatible with nitrocellulose in certain solvents only when another particular solvent is present.

The resins in the first class may be disposed of briefly with the simple and logical statement that they themselves are solvents of nitrocellulose. No limited miscibility is shown, because all the components are mutually miscible in all proportions. With resins that are not actually solvents of nitrocellulose, immiscibility is experienced in the presence of certain unfavorable solvents or solvent mixtures. It is this second type of phenomenon that will be discussed in the present paper.

Mechanism of Gum Blushing

Brown and Crawford (1) say that "as a general rule it may be said that nitrocellulose solvents are not good gum solvents, and vice versa. Gum solvents (diluent) sometimes precipitate nitrocellulose from solution when too much of the former is added in compounding a lacquer, and a precipitation of gum occasionally occurs when an excess of nitrocellulose solvent is added to a gum solution." They also state that "many liquids which dissolve nitrocellulose are also solvents for gums and resins—but few of these liquids will hold both materials in the same mixture." Finally, they say (2) that gum blush "is caused by an excess of gum non-solvents (usually nitrocellulose solvents) over gum solvents in the drying film." Other writers explain the phenomenon in different ways, but the consensus of opinion seems to be that some of the resin or nitrocellulose, or both, is precipitated during the drying of the lacquer film.

These explanations are, however, not satisfactory. It is incorrect to say that the addition of a nitrocellulose solvent to a resin² solution will precipitate part or all of the resin. This will take place only if the added material is a non-solvent for the resin that is in solution. Whether or not this added liquid is a solvent for nitrocellulose is coincidental. As mentioned above, nearly all of the nitrocellulose solvents in common use are solvents for the resins ordinarily used in connection with them. The trouble is that the nitrocellulose and resin are not always miscible in the presence of such a solvent.

From several careful experiments and numerous observations of the phenomenon of incompatibility, the author has concluded that the troublesome phenomenon is merely a manifestation of immiscibility in a polynary system (ternary in the simplest cases) in which all of the components are not miscible with each other in all proportions. Consider the system water-ethyl ether-ethyl alcohol. Water is miscible in all proportions with ethyl alcohol; so also is ethyl ether. But water and ether exhibit only a limited miscibility. If we start with a mixture of water and ether and add ethyl alcohol, two separate phases will continue to exist until considerable alcohol has been added. However, when sufficient alcohol has been added to the mixture, a homogeneous system of three components is obtained. Even after attaining this state, two phases may again be obtained by changing the temperature of the mixture. The same effect may be obtained by adding more water or more ether. At the time two phases separate from the previously homogeneous system, each phase contains each of the three components but in different proportions. The phases usually differ in density and refractive index; hence the mixture appears turbid at first, when globules of one phase are dispersed in the other phase. When the difference in the densities of the phases and their fluidities permit, a complete separation into two clear layers takes place, each of them homogeneous, and of a definite composition depending upon conditions of temperature and relative solubilities or miscibilities.

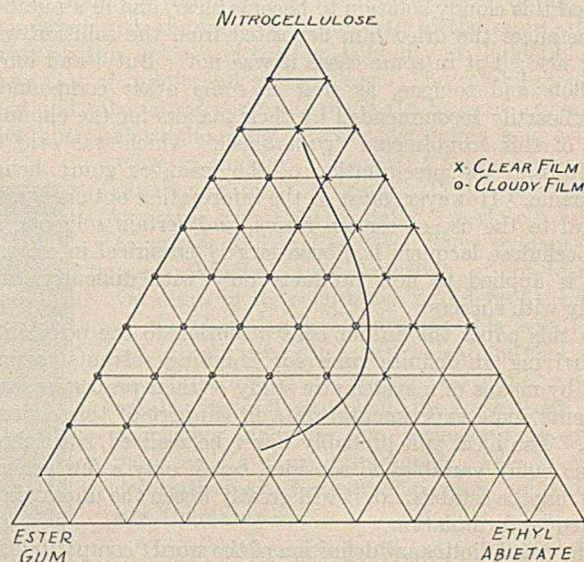


Figure 2—System Nitrocellulose-Ester Gum-Ethyl Abietate in the Single Solvent Cellosolve

The production of a turbid solution when nitrocellulose and a resin are placed in the same solvent, which may be a good solvent for each of them separately, is due to the fact

² The author prefers "resin" to the chemically incorrect term "gum." A gum is usually a water-soluble carbohydrate.

Table I—Behavior of Resins with Nitrocellulose in Nitrocellulose Solvents

OK—Clear solution and film.
 F—Clear solution but cloudy film.
 P—Clear solution and film with addition of 1 part plasticizer.
 A—Clear solution and film when diluted with equal volume of alcohol.
 H—Clear solution and film when diluted with equal volume of toluene.
 M—Clear solution and film when diluted with 80 toluene, 20 butyl alcohol.
 G—Clear solution and film with M and ester gum added.
 X—Cloudy film, all tests.

RESIN	HYDROCARBON SOLVENTS					ALCOHOL SOLVENTS						
	Ethyl acetate	sec-Butyl acetate	Butyl acetate	Amyl acetate	Butyl propionate	Acetone	Mesityl oxide	Diacetone alcohol	Ethyl lactate	Cellosolve	Cellosolve acetate	Butyl Cellosolve
Vinyl acetate	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
Rosin ^a	FP	FP	FP	FP	FP	FP	FP	OK	FP	OK	FP	OK
Ester gum	FP	OK	OK	OK	OK	M	OK	X	X	X	X	OK
Dammar ^b	OK	OK	OK	OK	OK	FP	OK	X	X	HM	HM	OK
Cumar	X	X	X	X	X	X	X	X	X	X	X	X
Amberol H-9	M	FP	FP	OK	OK	M	F	X	X	X	X	OK
Rezyl 12	OK	AM	AM	AM	AM	FP	OK	OK	OK	OK	OK	OK
Kauri	M	X	X	X	X	X	X	X	X	HM	X	OK
Pontianac	A	X	X	X	X	X	X	X	X	G	X	G
Manila	X	X	X	X	X	X	X	X	X	X	X	G
Shellac ^c	X	X	X	X	X	X	X	OK	OK	OK	X	OK

^a Evidently contains small amount of rosin oil (hydrocarbons).
^b Almost completely dewaxed.
^c Bleached, waxfree.

that the nitrocellulose and resin are not miscible in all proportions. Neither is precipitated. If this were true the precipitated materials would settle, but no sediment is found. The lacquer, if such it may be called, separates into two phases, one containing most of the nitrocellulose, the other containing most of the resin. The lacquer appears milky at first, but if allowed to stand will separate into two perfectly transparent layers.

Consider as analogous to the ether-alcohol-water system described above, the system nitrocellulose-ester gum-Cellosolve (monoethyl ether of ethylene glycol). The Cellosolve is a solvent for both the ester gum and the nitrocellulose, taken separately. When the two solutions are mixed, a separation into two phases takes place, producing turbidity, or incompatibility, but if allowed to stand for some time the mixture exhibits two clear transparent layers.

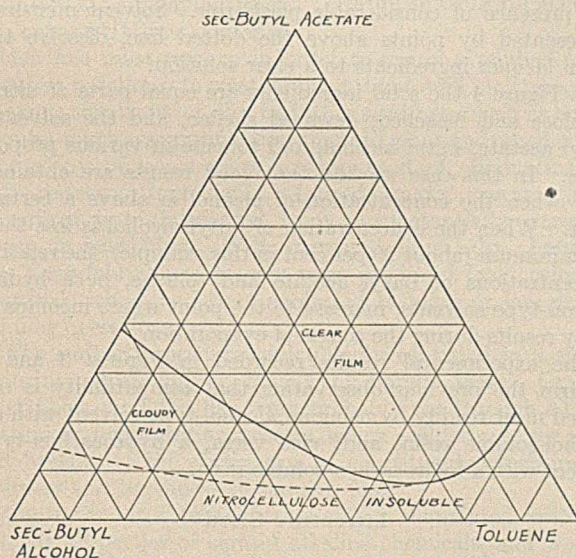


Figure 3—4 Nitrocellulose, 1 Dewaxed Dammar, 2 Plasticizer, in the System *sec*-Butyl Acetate-*sec*-Butyl Alcohol-Toluene

That the state of affairs existing in this mixture is similar to that in immiscible ternary systems of ordinary organic compounds is further demonstrated by the fact that when some of this turbid mixture is warmed to about 50° C. it becomes clear and homogeneous. It can also be cleared up by the addition of another suitable compound. It is well known that even small amounts of a fourth component materially displace the equilibrium of ternary systems. The fourth component may be another resin, but is usually another solvent, or a plasticizer, which may be considered a non-volatile solvent.

Effect of Nature of Resin and Solvent

In order to study the combinations of solvent and resin which produce clear films in the presence of nitrocellulose, the various resins and solvents have been divided into two groups—alcohol-type and hydrocarbon-type. The usual aliphatic esters are classed under the hydrocarbon-type, because they behave more like hydrocarbons than alcohols. The compounds containing a hydroxyl group are naturally classed as alcohol-type, as are the ketone solvents. Resins are classed according to their solubility in hydrocarbons or alcohols (3). Some resins are soluble in both hydrocarbons and alcohols, and in such cases the classification is made according to chemical structure or composition (4). In general, a solvent belongs to the alcohol class if it will dissolve refined shellac, and to the hydrocarbon class if it will dissolve cumar (coumarone) resin. A resin is in the alcohol-soluble class when it is almost completely soluble in 95 per cent ethyl alcohol and in the hydrocarbon-soluble class when it is almost completely soluble in toluene.

The more important solvents and resins are classified as follows:

ALCOHOL-TYPE SOLVENTS	HYDROCARBON-TYPE SOLVENTS
Ethyl alcohol	Toluene
Butyl alcohol	Xylene
Amyl alcohols	Petroleum naphtha
Acetone	Ethyl acetate
Mesityl oxide	Butyl acetates
Diacetone alcohol	Amyl acetates
Cellosolve	Butyl propionate
Cellosolve acetate	<i>sec</i> -Hexyl acetate
Butyl Cellosolve	
Ethyl lactate	
RESINS	RESINS
Shellac	Cumar
Kauri	Ester gum (rosin ester)
Pontianac	Dammar
Sandarac	Amberol resins (phenol-formaldehyde)
Manila	
Glyptal resins (Rezyls)	

By referring to the data of Table I it will be noted that when incompatibility exists in a mixture of nitrocellulose, resin, and solvent, the situation is often remedied by the addition of a solvent of the type opposite to that already present. For example, the cloudiness in a mixture of nitrocellulose, kauri, and Cellosolve (an alcohol-type solvent) can be cleared up completely by the addition of toluene (a hydrocarbon-type solvent). The same holds true to a lesser extent with resins. A lacquer made of nitrocellulose, pontianac, and Butyl Cellosolve gives a turbid or heterogeneous film, even when toluene, etc., are added to the solution. But the same lacquer will produce a clear film if some ester gum (a hydrocarbon-type resin) is added. The effect of alcohol-type and hydrocarbon-type ingredients appears to be complementary. This is not surprising, however, in view of the known effect

of alcohol and hydrocarbon mixtures on the solubility of nitrocellulose (5).

Effect of Plasticizer

Having thus examined qualitatively the incompatibility phenomena existing in certain lacquer solutions, let us consider the effect of varying the proportions of some of the ingredients, such as might take place in the actual formulation or manufacture of a nitrocellulose lacquer.

As pointed out previously, a solution containing nitrocellulose and a resin, which produces a cloudy or heterogeneous film upon drying, may be caused by the addition of a plasticizer to produce a clear and homogeneous film. That the effect depends upon the nature of the plasticizer as well as the amount added is shown by Figures 1 and 2. These charts represent graphically the behavior of various

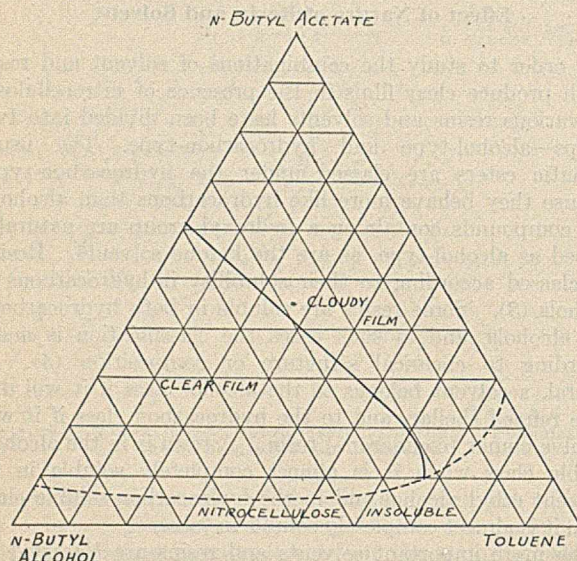


Figure 4—50 Nitrocellulose, 50 Bleached Shellac, in the System *n*-Butyl Acetate-*n*-Butyl Alcohol-Toluene

mixtures of nitrocellulose, resin, and plasticizer, all dissolved in the single solvent, Cellosolve. In both cases the resin is ester gum, and the plasticizer is dibutyl phthalate in Figure 1 and ethyl abietate in Figure 2. A test was made at each point of the chart indicated—a circle indicates that a cloudy film was produced, and a cross, a clear film. These charts show that, with this particular solvent, in order to obtain a clear film, the maximum plasticizer is required when the nitrocellulose and resin are present in approximately equal quantities, and that dibutyl phthalate is somewhat more effective than ethyl abietate in this respect.

Effect of Solvent Composition

A lacquer solution may be perfectly clear and homogeneous, but deposit a very bad cloudy film upon drying. The phenomenon familiarly called blushing is divided into three distinct kinds—the hydrocarbon blush, the moisture blush, and the gum blush. Only those vagaries of solvent compo-

sition which cause gum blush to develop in the evaporating lacquer film will be discussed here.

The development of gum blush when a clear lacquer solution evaporates is due to the widely different rates of evaporation of the solvent constituents. In the original solution the ratio of ester-alcohol-hydrocarbon (or whatever the solvents may be) is correct for obtaining compatibility between the nitrocellulose, resin, etc. But after a portion of the solvent has evaporated, it may be found that the concentration of one component, inimical to good compatibility, has greatly increased with respect to the others. Whether the component which increases in concentration—and one of them must increase except in the rare instances of constant-evaporating mixtures—is an ester, an alcohol, or a hydrocarbon depends upon the relative evaporation rates of the individuals present; and whether such an increase in the concentration of one of the solvent ingredients will cause incompatibility to develop will depend upon the nature of the resin present in the lacquer. Thus an increase in the relative concentration of alcohol as the solvent evaporates will probably cause trouble with certain hydrocarbon-type resins, and likewise an increase in the concentration of a hydrocarbon solvent will cause trouble with an alcohol-soluble resin. Examples of these two possibilities are given in Figures 3 and 4.

In Figure 3 the solid ingredients are 4 parts nitrocellulose, 1 part dewaxed dammar resin, and 2 parts plasticizer. The solvent mixtures used were composed of *sec*-butyl acetate, *sec*-butyl alcohol, and toluene, in various proportions, as represented by points on the chart. It will be seen that after the concentration of alcohol in the original solvent mixture is increased beyond certain limits, an incompatibility develops during the drying on account of the excess of alcohol, which is hostile to the compatibility of nitrocellulose with dammar (a hydrocarbon-type resin), even in the presence of considerable plasticizer. Solvent mixtures, represented by points above the dotted line, dissolve the given lacquer ingredients to a clear solution.

In Figure 4 the solid ingredients are equal parts of nitrocellulose and bleached, dewaxed shellac, and the solvents, butyl acetate, butyl alcohol, and toluene in various proportions. In this case we find that good results are obtained only when the concentration of alcohol is above a certain limit. When the concentration of butyl alcohol is less than the minimum (about 20 per cent in this example), the relative concentrations of butyl acetate and toluene, both hydrocarbon-type solvents, increase to the point where incompatibility results during the course of evaporation.

The experimental results recorded in Figures 3 and 4 confirm the previous observation that compatibility is obtained most readily by using an alcohol-type solvent with an alcohol-soluble resin, and, vice versa, a hydrocarbon-type solvent with a hydrocarbon-soluble resin.

Literature Cited

- (1) Brown and Crawford, "Survey of Nitrocellulose Lacquer," p. 9 (1928).
- (2) *Ibid.*, p. 19.
- (3) Calvert, *IND. ENG. CHEM.*, **21**, 213 (1929).
- (4) Hofmann and Reid, *Ibid.*, **21**, 955 (1929).
- (5) Hofmann and Reid, *Ibid.*, **20**, 687 (1928).

The Sugar Situation in China—The latest reports state that there are ten sugar refineries and six sugar factories in China, the great bulk of the sugar being made by small mills employing crude processes. The three qualities are green (dark brown), brown (light brown), and white. The sugar is dark brown as it comes from the brewing vats and is bleached by exposure to the sun. The green and brown varieties are only slightly bleached, and the white is subjected to an extended bleaching process.

The five kinds of sugar imported into China are brown, white, refined, cube or loaf, and rock or sugar candy. The brown sugar is mixed with native sugar and also goes into cheap confectionery, to bakers, and to native doctors. The white sugar is used in the better-class households and for higher-priced candies, cakes, and pastries. Sugar candy is imported in sacks and is repacked into cartons and tins upon arrival and is in high favor as a gift.

Purified Wood Fiber¹

A Study of the Physical and Chemical Properties

Geo. A. Richter

BROWN COMPANY, BERLIN, N. H.

SINCE early times man has endeavored to extend his use of cellulose and cellulose products. Centuries ago he discovered that he could, by suitable maceration of fiber and possibly by some extraction of undesirable constituents, convert plant materials into sheets of interfelted fibers, which might serve as paper, textiles, and the like. He later found that some plants yield more favorably than others to this conversion process and that a suitable modification in the process would in many cases result in characteristic differences in the product.

Later he learned that all plant tissues consist in general of a fibrous constituent of marked durability, together with an accompanying mass of cementitious material

which one must remove in order to secure a product of the greatest resistance to weather, heat, light, and moisture. He became cognizant of the fact that seed hairs such as cotton require much less purification than do grass and wood fibers. For many purposes there was no need of eliminating the less resistant ingredients. Indeed, many coarse textile coverings were fabricated from a substantially unrefined grass or bast fiber. With increased knowledge, however, the finer fabrics and papers were produced from cellulosic materials which had been subjected to more or less drastic refining operations.

The earliest procedure undoubtedly consisted in a simple scouring, steaming, or boiling of fibrous mass. Grasses, bast fibers, and the like were probably put through a crude retting or fermentation process, which yielded a softer product because of the elimination of constituents which impart stiffness and harshness to the raw fiber.

Centuries later technicians became acquainted with the solvent properties of certain alkaline chemicals, and worked out ways of using such chemicals advantageously. It became evident that hot alkaline solutions have the power of partly removing undesirable impurities such as waxes, resins, and semi-cellulose groups without severe injury to the cellulose itself. This general principle of purification of cellulosic material is obviously based on the fact that a virgin, ungraded cellulose is very resistant to alkalis, and that much of the non-cellulosic material will be partially solvated in alkali at elevated temperatures.

The increasing knowledge of chemical behavior quickly led to the utilization of raw materials which had not previously been used for textiles or papers. The known treatments were applicable only to raw products of the grass, bast-fiber,

An understanding of the significance of purified wood fiber in modern industry demands a brief review of the successive advances made in the cellulose field since early times. The present article suggests the reasons for each step in this progress toward the preparation of highly purified cellulose products from other sources than cotton. The tests which are used to characterize cellulose products are interpreted and tables are submitted to illustrate differences in chemical analysis of cellulose which has been prepared from various raw materials. Succeeding articles in the series will extend the study of those characteristics which have differentiated cotton from ordinary wood pulps and which have given cotton its unique position in the cellulose industry. Experimental evidence will be submitted to show that these dissimilarities are only superficial and that notable advance has been made in the preparation of wood celluloses which have characteristics supporting the generally accepted theory that all natural cellulose, from whatever source, is fundamentally the same, and that the differences in physical and chemical properties of the ordinary wood pulps and cotton may be attributed to the relative crudeness of the methods employed for isolation of cellulose from its accompanying impurities.

as lignin, wood gums, and the like.

The discovery of the value of alkali for this purpose immediately suggested the utilization of natural resources of unlimited and ever renewed abundance, and for this reason marks the beginning of a new epoch in the cellulose industry.

The pulping of wood by means of alkali results in the product known technically as soda pulp. Until quite recently soda pulp was produced chiefly by the alkaline digestion of short-fibered, deciduous woods. This restriction was based upon the observation that a soda pulp produced from the longer-fibered, coniferous wood was brown and very difficult to bleach to a fair degree of whiteness, whereas the pulp obtained from most deciduous woods could be brought to a reasonably high degree of whiteness and could therefore be used in white or light-colored papers in mixture with cotton or linen. Soda pulp was originally produced almost wholly from aspen and poplar wood, although certain grades of birch, beech, and other hardwoods are now being used successfully. All these woods yield a short-fibered pulp.

Inasmuch as it is almost impossible to produce a paper of suitable physical strength from a furnish comprising a soda pulp alone, this product was and still is used mainly to cheapen the furnish of rag papers and to impart certain modifications in texture, softness, and feel, which characteristics are more difficult to obtain with the long-fibered cotton alone.

Of late certain major developments in the wood-pulp industry have led to alkaline pulping processes which allow the preparation of a somewhat more easily bleachable pulp from the long-fibered coniferous woods. It is still very difficult, however, to secure maximum whiteness of fiber without extreme sacrifice in the physical strength of papers produced therefrom, except by specially developed refining processes which will be discussed in subsequent articles in this series.

and seed-hair families. In spite of the abundance of wood, practically no use had been made of it for textiles or paper, since the crude retting and macerating treatments were not able to liberate fiber from the dense and heavily lignified wood substances.

Soon after caustic soda became available in commercial quantities the use of alkalis in the cellulose industry became widespread, not only in preparing cotton and linen for textiles, but also in the paper industry, where caustic soda was employed in the treatment of cotton and linen rags prior to conversion into paper. Somewhat later it was used to liberate cellulose fibers from solid wood material by reason of its solvent action on a major portion of the cementitious matter which we now classify

¹ Received December 19, 1930.

In 1866 there was a second discovery and development which added further impetus to the utilization of chemical wood pulps in the paper industry. Benj. C. Tilghman discovered the solvent action of sulfites on lignin and C. D. Ekman assisted in the development of what is now known as the sulfite process.

Sulfite groups react more readily with lignin when in the presence of acids. This fact resulted in a preference for the bisulfite or acid sulfite solutions for pulping wood. Such acid sulfite solutions remove both lignin and wood-gum groups more effectively than do sodium hydroxide solutions, as is evidenced by the lower temperatures needed in the bisulfite process and also by the fact that many coniferous woods can be converted into sulfite pulps which are easily bleached to high whiteness.

If a soluble sulfite is used in the absence of acid, much higher temperatures are necessary to effect fiber isolation. The resulting pulps contain a higher proportion of lignin and wood gum and they require larger amounts of oxidant for conversion into white products.

The past forty years have witnessed great strides in the paper industry, partly as a result of the introduction of sulfite pulp. Such a comparatively long-fibered white stock as could be obtained by the sulfite process from coniferous woods opened up possibilities which were quite unknown before. The sulfite pulps yield readily to hydration and because of length of fiber can be converted into satisfactory paper without the addition of rag or linen stocks; or they may be employed as a part of the furnish in a great variety of papers where color, strength, and cleanliness are essential.

It is very evident that, as the knowledge of the chemistry of wood and other raw cellulosic materials has grown, there has been a continued effort to utilize all types of plant substances and to improve the quality of the liberated fiber by changing the methods of eliminating the non-cellulosic constituents which are present in the natural state.

Some investigators have had in mind primarily the improvement of fibers for paper-making; others were interested especially in the development of cheap and abundant raw materials for cellulose esters—for instance, during the war, cellulose nitrate. It is obvious that the requirements of these two major fields of use may not coincide in any particular; but as a matter of historical fact the two fields have actually overlapped to a surprising degree. Paper-making and esterification will be discussed separately in this series of articles, not because of any fundamental difference of viewpoint, but simply for the sake of convenience.

Identification of Natural Cellulose

In the plant world cotton occupies a unique position. It is representative of a raw material which in its natural state is very high in cellulose and from which the non-cellulosic impurities can be removed quite easily and completely. A long-staple cotton contains comparatively small amounts of impurities, as illustrated by the analysis given in Table I. All other plant products are lower in cellulose content, and it is usually correspondingly more difficult to isolate cellulose which shall be comparatively free from non-resistant cellulose, pentosan groups, oxycellulose, and lignin. Table I typifies the differences in analysis of various plant materials.

It is to be noted that, while cotton appears to be in a class by itself, wood, in its various species and types, exhibits wide variations in the proportions of impurities accompanying the cellulose.

Because of the relative absence from raw cotton of non-cellulosic constituents, there has been no great problem in its refinement to a product of high purity. This is strictly true only in those cases where the long-staple raw fiber is purified directly; it is more difficult to refine short-fibered

cotton such as linters, which are richer in impurities. Neither is the refining process necessarily simple in case the long-staple cotton has been converted first into fabric and cordage and is to be re-used for chemical or paper-making purposes. Most textile operations deposit characteristic impurities in the form of waxes, sizing, and color, which are more or less firmly fixed on the fiber and which resist the action of chemical refining agents. It evidently follows that, since most cotton enters the paper and cellulose-esterification industries either by first passing through the textile stage or else directly as the relatively impure linters, the refinement of cotton for paper and for chemical conversion offers more difficulties than are at first apparent. Even so, however, this refinement is in many cases less difficult than when wood substance is employed as a base material.

Table I—Analysis of Raw Cotton and Various Woods^a

	PENTOSANS	LIGNIN	CCl ₄ EXTRACTABLE
	%	%	%
Raw cotton	1.18	1.7	0.62
White spruce	9.3	30.0	{ 0.8 (sapwood) 0.65 (heartwood)
Yellow poplar	23.7	27.0	
White birch	29.1	28.0	{ 1.16 (sapwood) 1.52 (heartwood)
Slash pine (southern)	5.16	32.3	1.21 (composite sapwood and heartwood)
Loblolly pine (southern)	5.35	31.5	1.08 (composite sapwood and heartwood)
Western hemlock	7.2	33.9	..
Eastern hemlock	12.0	34.5	..
Douglas fir	6.3	37.6	..
Eastern fir	12.2	34.3	..
Beech	22.4	33.4	{ 0.27 (sapwood) 0.28 (heartwood)
Sugar maple			{ 0.2 (sapwood) 0.23 (heartwood)

^a Total cellulose determinations of wood substance have been omitted because of inconsistencies in laboratory results. The author prefers to postpone publication of total cellulose values of wood substance until more reliable data can be obtained. Miscellaneous findings from other laboratories are given in "The Chemistry of Wood," by L. F. Hawley and Louise E. Wise, 1926.

An ideal purification of cellulose would completely eliminate non-cellulose groups and would cause no chemical or physical injury to the cellulose itself. Such a perfect treatment has never been realized. The known chemical refining agents remove non-cellulose constituents more or less effectively, but in no case does the elimination take place without some unavoidable injury to the cellulose. This partial degradation may be evidenced in many ways, such as by change in fiber structure, by the formation of so-called "hydrocellulose," or by a marked change in the viscosity of its cuprammonium solution. It is this secondary effect on the cellulose itself which makes it more difficult to procure uninjured cellulose from a cotton fabric or rag than from the virgin fiber. The same difficulty is encountered when wood substance is converted into pulps or fiber of substantial purity.

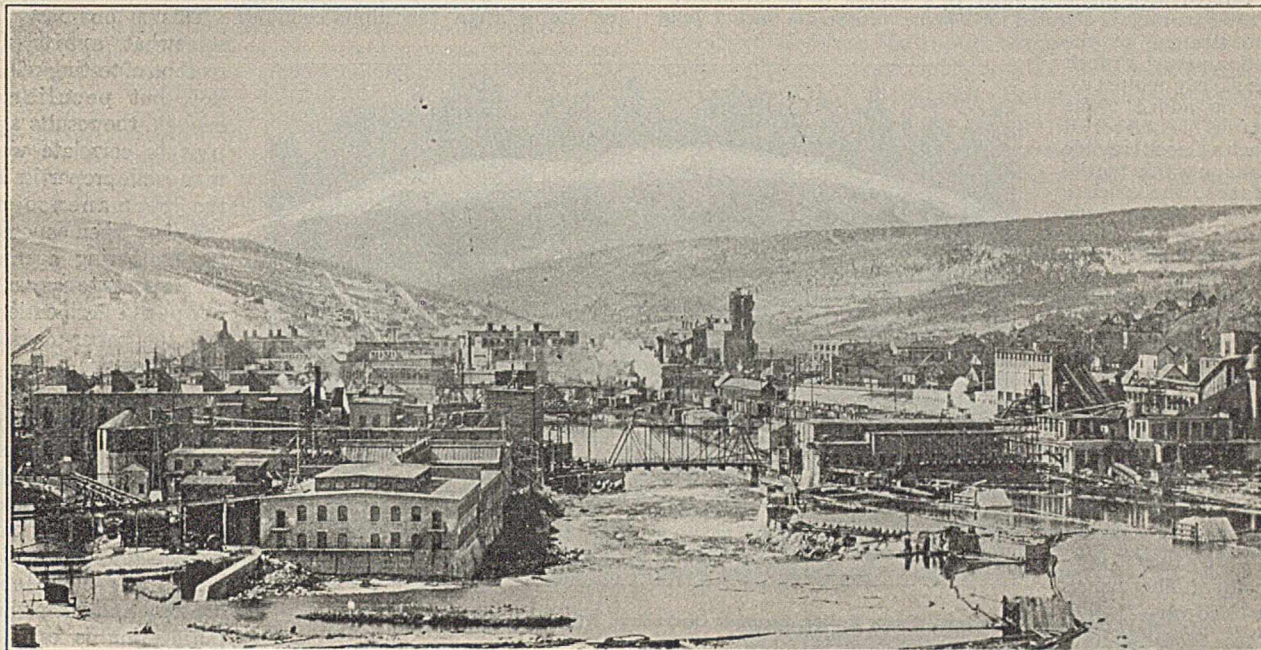
With proper care it is possible to select a refining sequence in which there is, first, a major removal of impurities without a drastic degradation of cellulose and, second, a final removal of residual impurities and of such degraded cellulose as was unavoidably formed in the first stages of treatment. If, however, the delignification at any stage has been sufficiently drastic to effect profound changes in the cellulose, it is practically impossible to restore the natural cellulose characteristics, because such a severe preliminary treatment usually affects the fiber structure in a marked manner.

Schorger (1) has recently summarized some of the procedures which have been recommended for the purification of wood pulps to contain high percentages of alpha-cellulose. When the purification steps are practiced on a sulfite pulp, the treatment may involve a partial delignification of the raw fiber by means of chlorine or its equivalent, and a subsequent digestion with an alkaline liquor which at elevated

temperatures will remove part of the non-alpha-cellulose constituents. To obtain a final white product it is often necessary to bleach the alkaline-treated stock with hypochlorite under carefully controlled conditions. The procedure may be varied considerably depending on the characteristics of the original fiber and upon the qualities desired in the finished product.

ments. Even where there is no evidence of accompanying impurities, the cellulose thus isolated may itself have undergone profound changes, as manifested by reduction in cuprammonium viscosity and change in fiber structure.

Method. The method used for the determination of total cellulose is a modification of that of Cross and Bevan ["Cellulose," p. 95, Longmans, 1916], in which is employed the crucible and



Brown Company Mills with White Mountains in Background

Units of Characterization

The degree of purity of a cellulose product may be expressed in many ways. The units by which this purity is measured depend usually upon the viewpoint of the investigator and upon the use for which the cellulose is intended.

Oftentimes the cellulose is defined indirectly in terms of physical and chemical behavior rather than by actual percentage composition. As examples of this type of evaluation, one may cite the permanence tests used to determine the probable life of papers and also the standardized esterification procedures which are employed in expressing the worth of a fiber for conversion into acetates, nitrates, and the like. In the remainder of this article the most important tests which are accepted as measures of the relative value of cellulose products will be defined briefly. No special effort will be made to point out the full import of such tests as they are applied in different fields of the cellulose chemical industry. A more complete interpretation will be given as specific cases arise.

Chemical Tests

TOTAL CELLULOSE—The total-cellulose content of a product represents that portion which resists the solvent action of successive treatments with chlorine and hot sodium sulfite solutions. The resulting residue may contain appreciable amounts of impurities which have also resisted the action of the refining agents, and in some cases contains degraded cellulose which is formed by hydrolysis or otherwise. A low total-cellulose content will obviously signify the presence of large percentages of impurities in the original fiber, but a high total-cellulose value is not always indicative of a high degree of purity. Resins, insoluble ash, and pentosan groups are not always removed effectively by this sequence of treat-

carbon filter used in the modification of Sieber and Walter [Schorger, "Chemistry of Cellulose and Wood," p. 514, McGraw-Hill, 1926]. Groundwood samples are first extracted with benzene-alcohol (32 parts alcohol and 68 parts benzene) for 6 hours, dried by suction, and washed with hot water. Kraft and other unbleached pulps are given, as a preliminary treatment, a 30-minute boil with 1 per cent sodium hydroxide solution (1 gram bone-dry pulp), and are then filtered into the chlorination crucible and washed with hot water. In the case of bleached pulp no pretreatment is necessary, so that a test portion representing 1 gram of bone-dry original material is placed directly in the crucible and moistened. Washed chlorine gas is drawn through the crucible for 30 minutes. The pulp is washed with warm water, treated for 3 minutes with a 25-cc. portion of boiling 2 per cent sodium thiosulfate solution, and then rewashed with warm water using suction. The residue is then treated with 25 cc. of 0.1 per cent potassium permanganate solution for about 2 minutes and after washing is decolorized with 25 cc. of cold sulfurous acid solution. After washing well with cold water, the pulp is rechlorinated for 15 minutes and is retreated as before. The residue is then rechlorinated for one or more additional 15-minute periods each, followed by washing treatments until the residue is white. In the case of bleached pulps a single 1-hour chlorination period is given, this being followed by the treatments and washings as outlined above. The residue is dried to constant weight at 105° C. and the results reported as per cent total cellulose based on bone-dry original material.

LIGNIN—Lignin is that part of a cellulosic material which resists the solvent action of 72 per cent sulfuric acid under carefully prescribed conditions. It is assumed that all the cellulose will be hydrolyzed and converted into soluble products by this treatment. Suitable correction is made for the mineral content of the residue. The lignin content of a given type of fiber correlates well with the bleachability of the fiber, although this measure of bleachability cannot be applied indiscriminately to all types of cellulose. As an example, it is well known that a sulfite pulp of lignin content equal to that of a corresponding kraft pulp can be bleached

to whiteness by the use of less oxidant than the kraft pulp would require.

Method. Approximately 1 gram of bone-dry fluffed pulp is weighed accurately and placed in a 400-cc. beaker. Twenty cubic centimeters of 72 per cent sulfuric acid are added and the mass is well mixed with a stirring rod. After a 15-minute standing period 70 cc. more of the acid are added and the mixture is stirred and set aside for a period of 18 to 24 hours. It is then diluted with distilled water to a volume of about 375 cc. and, after stirring, is digested for 2 hours on a steam bath. Just before the end of the digestion period a pinch of previously ignited asbestos is added. The mixture is filtered through a Gooch crucible containing a thin mat of asbestos, the crucible and mat having been previously ignited. After the mixture has been thoroughly washed with hot, distilled water, the crucible and contents are dried to constant weight at 105° C. The crucible is then ignited, cooled in a desiccator, and reweighed. The loss in weight upon ignition is calculated as ash-free lignin.

PENTOSANS—Pentosans are those constituents in fiber which upon hydrolysis yield pentoses. A cellulose, on the other hand, will hydrolyze to produce hexoses or, more specifically, dextrose. In the analysis the pentosans are converted by hydrolysis to pentoses and finally to furfuraldehyde, which is determined by precipitation and calculation. In some instances the methyl pentosans are determined separately.

Differences in amount of pentosan present reflect differences in both the physical and the chemical behavior of the fiber. From the standpoint of cellulose purity alone the pentosan groups must be considered as impurities. In many cases, however, the pentosans are highly desirable constituents and impart characteristics which make the fiber peculiarly suitable for certain purposes; pentosan-free cellulose would not serve in these cases at all. For example, the semi-transparent Glassine papers and the strongest kraft papers possess their characteristic transparency or strength by virtue of the pentosans present in the pulp. Pentosans are often objectionable in cellulosic materials which are intended for esterification. For example, there appears to be evidence that the presence of pentosans interferes with the proper acetylation of cellulose.

All types of raw wood fiber contain substantial quantities of pentose-forming groups, whereas raw cotton contains less than 1 per cent of pentosans. Ordinary wood pulps contain from 3 to 12 per cent. Purified wood pulps may be prepared under conditions which will yield a product containing less than 1 per cent pentosans. The refinement may also be carried out in such a way as to leave a somewhat higher percentage, so as to meet particular requirements in the paper field.

Method. The method for pentosans determination is that of the Association of Official Agricultural Chemists [Methods, pp. 96-7 (1920)] with the following exceptions: A sample of exactly 2 grams of bone-dry material is used and the distillation carried out in a 500-cc. flask. A total volume of 270 cc. is distilled over; after the addition of the acid solution of phloroglucinol the volume is made up to 400 cc. with 12 per cent hydrochloric acid

solution. The mixture is heated on the water bath at 80-85° C. for 2 hours and is then allowed to cool to room temperature. The weight of phloroglucinol obtained times 0.785 is taken to be the amount of pentosans present in the 2-gram sample.

ALPHA-CELLULOSE—Alpha- or resistant cellulose is that portion of a fiber which is not dissolved by exposure to 18 per cent sodium hydroxide solution at normal temperature. It is generally assumed that the portion which dissolves is less stable than the alpha-cellulose. This is obviously a

somewhat arbitrary method of testing cellulose, but peculiarly enough, the results appear to correlate well with such properties as the permanence of cellulose when exposed to weathering agents, the response to easy and proper esterification, and the paper-making characteristics.

Cotton, when properly purified, may be very high in alpha-cellulose content. Other raw materials, such as wood fiber, can be refined to an equally high alpha-cellulose content, and when this purification is carried

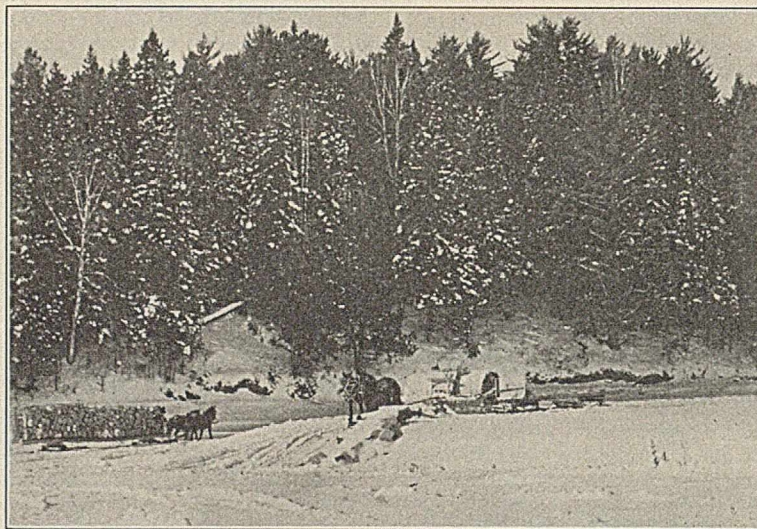
out properly the product appears to equal cotton as a paper-making furnish and as a basic material for esterification. On the other hand, many chemical treatments, the most potent of which are oxidation and hydrolysis, are able to degrade either cotton or wood fiber, originally high in alpha-cellulose, to products which are comparatively low in alpha-cellulose. When this occurs, the fiber undergoes major changes in its physical and chemical properties.

As in the case of total cellulose, one must guard against unintelligent interpretation of the alpha-cellulose determination. To appreciate this caution one need only consider a case in which a groundwood fiber is thus treated. The residues will contain a large proportion of lignin and will not represent a true alpha-cellulose value.

BETA-CELLULOSE—Beta-cellulose is that part of the dissolved fiber which will be reprecipitated when the 18 per cent caustic soda extract from an alpha-cellulose determination is treated with acid. This arbitrarily classified ingredient is also very indefinite in character. The recovered precipitate may on further examination show the presence of such groups as pentosans, resins, and lignin, which may have been partly removed from the original fiber and which are reprecipitated to some extent when the alkaline extract is acidified.

In a material which is low in lignin content a high beta-cellulose value points strongly to the presence of hydrolysis products. A weak, hot acid treatment of cotton or purified wood fiber will reduce the alpha-cellulose and raise the beta-cellulose content very markedly. Oxidation of cellulose, unless carried out under strongly alkaline conditions, will usually result in greater changes in gamma-cellulose than in beta-cellulose.

GAMMA-CELLULOSE—Gamma-cellulose is that portion of the 18 per cent sodium hydroxide extract which does not precipitate when the liquor is acidified. This percentage varies. It appears to be mostly dependent upon the presence of oxidation products in the original fiber. Whereas the



Snow Roller, Lumber Operation, Richardson Lake, Maine

beta-cellulose content may for some requirements be purposely raised, as in the preparation of a base material for low-viscosity nitrates, the gamma-cellulose appears to have no value and is to be avoided in all cellulose products.

Method for Alpha-, Beta-, and Gamma-Cellulose. The pulp material in the form of loose shreds or of $1/4$ - to $3/8$ -inch (6- to 9-mm.) squares cut from thin sheets is allowed to become air-dry. A 10-gram portion is divided into two exactly equal parts, the division being made with the parts each resting upon one of the pans of an analytical balance. One part is dried to constant weight at 105°C .; its bone-dry weight represents the amount of sample taken for the alpha-cellulose determination. The other part is placed in a 400-cc. beaker. To it are added from a pipet 50 cc. of 18 per cent sodium hydroxide solution at 20°C . The mixture is washed with the flattened end of a glass rod until complete disintegration has taken place. After adding 50 cc. more of the 18 per cent caustic solution and stirring well with the rod, the beaker containing the mixture is set into a water bath maintained at 20°C . and is allowed to stand for 30 minutes from the time the first portion of caustic reached the pulp.

A disk of new nainsook cloth is dried at 105°C . and is weighed in a weighing bottle. The weighed cloth is then fitted into a 4-inch (10-cm.) Büchner funnel, the funnel placed in a clean filter flask, and the flask connected to a suction apparatus with a Y-connection provided so that the suction can be conveniently released or applied. At the expiration of the 30-minute period 300 cc. of distilled water at room temperature are added to the caustic-pulp mixture in the beaker and the whole mass is well mixed. The contents of the beaker are washed quantitatively into the funnel, the pulp mass is spread evenly over the cloth, and suction applied. The edges of the pad are pressed down with a stirring rod. The pad of pulp formed upon the cloth is not disturbed during the remainder of the procedure. The pulp mat is washed with 1 liter of distilled water at room temperature in several portions, the suction being relieved before each addition of water. Finally, a solution of 20 cc. of glacial acetic acid in 80 cc. of water is poured over the pulp, allowed to stand for a few moments, and then drawn off. The filtrate and washings are transferred at this point to a 2-liter beaker and are set aside for the determination of beta-cellulose. The pulp mat is then washed with 1 liter of boiling distilled water in several small portions, is drawn as dry as possible with suction, and is dried in the oven to constant weight at 103 – 105°C . The hot-water washings are discarded. The weight of the residue, corrected for the weight of the cloth, is calculated as per cent alpha-cellulose, based on the bone-dry original material.

The filtrate from the alpha-cellulose determination is acidified with acetic acid and is heated without active boiling for 1 hour. A pinch of previously ignited asbestos is added and the suspended matter filtered off into a Gooch crucible which has been previously ignited and which contains a thin mat of asbestos. The crucible and contents are dried to constant weight at 105°C ., weighed, ignited, and reweighed. The loss in weight is calculated as per cent beta-cellulose based on the original bone-dry sample.

The sum of the alpha- and beta-cellulose percentages is subtracted from 100 per cent and the difference reported as gamma-cellulose.

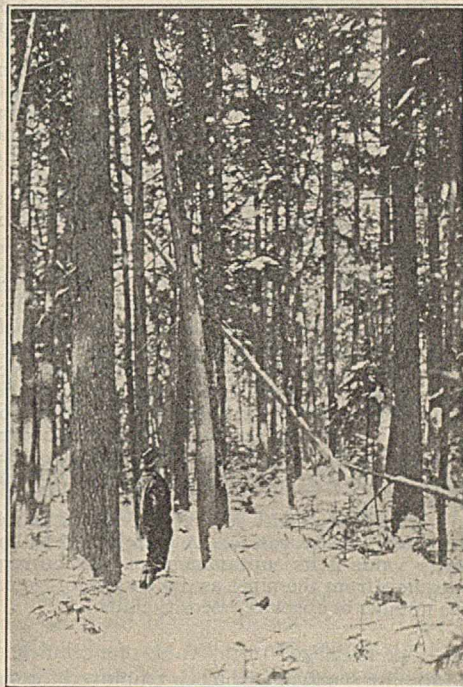
7.14 PER CENT SODA-SOLUBLE—Some investigators prefer to measure non-resistant cellulose by a treatment of the fiber with a boiling 7.14 per cent sodium hydroxide or a boiling 10 per cent potassium hydroxide solution. This test has often been considered to be equivalent (inversely, of course) to the alpha-cellulose determination. In some cases the two tests may correlate reasonably well, but this is not necessarily so. It is easily possible to prepare cotton or wood cellulose which will have a sum total of alpha-cellulose and 7.14 per cent soda-soluble well over 100 per cent. A normal bleached sulfite pulp is an example of such a product. High soda-solubility is usually accompanied by a high copper number, but the alpha-cellulose content of the fiber may be high at the same time; for instance, it is possible to bleach or oxidize a cotton or wood fiber which is high in alpha-cellulose in such a manner as to give a high soda-solubility and copper number without materially reducing the percentage of alpha-cellulose.

Method. The procedure followed is that given by D. F. J. Lynch [IND. ENG. CHEM., 22, 952 (1930)] and described by him as "the determination generally used by cellulose nitrators."

A 25-cc. excess of acetic acid was employed and the undissolved cellulose collected upon an asbestos mat placed in a Gooch crucible.

COPPER NUMBER—The copper number of a pulp is simply a measure of its power to reduce Fehling's solution. In general, either mild oxidation or mild hydrolysis of the cellulose—the former producing the so-called oxycellulose, the latter, hydrocellulose—will increase its reducing power and hence its copper number. It is possible, however, actually to decrease the copper number by a controlled oxidation of the cellulose under suitable conditions. Acid oxidizing agents raise the copper number much more markedly than alkaline ones, possibly because the alkaline agent progressively dissolves the oxycellulose as it is formed; or the acid oxidant may exert a hydrolytic as well as an oxidizing effect.

Method. A 3-gram sample of bone-dry shredded pulp is placed in a 1.5-liter round-bottomed flask, a water-jacketed reflux condenser is attached to the flask, and the pulp suspension quickly brought to the boiling point. Portions of 50 cc. each of copper sulfate solution (69.3 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals, c. p., dissolved and made up to 1 liter) and alkaline Seignette solution (346 grams c. p. sodium potassium tartrate dissolved and made up to 1 liter) are separately brought to the boiling point in small beakers. The two boiling solutions are mixed and the mixture at once poured through the condenser tube and into the boiling pulp suspension. The liquid is kept actively boiling for exactly 15 minutes and is then filtered through a small Büchner funnel provided with a mat of asbestos. The residue on the filter is washed free from cupric copper with hot water. The filter mat with the collected material is returned to the flask, 50 cc. of 6.5 per cent nitric acid are added, and the mixture is brought to the



Timber Stand, Richardson Lake, Maine

boiling point. As soon as all the cuprous oxide has been dissolved, the mixture is poured through the Büchner funnel into a clean suction flask. The first filtrate is returned through the filter mat. The copper solution is evaporated to a volume of about 100 cc., cooled, neutralized with ammonium hydroxide, and acidified with a slight excess of acetic acid. Five grams of potassium iodide are then added and the liberated iodine titrated with 20 *N* sodium thiosulfate using starch indicator. In case the end point has not appeared when so much as 25 cc. of the thiosulfate has been added, 2 or 3 grams more of the iodide are added and the titration continued. The copper number is the number of grams of copper reduced by 100 grams of bone-dry pulp.

VISCOSITY—Cellulose may be characterized by the viscosity of its solution in cuprammonium hydroxide, prepared under carefully prescribed conditions. This determination is of great interest in controlling the preparation of cellulose esters. The test is sometimes regarded as a measure of the size of the molecular or micellar units. It is, however, seriously affected by the presence of hydrolysis or oxidation products, which often confuse the interpretation of viscosity figures. It is readily seen that a low-viscosity result may in reality connote a mixture of fibers of very low and very high viscosity—such a mixture as may be formed by a selective reaction on surface portions of fiber during a treatment or, more simply, by blending two components. The viscosity of fiber does not necessarily correlate with alpha-cellulose content, nor does it follow that a cellulose high in soda-soluble constituents is correspondingly low in viscosity. Some reagents will simultaneously effect a decrease in viscosity and an increase in alpha-cellulose content—for instance, a treatment with mercerizing caustic soda solution. High temperature or acid conditions are also conducive to the reduction of viscosity. Possible correlation between viscosity and permanence of fiber will be discussed later in this series of papers.

Method. The sample is slushed with distilled water until a smooth suspension is obtained. The suspension is poured into a 5½-inch (14-cm.) Büchner funnel fitted with a piece of nainsook cloth. After removing as much water as possible with suction, the suction is released and 150 to 175 cc. of redistilled acetone are poured over the pulp mat and then drawn off. The pad is dried by passing through and around it a current of air warmed to 105° C. It is then fluffed in a metal can, 5½ inches (14 cm.) in diameter and provided with a fiber-board cover, using as a disintegrator a star-shaped piece of 1/16-inch (1.6-mm.) brass, 2½ inches (6.4 cm.) in diameter and turned by means of a direct connected motor at from 5000 to 6000 r. p. m. The fluffed pulp is dried for 20 minutes at 103–105° C.

A 6-gram portion of bone-dry fluffed pulp is weighed out and is added to a 300-cc. Erlenmeyer flask together with 9 grams of so-called "copper hydrate" powder. The "copper hydrate" is in reality basic copper nitrate corresponding in composition to the formula $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$; it must contain less than 1 per cent water-soluble matter and less than 0.4 per cent moisture. After mixing the pulp and copper hydrate powder in the dry state, 225 ± 0.5 cc. of 28 per cent ammonia solution are added, the flask is stoppered and is shaken vigorously in a mechanical shaker for 800 strokes over a 2-minute period. The flask is then placed in a water bath kept at 25° C. for a period of 28 minutes from the time shaking was commenced. The cuprammonium solution is blown up into the pipet by means of air pressure. The flow from the pipet is started at exactly 30 minutes from the time shaking was started. The outflow time is converted into viscosity units by reference to the pipet calibration curve.

The pipet used is of the regular 100-cc. glass volumetric-apparatus type. Before calibration and use the constricted tip is cut off and the cut end fire-polished. In use the pipet is inverted so that the lower end is the one originally intended to be the upper.

The pipet is calibrated with several glycerol-water solutions of known absolute viscosity values. A pulp is said to have a certain viscosity value if its cuprammonium solution requires the same time to flow from the pipet as did a glycerol-water solution of the same number of absolute viscosity units.

RESINS—The so-called "resin" value of a cellulose is largely dependent upon the solvent which is employed for the extraction. Ether, acetone, carbon tetrachloride, and alcohol extract unequal amounts of soluble material. The relative amounts which each of these solvents can remove vary with different raw materials and are undoubtedly related to the character of the resins and waxy groups which are present in the fiber. In some instances the solvent will remove water-soluble constituents, and even a hot-water extraction will remove material which can also be collected by solvent treatment. In the work which is discussed in these articles, no great emphasis is placed on the solvent-soluble material, although there are included some values obtained by the use of carbon tetrachloride.

Determination. A 10-gram sample of bone-dry shredded pulp is extracted completely in a Soxhlet extractor using carbon tetrachloride as a solvent. The extract is evaporated to dryness at 100–103° C. and the weight of extracted material determined.

Paper-Making Tests

FIBER DIMENSIONS—Although there are well-known and generally satisfactory methods for determining the average fiber length of a sample of pulp, the results thus far have not had any great significance to the paper maker. No doubt this is mainly because the mechanics of even the simplest strength test of paper is so imperfectly understood. It has generally been assumed that increased length of fiber means increased physical strength of the paper which can be produced therefrom. This assumption becomes an absurdity unless duly limited. It is true that a paper of high tearing strength cannot be made from a very short fibered pulp. On the other hand, extremely long fibers cannot be successfully incorporated in a sheet, since they must be deliberately reduced in length by cutting and by beating in order to secure a paper of reasonably good formation and appearance. One rarely finds fibers exceeding 4 mm. in length in any except very special papers. The proportions of fibers of different length present in a pulp possibly play a part in the properties of the paper which can be made from it, but as yet no quantitative relationship has been found.

Fiber thickness and shape are also practically unknown influences in paper-making. The "brooming" or fraying of fiber during the beating operation appears to be of much greater significance.

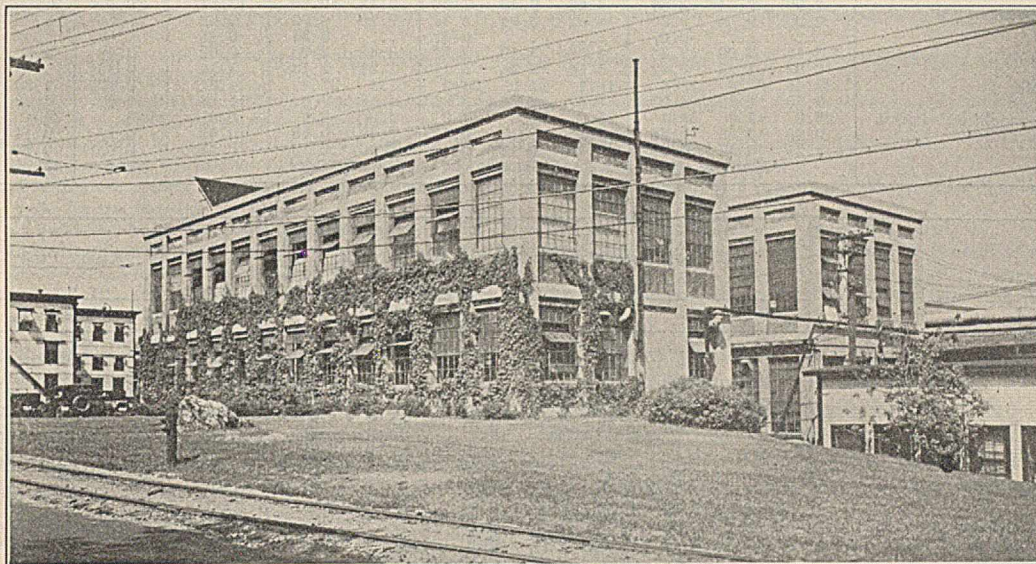
Fiber Length Determination. A representative portion of the sample is disintegrated in water to a smooth suspension which is diluted so that a drop from a standard dropper (a glass tube with a 4-mm. opening) will contain approximately twenty-five fibers. The desired concentration will be about 0.38 gram of pulp per liter. Eight drops of the well-agitated dilute suspension are separately transferred to glass slides, the drops are dried down by placing the slides in a cabinet through which is flowing a current of warm air. Each slide, in turn, is placed upon the platform of a dissecting microscope. A drop of standard iodine-calcium chloride solution is placed upon the fibers. The standard solution is prepared by mixing 15 parts of a solution of 59 grams calcium chloride in 100 cc. of water with 1 part of a solution of 21 grams potassium iodide and 1 gram of iodine in 50 cc. of water; the mixed solution is allowed to stand for 24 hours and is then decanted into a dark glass bottle. The surplus stain upon the slide is decanted from the fibers, care being taken that no fibers are lost in the operation. With a pair of dissecting needles every fiber on the slide is straightened out and is drawn towards the middle of the slide. The fibers are arranged so that they lie side by side and parallel to the longer side of the slide; they are then covered with a glass and the edge of the cover glass is wet with a small amount of the stain. The prepared slide is then mounted on the mechanical stage of a compound microscope provided with a filar micrometer and a 16-mm. objective. The micrometer reading is recorded for the length of each of two hundred separate fibers. The total of the micrometer readings multiplied by the micrometer factor (converting readings into millimeters) and divided by 200 gives the average fiber length of the pulp in millimeters.

HYDRATION—The paper-making properties of cellulose may be attributed to its behavior in water, which is quite different from the behavior of wool, silk, or hair. The exact mechanism of hydration by beating is not fully understood, but regardless of theory it is an established fact that if a normal cellulose is subjected to a rubbing or pounding action in the presence of water the fiber swells and then becomes slippery or slimy; in this condition the beaten stock will retain water tenaciously. It is still a debatable point whether this change takes place because of an increased surface of fiber exposed or because of a partial loosening of fiber structure; at any rate, hydration is evidently a special case of the solvation of a colloid, complicated by the fact that the latter has an organized structure.

Different types of cellulose will hydrate at different rates and to different degrees. Certain forms, such as mercerized fiber and regenerated cellulose, resist hydration to such an extent as to be considered useless as paper-making material (2). Virgin cotton resists hydration more than does most chemically treated cotton. A kraft pulp requires a more severe beating than does a sulfite fiber. A purified wood fiber simulates cotton in that it resists hydration and requires a longer beating time than does a sulfite pulp.

sumers. The test is greatly influenced by fiber length, by the flexibility of the sheet, and by the character and amount of the cementitious cellulose gel which bonds the fibers together.

Sulfite pulp and short-fibered soda pulp yield papers of low tearing resistance. A high-quality rag or cotton stock will produce a sheet with a high tearing resistance, as will purified wood fiber which has been properly prepared. The high tear values of the cotton and the purified wood fiber



Research Laboratory, Brown Company

The rate and degree of hydration may be studied in several ways. Space forbids a present discussion of the various chemical tests which have been used. The paper maker measures hydration by a "slowness test," which is expressed in terms of the time required for water to drain from the beaten stock which is retained on a wire screen under standard conditions. He thus attempts to establish a direct relationship with the rate of removal of water from the beaten fiber on the wire screen of the paper machine. It is quite evident that this method of determining suitability of beaten stock does not discriminate between actual hydration and the subdivision of fiber caused by the cutting action of the beater. For want of a better method, however, it is employed quite universally and serves its purpose very well. The evaluation of a pulp or a rag stock requires the study of the rate of hydration and of the character of the sheet which can be produced from the partly gelled stock.

POP TEST—The pop or puncture test is probably used more and in itself signifies less than any of the other commonly accepted paper tests. Although closely related to the tensile strength of the sheet, it is actually a complex function of strength, stretch, and tear. The results are also profoundly affected by the presence of such cementitious matter as wood gums, starch, or glue. The pop test has been used as a standard for so many years, however, both by manufacturers and by paper users, that it must still be considered when a sheet of paper or sample of paper-making pulp is to be evaluated.

TEAR TEST—The tear test is intended to determine the total resistance offered when a sheet is torn for a definite distance, starting from a cut in one edge. The Elmendorf tester is generally accepted as the best present-day instrument for this purpose. The tear resistance of a paper is obviously of great practical importance and is demanding ever increasing attention from paper makers and paper con-

sumers. The test is greatly influenced by fiber length, by the flexibility of the sheet, and by the character and amount of the cementitious cellulose gel which bonds the fibers together.

may be partly explained by the increased softness and flexibility of paper made from them, while the presence of sizing agents which impart stiffness and some brittleness will cause a decrease in the tear value of any type of paper. It is well known that the use of glue or gelatin as a surface size for high-grade papers produces this effect.

FOLDING ENDURANCE—The flexibility and resistance to breakage by continued reversed fold are determined by flexing a paper under slight tension until a break occurs. In practice, two sets of test sheets are cut at right angles so as to include breaks both in the direction and across the direction of travel of the wire on the paper machine. In recent years this criterion of physical strength has assumed much greater importance than formerly and has become an important paragraph of practically all paper specifications. The fold test is influenced by many factors, among which are the character of the basic fiber, the length of fiber, the elasticity of the sheet, the softness or stiffness, and the type of sizing.

Most white wood-pulp papers have decidedly less folding endurance than do high-grade cotton rag papers. A low-grade cotton which has been drastically treated with chemicals during the purification steps yields a paper of inferior folding quality, and is in many cases exceeded in this respect by the better grades of sulfite papers. A spruce wood pulp which has been carefully purified to an alpha-cellulose content of from 93 to 97 per cent may be converted into a paper which has as high a folding endurance as the better grades of rag papers. In this respect it differs sharply from sulfite pulp.

TENSILE STRENGTH—The tensile strength is, as the term signifies, a measure of the load necessary to break a given standard width or cross section of paper. This is sometimes expressed in kilograms, but is preferably stated in terms of breaking length, which obviously corrects for differences in

Table II—Chemical Characteristics of Cellulose Products

CHARACTERISTICS	UNBLEACHED CONIFEROUS SULFITE PULP			UNBLEACHED HARDWOOD SULFITE PULP			BLEACHED SULFITE PULP		BLEACHED ASPEN SODA PULP	ABSORBENT COTTON	COTTON LINTERS		
	A	B	C	D	E	F	Coniferous	Hardwood			I	J	K
							%	%	%	%			%
Total cellulose	96.67	93.65	92.22	91.94	96.52	90.65	99.78	99.32	98.73	100.0	100.0
Alpha-cellulose	87.80	87.62	87.72	86.52	86.86	86.32	84.82	83.39	81.47	99.70	98.97	97.67	98.17
Beta-cellulose	2.90	2.54	2.89	4.66	9.40	7.36	7.48	10.66	15.84	<0.5	...	1.97	1.63
Gamma-cellulose	9.30	9.84	9.39	8.82	3.94	6.32	7.70	6.06	2.62	0.35	0.20
Fiber length	3.16	2.90	2.36	...	3.10	2.72	...	0.42	0.44	0.48
Copper number	4.56	3.10	2.72	3.42	3.08	2.62	0.58	1.52	0.84	1.24
Lignin	3.03	3.23	7.42	5.10	3.34	5.15	1.24	2.16	1.16	0.33	...	0.06	0.04
7.14% soda-soluble	22.46	21.8	21.6	18.1	24.0	23.2	27.1	27.4	22.2	0.107	2.25	5.29	3.50
Pentosans	3.70	4.29	4.27	8.47	8.34	8.25	4.18	9.3	11.68	0.69	0.66	0.54	0.46
Viscosity in cuprammonium solution	26.0	14.0	50+	24.0	28.0	17.0	3.0	3.0	0.6	680	30+	1.5	2.60
Resins (CCl ₄ -extractable)	0.80	0.55	0.66	1.16	...	0.53	0.59	0.68	0.43	0.24	0.14	0.01	0.07
Ash	0.25	0.37	0.10	0.38	0.18	0.17	0.16	0.19	0.53	0.05	0.14	0.05	0.10
Color	Light tan			Light tan			White	White	White	White	White	...	White

CHARACTERISTICS	RAG PAPER-MAKING STOCKS						CONIFEROUS GROUNDWOOD	KRAFT PULPS				
	N	O	P	Q	R	S		T	U	V	W	X
	%	%	%	%	%	%	%	%	%	%	%	%
Total cellulose	...	98.36	55.0	93.00	93.50	94.30	92.27	91.75
Alpha-cellulose	75.46	92.94	94.84	97.97	94.71	95.23	94.91	91.73	92.27	90.80	94.04	94.60
Beta-cellulose	14.22	4.26	2.68	1.94	4.87	4.14	2.96	0.50	0.16	0.50	<1.0	<1.0
Gamma-cellulose	10.32	2.80	2.48	0.13	0.61	0.63	3.03	7.77	7.57	8.70
Fiber length	0.60	0.75	0.58	0.64
Copper number	4.64	1.94	1.08	1.14	1.82	1.46	4.06	...	1.16	...	2.0	5.10
Lignin	...	0.26	0.33	29.8	6.3	4.05	4.80	7.73	7.55
7.14% soda-soluble	23.8	12.90	6.37	4.65	11.82	2.53	18.6	10.7	15.3	12.0	7.5	6.18
Pentosans	0.39	1.03	0.52	0.71	0.57	0.63	7.7	7.92	9.5	7.45	8.85	5.64
Viscosity in cuprammonium solution	0.40	3.50	5.30	11.60	0.80	2.30	Insol.	26.8	20.0	33.0	Insol.	Insol.
Resins (CCl ₄ -extractable)	0.06	0.05	0.10	0.07	0.06	0.12	0.39	0.12	0.05	0.08	0.08	0.12
Ash	0.53	1.36	0.05	0.17	0.48	0.15	0.38	0.47	0.58	0.81	0.54	0.60
Color	Yellow	Gray	White	White	White	White	Buff	Brown	Brown	Brown	Brown	Brown

CHARACTERISTICS	PURIFIED WOOD FIBER												
	AA	BB	CC	DD	EE	FF	GG	HH	II	JJ	KK	LL	MM
	%	%	%	%	%	%	%	%	%	%	%	%	%
Total cellulose	97.20	99.4	98.9	99.63	98.98	99.35	99.21	99.63	100.0	99.73
Alpha-cellulose	94.32	95.13	93.93	94.32	92.79	94.85	95.53	94.97	95.50	97.20	98.39	98.50	96.45
Beta-cellulose	1.21	1.99	2.07	1.59	1.98	2.51	...	2.78	0.93	2.50	1.42	1.40	0.90
Gamma-cellulose	4.45	28	4.60	4.09	5.23	2.64	...	2.25	3.57	0.30	0.28	0.10	2.65
Fiber length	0.83	0.75	0.90	0.86
Copper number	1.22	1.30	0.96	0.90	1.00	1.30	1.06	1.12	1.54	1.55	0.98	1.13	1.18
Lignin	1.06	0.48	0.52	0.54	0.57	0.4	0.20	0.13
7.14% soda soluble	7.73	7.00	6.65	6.42	7.25	8.30	6.62	6.74	6.50	1.90	5.25	3.85	4.20
Pentosans	3.28	2.98	4.35	3.93	4.02	2.28	1.87	2.18	2.45	2.09	0.99	0.93	2.35
Viscosity in cuprammonium solution	38.0	17.0	10.5	6.7	7.1	5.9	5.1	6.6	5.0	2.85	3.08	1.65	4.5
Resins (CCl ₄ -extractable)	0.12	0.07	0.13	0.06	0.19	0.15	0.10	0.04	0.05	0.11	0.09	0.14	0.04
Ash	0.12	1.11	0.17	0.18	0.14	0.12	0.08	0.08	0.09	0.07	0.05	0.02	0.05
Color	Light gray	White	White	White	White	White	White	White	White	White	White	White	White

CHARACTERISTICS	PURIFIED WOOD FIBER												
	NN	OO	PP	QQ	RR	SS	TT	UU	VV	WW	XX	ZZ	AAA
	%	%	%	%	%	%	%	%	%	%	%	%	%
Total cellulose	99.55
Alpha-cellulose	96.70	96.38	95.6	94.69	97.00	96.25	95.60	95.10	95.56	96.23	96.30	95.43	95.6
Beta-cellulose	0.89	2.77
Gamma-cellulose	2.41	0.85
Fiber length	...	0.43
Copper number	0.88	1.06
Lignin	...	0.27	1.36	0.06	1.7
7.14% soda soluble	5.7	5.72
Pentosans	1.87	2.82	0.6	0.94	1.09	2.0	2.2	1.2	0.71	1.08	0.50	1.00	0.60
Viscosity in cuprammonium solution	3.9	5.8	0.5	9.5	5.8	...	0.80	1.0	...	1.13	...
Resins (CCl ₄ -extractable)	0.02	0.10
Ash	0.07	0.07
Color	White	White	White	White	Buff	Buff	Buff	Buff	White	Buff	White	White	White

Legend to Table II

A and B—Pulps produced by cooking a mixture of spruce and fir with a sulfite acid for 10.5 hours. The sulfite acid contained about 1 per cent combined and 4.5 per cent free sulfur dioxide. Maximum cooking temperature was 145° C.

C—A sulfite pulp which was cooked with an acid containing about 2.5 per cent combined and 5 per cent free sulfur dioxide. Cooking time was 10 hours. Maximum temperature was 150° C.

D, E, F—Pulps produced by digesting a mixture of birch, maple, and beech under conditions very similar to those maintained in A and B.

G and H—Bleached sulfite stocks made by bleaching raw stocks such as A and E with hypochlorite.

I—A commercial grade of bleached soda pulp which was made from aspen wood.

J—A medical grade of absorbent cotton.

K, L, M—Three grades of cotton linters which have been purified for conversion into cellulose nitrates. The sample K, which has higher viscosity, is used in preparation of cellulose nitrate films.

Legend to Table II (Continued)

N, O, P, Q, R, S—Six different grades of so-called rag half-stocks. All of these samples were cooked and bleached for use in the beater. The commercial grade of rags used in each case was: (N) thirds and blues; (O) blue overalls; (P) white shirt cuttings; (Q) new white rags; (R) fancy shirt cuttings; (S) pink corset cuttings.

T—A commercial grade of groundwood which was produced for newsprint.

U, V, W—Three samples of kraft pulps. These pulps were produced by a digestion of coniferous wood (spruce and pine) with an alkali liquor in which 40 per cent of the total active alkali is present as sulfide. The maximum temperature of cooking in all cases was about 165° C. and the cooking time about 4.5 hours.

X—A commercial sample of kraft made in the Southern States and presumably from southern pine species.

Y—A kraft fiber produced from a western hemlock. The cooking conditions are similar to those given in U, V, W.

AA—An unbleached coniferous fiber which was made by treating a prechlorinated sulfite stock with alkali at 100° C.

BB—A fiber which was obtained by bleaching a stock such as given as AA. The high viscosity of the cuprammonium solution is important in some fields of esterification.

CC—A purified wood fiber in which the reconditioning conditions were selected so as to emphasize good physical strength in the paper which can be produced therefrom.

DD and EE—Two grades of purified wood fiber in which good paper-making characteristics are desired. The raw stock from which this fiber is made is cooked so as to avoid injury of fiber length.

FF—A purified fiber which is designed particularly for conversion into xanthates. For this type of fiber it is necessary to maintain a high alpha-cellulose and a uniform viscosity of ester solutions which are made therefrom.

GG, HH, II—Three samples of wood cellulose which have been prepared specifically for conversion into cellulose nitrates. For this grade of fiber it is necessary that the resin content be very low and that the color of fiber be of exceptional degree of whiteness.

JJ, KK, LL, MM, NN—A variety of purified wood fiber products in which emphasis is laid on lower pentosans and very low soda-soluble constituents. Such types are of value for esterification purposes.

OO—A purified wood fiber which was made from poplar wood. Such a fiber has value for both paper and esterification purposes.

Samples PP to AAA were prepared by digesting wood substance in a series of steps in which temperatures and chemical concentrations are chosen to emphasize pulps which are high in alpha-cellulose and low in pentosans.

Samples RR, SS, TT, UU, and WW were not bleached. PP, QQ, VV, XX, ZZ, and AAA represent pulps which are comparable to bleached cotton in color.

the weight of the sheet and allows one to make direct comparisons. Tensile strength is of great importance in many special papers. It may be affected profoundly by fiber pattern within the sheet, by the conditions under which the wet has been dried, by the degree of hydration of the pulp during beating, and by the nature of the fiber. In the great majority of machine-made papers the tensile strength is higher in the machine direction than across the sheet; this is the result of non-uniform arrangement of fibers in the sheet, together with directional tension during the drying process.

Discussion of Data

The above discussion of the methods which are used to characterize cellulose products will be of assistance in the interpretation of the chemical characteristics which are summarized in Table II. These data are for the most part expressed in units which are generally accepted by investigators in this field of work. Exceptions will be noted. The listed data were secured in the Research Laboratory of the Brown Company, and inasmuch as the technic and the procedures are identical for all samples, the data are more directly comparable than is the case when attempts are made to compare analytical figures which are assembled from a number of laboratories.

From this table it appears evident that, while the bleached sulfite wood pulps are as high in total cellulose as the purified wood fiber and the cotton products, they are consistently lower in alpha-cellulose content. The lower alpha-cellulose values for the bleached sulfite fiber as compared with the corresponding unbleached sulfite pulps may be due in part to the presence of lignin in the alpha-cellulose residue from the unbleached fiber.

Bleached soda pulp which is prepared from aspen wood is appreciably lower in alpha-cellulose than are the coniferous sulfite products. The soda pulp has a higher pentosan value than the sulfite fiber. This difference is partially the result of a higher initial pentosan value in the aspen wood; besides, the acid sulfite digestion is more effective than alkali in the removal of pentosan groups. As one would suspect, the kraft pulps simulate the soda pulps in that they also reflect the higher pentosan content of the original wood. The sulfite pulps which were produced from spruce and hardwood, respectively, show differences in pentosans which may be traced back to the analysis of the raw woods.

All ordinary sulfite wood pulps are relatively high in those resinous groups which respond to carbon tetrachloride extraction. The purified wood fiber and the cotton stocks contain much less of these constituents. This applies also to the kraft pulp. The alkaline nature of the digestion is undoubtedly responsible for the low content of resinous material in the kraft pulps.

The very low pentosan values found in many of the purified wood-fiber products prove quite conclusively that it is possible to simulate cotton in this respect. Some of the wood products which contain the least pentosans have paper-making characteristics of outstanding quality, as will be shown in the second article of this series.

The solubility of the material in boiling 7.14 per cent sodium hydroxide solution is very marked in the case of sulfite pulps of all types. Many of the kraft products show relatively high solubility, but in general less than the acid-digested fibers, which apparently suffer by acid hydrolysis. The cotton linters are usually quite low in soda-soluble materials. Paper-making rag stocks of the best grades compare favorably with the cotton linters in this respect, as do many of the purified wood fibers. It appears that a chemical overtreatment of rag stocks will result in a high percentage of soda-soluble constituents. The soda-solubility of a purified wood fiber may be controlled as desired by a proper selection and sequence of refining steps in its manufacture.

A survey of the values listed in Table II shows that it is possible to prepare refined cotton stocks or purified wood products which have alpha-cellulose contents ranging from 92 to 97 per cent. There is much testimony that low alpha-cellulose values in the case of cotton signify extreme severity in the refining treatments, whereas in general low values in the case of purified wood fibers suggest relatively mild purification steps. It is to be noted, however, that a high alpha-cellulose wood fiber will also sacrifice its alpha-cellulose content if it is overtreated.

The alpha-cellulose values of the kraft pulps and the groundwood sample are obviously absurd inasmuch as a very high percentage of the original ligneous matter resists the action of the 18 per cent caustic soda solution and remains with the residue which is assumed to be alpha-cellulose. This absurdity emphasizes the need of intelligent interpretation of alpha-cellulose results.

Literature Cited

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Corrosion of Metals by Phosphoric Acid¹

Peter R. Kosting and Conrad Heins, Jr.

FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

THE increasing interest in the manufacture and use of phosphoric acid has created the need for information concerning the corrosion resistance of construction materials to that acid. Present-day manufacturers, in an effort to combat the expensive corrosion which adds to the cost of the acid, have made laboratory corrosion tests of various alloys, but quite often have not been able to correlate the results with those of plant installations.

Results of Previous Investigations

From the literature dealing with the action of phosphoric acid on materials of construction, much data of a general nature may be obtained, but little quantitative information. The following paragraphs summarize these data.

Many alloys have been mentioned as being of use around the phosphoric acid plant (5, 8, 13, 16, 24, 28, 42, 43, 49). Bronzes of aluminum and of tin are used as condenser tubes to recover steam from its reaction with phosphorus (24). Drying the air used to burn phosphorus to the pentoxide protects the metal vessels from corrosion (36).

Much has been claimed for the new stainless steels. To resist pure, boiling 85 per cent acid, the 24 Cr-15 Ni-3 Si alloy is recommended (31, 34); for pure, boiling 45 per cent acid, the 18 Cr-8 Ni alloy (34); at lower temperatures these austenitic steels are very resistant to all concentrations of acid (22, 40, 41). Alloys of the cutlery type are slightly attacked by phosphoric acid (4, 21, 22, 33, 44). The corrosion of stainless steels increases with acid concentration (21, 33, 44).

Among the non-ferrous alloys, aluminum is not to be recommended (7, 25). Alloys of copper with silicon (15) and with aluminum (2, 26) are reported as being resistant to dilute phosphoric acid. Monel metal has also been used with dilute acid (12, 25, 32). Tin is said not to be attacked by the acid (23). The wires in Cottrell precipitators used in the manufacture of phosphoric acid have been made of nichrome and even silver (49).

Metals which are carefully coated with Bakelite (3, 11) are said to resist dilute phosphoric acid, even when subjected to abrasion. Rubber-lined tanks, also, are reported resistant (17, 18). A specially precipitated latex has been developed which, when vulcanized, does not color the acid (10). The maximum temperature which rubber withstands when in the presence of 75 per cent acid is 50° C. (125° F.) (9). It is said that coatings of alkali metal fluosilicates protect the apparatus in evaporating crude acid (29). The reaction that takes place when parkerizing (the process of making iron rustproof by dipping it into a dilute solution of phosphoric acid con-

This paper gives data on the corrosion of metals by C. P. and crude phosphoric acids. Accelerated corrosion tests on 52 metals and alloys were carried out under various conditions, using 10, 25, 50, and 85 per cent C. P. acids, and dilute and concentrated acids. The effects of temperature, aeration, and purity of solution were investigated, and the physical appearance of the different metals after exposure was noted.

It was found that temperature rise increases the rate of corrosion. One non-ferrous alloy showed a maximum rate between 75° and 85° C. In concentrated acid, the corrosion rates of stainless steels suddenly increase near the boiling point. The purity of the acid affects the resistance of metals to phosphoric acid. Products of corrosion tend to increase the corrosion of the special bronzes and bronzes. Halogens destroy the passivity of stainless irons and steels and so cause rapid corrosion. Arsenic, hydrochloric acid, pine oil, mucilage, and pyridine inhibit the attack of concentrated acid on iron. Sulfuric acid increases the corrosion rate of iron, bronzes, etc., but cuts down the corrosion of lead. Aeration increases the corrosion of non-ferrous metals and alloys.

taining many different phosphates) ceases in a short time, owing to a phosphate film depositing on the iron.

Silica ware is described as being resistant to phosphoric acid under all conditions (8, 42). The maximum temperature at which this material can be used is 400° C. (38). At this temperature one deals not with orthophosphoric acid but with the pyro- and even the meta- acid, both of which are considered more corrosive than the former. Quartz filter stones seem to resist 50 per cent acid much better than the common grades of filter stone (46). Glass is even dissolved by solutions of sodium acid phosphate (48).

Starch, gelatin, quinoline, pyridine, aldehydes, pine oil,

arsenic, sulfate, and other materials, may be considered inhibitors of the attack of phosphoric acid on iron (1, 5, 19). Because of the presence of inhibitors, concentrated crude acid is shipped in steel tank cars. For the same reason no lead is used for building apparatus at a plant where concentrated crude acid is handled in making the different sodium salts (13).

The quantitative data on corrosion by pure phosphoric acid as obtained from the literature and private communications were recalculated to give corrosion rates in centimeters per day and are listed in Table I. In some cases densities had to be assumed. Wherever possible, the conditions of test have been indicated.

Description of Tests

The plant conditions which must be simulated when making accelerated corrosion tests in the laboratory involve high temperature, agitated solutions exposed to the air, and the presence of many impurities in solution. Crude acid, made by the sulfuric acid method, contains organic matter, arsenic, fluorides, fluosilicates, sulfates, etc. Crude acid made by the furnace method may be expected to contain, besides fluorides, fluosilicates, etc., traces of the meta- and pyrophosphoric acids, if the temperature at the time of Cottrell precipitation, or even of concentration, be high. The effects on corrosion of the addition to C. P. acid of impurities such as found in the former crude acid were studied in a cursory manner.

Materials

Altogether, 52 metals and alloys were tested in phosphoric acid of at least one concentration. They were obtained from a large number of sources and were tested in the "as received" condition as regards heat treatment. Their compositions are listed in Table II. The general physical properties of a number of the metals and alloys used in the tests are given in the chart "Materials of Construction for

¹ Received November 11, 1930.

Table I—Corrosion by Phosphoric Acid

SAMPLE	COMPOSITION	ACID CONCENTRATION											
		DILUTE			MEDIUM			CONCENTRATED					
		Acid	Temp.	C. R.	Acid	Temp.	C. R.	Acid	Temp.	C. R.	Acid	Temp.	C. R.
		%	° C.	Cm. per day	%	° C.	Cm. per day	%	° C.	Cm. per day	%	° C.	Cm. per day
METALS		Poor in all concentrations											
Aluminum (7) ^f		65	17/20	0.0042	72	17/20	0.0039						
Tank car steel ^f	0.23 C	65	17/20	0.018	72	17/20	0.016						
Mild steel (33)	0.35 C	66.3	18/20	0.014	80	17/20	0.010						
Lead ^f		65	17/20	0.00003	72	17/20	0.00003						
NON-FERROUS ALLOYS													
Alcumite ^a		20	80	0.00020 (max.)									
Barberite ^c		40	Rm	nil	85	Rm	nil						
Bronze (15)	15 Sn	50	Rm	nil	85	71	0.000007						
Bronze (26)	87 Cu; 9.8 Al; 3.1 Fe	30	b. p.	0.0027%/hr.									
Bronze ^b	Lead phosphor	10	22	0.000020	35	22	0.000013						
Hastelloy D ^g	Ni; Al; Si; Cu	30		0.00024	30		0.00024				85	70	0.00002
Hytens ^b		30		0.000041							85	160	0.00050
Monel metal ^b		30		0.000078									
Monel metal ^f		65	17/20	0.000003	72	17/20	0.000002						
Red brass (15)		30	b. p.	0.019%/hr.									
Resistac ^b		30		0.00036									
Rotoxit (15)		30	b. p.	0.00087%/hr.									
Still metal ^b		30		0.00025									
FERROUS ALLOYS													
Anka (33)	15.2 Cr; 11.4 Ni	5	18/20	nil	25	18/20	nil	66	17/20	0.00016			
Corrosiron ^d		2.9		nil	17.6		0.45%						
Duriron ^e		10	82/88	0.0000020	25	82/88	0.0000030				87	82/88	0.0000030
Hastelloy A ^g	Ni; Mo; Fe	10	15/20	0.00000017	25	15/20	0.00000021				87	15/20	0.0000013
Hastelloy C ^g	Ni; Mo; Fe	10	70	0.00001							85	160	0.0040
KA-2A	Ni; Mo; Fe	40									85	70	0.000009
	17-20 Cr; 7-10 Ni	45	b. p.	0.00001							85	160	0.01
Resistal 7 (31)	25 Cr; 15 Ni; 1 1/2 Si	45									80	110	0.0096
Stainless steel (33)	12.6 Cr; 0.3 C	5	18/20	0.00015							80	115	0.041
Stainless steel (22)	12-14 Cr	5		Slight attack	25		Slight attack	66.3	18/20	0.0015			
Staybrite (22)	18 Cr; 8 Ni	50		nil	25		nil	50		nil			
Stellite (20)	50-60 Co; 30-40 Cr; 8-20 W	66	18/20	0.00035							75	Slight attack	
V2-A (33)	20.4 Cr; 8.6 Ni										and 100	Slight attack	
NON-METALLIC													
Alumina (6)	Filter plate	Resistant to all concentrations											
Prodorite (50)	Pitch aggregate	Resists fumes from acidulated crude phosphates											
Quartz (46)	Filter plate												
Vitreosil (38)		Excellent up to 400° C.											

^a Alcumite Corp., Bull. 1 (1925).

^b American Manganese Bronze Co., Tabulation of Corrosion tests

^c Barber Asphalt Co. Letter. 24-hour test.

^d Bethlehem Foundry and Machine Co., "Corrosion."

^e Duriron Co., Bull. 116 (1920).

^f Fertilizer and Fixed Nitrogen Investigations Laboratory, Rept. 1920, breaker tests.

^g Haynes Stellite Co. Letter, 1930.

^h Ludlum Steel Co., Bull. K1, 1929.

Chemical Engineering Equipment," (30), while Table III lists the physical properties of some alloys not given in this chart.

The c. p. phosphoric acid used was the product of both the J. T. Baker Chemical Company and the Mallinckrodt Chemical Company. The dilute and concentrated crude acids were commercial products freshly made by the sulfuric acid method. They were stored in paraffin-coated bottles to prevent any loss of fluorine by its reaction with the glass. Much of the suspended matter was allowed to settle out of the acid prior to its use in the tests. Table IV lists the composition of these acids as used in the tests.

Apparatus and Experimental Method

The first series of tests was made in open beakers, using, for the most part, concentrated acid. The temperature of solution was maintained at $95^{\circ} \pm 5^{\circ}$ C. When dilute solutions were used, or when the solutions were aerated, condensers were used to prevent evaporation. The second series of tests was made with the aerated solutions. The air was neither purified nor controlled. Supplied to the laboratory at relatively low pressures, the flow varied from hour to hour and fell to almost nothing over night. The final form of apparatus is similar to that described by Pratt and Parsons (39), and diagrammatically shown in Figure 1.

A copper bath, $50 \times 7 \times 7$ inches ($127 \times 17.8 \times 17.8$ cm.), was thermally insulated by means of a felt-lined wooden box (1 and 2 of Figure 1). The water was heated by two glass-covered coils of nichrome wire (3). One coil extended di-

agonally across the bottom and the other extended around all four sides. A horizontal shaft with three propellers was coupled (23) to the end vertical shaft to serve as an agitator (4). A mercury thermoregulator (22) operating a Mercoid relay kept the temperature constant within 0.3° C. The temperature difference between the ends of the bath was 0.2° C. at 65° C.

Straight-walled beakers (5), $2 \frac{3}{8} \times 4 \frac{1}{4}$ inches (6.03×10.8 cm.), were made with small inside and outside ridges at the top. The outside ridge prevented the beaker from slipping through the copper washer used to suspend it in the bath and the inside ridge prevented the rubber stopper from slipping out. The rubber stoppers (6) had five holes, one for a thermometer (7), one each for air inlet (11) and outlet, one for specimen holder (8), and a glass bushing with mercury cup (12) passed through the fifth hole in the center. Propellers (10) with inverted cups for the mercury seal (12) were rotated from vertical shafts at 360 r. p. m.

Air from high-pressure cylinders was used for aeration. Control was maintained by means of a flowmeter (25), and a constant gas-flow regulator (29) similar to that used by Kuntzel (27). Sulfuric acid (27) and potash sticks (26) were used for purification. After bubbling through 25 per cent phosphoric acid (24) and passing through a 12-inch (30.5-cm.) condenser, the air was considered to be in the same condition as it would be after passing through the test solutions. This air was bubbled at the rate of 95 cc. per minute through four solutions in series, 50, 25, and 10 per cent c. p. acids and dilute crude acid, passing through 12-inch (30.5-cm.) condensers (18)

Table II—Analyses of Metals and Alloys

SAMPLE	Cu	Ni	Fe	Mn	Mg	Si	Sn	Zn	Pb	Al	C	Bi	Sb	Cr	Co	Mo	Misc.
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
METALS																	
1 Aluminum sheet																	
2 Chromium											1. ± ^a			96-97 ^a			
3 Copper (electrolytic)	99.993 ^b		0.007														P, O; Ag, 0
4 Iron (Armco)			(b) 0.01	0.01		0.005					0.028						
5 Lead	0.05		0.006	0.01			0.02	0	99.9				0.01	0			As, 0
6 Nickel (rolled)	0.08	(b)	0.28	Trace		0.14											Ag, 89.9
7 Silver	7.9																
8 Tantalum																	
9 Tin							99.45										
10 Zinc								99.9									
NON-FERROUS ALLOYS																	
11 Admic	67.1	28.3	0.30	1.48	0.10		1.19	1.75									
12 Alcumite G	87.4		3.75	0.96							7.80						
13 Alpac	0.10		Trace			11.3					88.6 ^b						
14 Ambrax	73.4	19.5	0.13	0.48	0.11			6.39	0								
15 Ampco 12	88.9	0	2.84	0.05	0.11	0	0	0	0		8.13						
16 Ampco 18	85.5	0	4.28	0.05	0.15	0	0	0	0.03		9.97						
17 Barberite	88.1	5.28	0.42	0.10	0.28	1.28	4.40	0	0.06	0	0.03						
18 Low brass A	85.1	0	0.16	0				14.7	0								
19 Low brass B	87.5	0	0.12				0	10.5	2.57								
20 Machine brass	66.3							32.5	0.87								
21 Tobin bronze	60.1		0.10				0.86	39.1	Trace								
22 Yellow brass J. C. T.	62.6		0.18				0.10	34.5	2.55								
23 Everdur	95.5	0	0.15	1.22	0.19	2.97											
24 Hastelloy D	3.37	(b)	1.05			10.8											
25 Hills McCanna 42	89.0		3.11								2.36						
26 Hills McCanna 45	88.6	0	1.33	0.25	0.25	0	0				7.76						
27 Hills McCanna 52	74.1	15.8	3.71	1.16		0.05					9.92			0			
28 Hills McCanna 55	27.2	65.8	2.37	0.99	0.21	2.75					5.55			0		0.34	
29 Hytensl	67.8		1.88	2.95			0	22.5	0		4.97						
30 Illium G	7.90	60.2	1.80 ^b	0.39		0.74					0.50	0.31			21.5		4.63 W, 1.99
31 Illium 50	4.49	31.8	47.0 ^b	0.17		0.59					0.80	0.43			11.3		2.51 W, 0.89
32 Lead A																	
33 Lead B																	
34 Lead C																	
35 Lead D																	
36 Mond 70	26.3	68.9	1.10	3.51	0.17	0.03					0.08						
37 Monel	28.4	66.9	2.19	2.10		0.014					0.18						
38 Nichrome IV	0	74.5	0.80	2.06	0.03	0.35					0.22						Cr ₂ O ₃ , 1.18
FERROUS ALLOYS																	
39 Allegheny (18-8) metal	0.13	8.49	(b)	0.47		0.17					0.17				18.1		V, 0.0
40 CrV ₃			(b)								0.35				7.7		V, 0.18
41 CrV ₄			(b)								0.35				14.4		V, 0.18
42 Durimet	0.10	33.7	(b)	1.75		4.38									11.7		
43 Duriron																	
44 Enduro (C. L. P.)	0.06	0.37	(b)	0.45		0.62					0.08				18.1	0	V, 0.05
45 Fahrite	0.10	38.9	(b)	0.71		0.50					0.74				17.3	0	V, 0.03
46 Hastelloy A		(b)	22.2	2.47	0	0.18									0	19.4	
47 Hastelloy C		(b)	9.2	0.20		1.06									11.4	18.7	W, 3.05
48 KA-2	0.12	10.2	(b)	0.17		1.26					0.12				18.4		
49 Non-corrodite-12-22	0.0	12.14	(b)	0.0		0.61									22.4		
50 Silchrome	0.07	0.39	(b)	0.30		2.89					0.33				18.6		V, 0.39; W, 3.5
51 Uniloy 1409	0.05	0.64	(b)	0.27		0.19					0.094				12.4	0	V, trace
52 Uniloy 2825	0.04	0.17	(b)	0.26		0.13					0.30				28.4	0	V, trace

^a Manufacturer's analysis.^b By difference.Table III—Properties of Alloys^a

SAMPLE	ULTIMATE STRENGTH		YIELD POINT		REDUCTION OF AREA	ELONGATION	DENSITY	MACHINE QUALITIES	FORM AVAILABLE ^b	METHOD OF FABRICATION ^c
	Lbs./sq. in.	Kg./sq. cm.	Lbs./sq. in.	Kg./sq. cm.						
32 Lead A	7,700	541			14	16	10.6	Good	B, C, CR S, T, W	B, Br, F R, SS, W
33 Lead B	2,570	181				48	11.5			
34 Lead C	2,990	210				38	11.3			
35 Lead D	3,420	240				36	11.3			
36 Mond 70	89,000 91,000	6260 6400	58,000 63,000	4080 4430			8.9	Same as mild steel	C, HR, W R, CR, Fr	All

^a Terms are the same as in chart, "Materials of Construction for Chemical Engineering Equipment (30)" which this supplements.^b Forms available: B, bar; C, castings; CR, cold-rolled; Fr, forgings; HR, hot-rolled; S, sheets; T, tubing; W, wire.^c Method of fabrication: B, brazing; Br, burning; C, casting; DD, deep-drawing; F, flanging; R, riveting; SS, soft-soldering; W, welding.

between each solution. A flowmeter at the exhaust end immediately showed the occurrence of leaks in the system.

With a flow of air of 95 cc. per minute, 25 per cent acid was concentrated to 25.5 per cent when maintained at 65° C. for 24 hours. The air bubbles were large and rose to the surface of the solution in a straight line slightly distorted by the motion of the liquid produced by the propeller at the bottom of the beaker. The flow of air could be varied through wide limits without affecting the corrosion rates. The pressure drop over the four beakers was 1.11 cm. of mercury. The effect on the rate of corrosion due to increased solubility of oxygen brought about by this difference in pressure was found to be less than the experimental error.

Aerated tests with the concentrated crude acid could not be completed owing to a crystalline deposit blocking up the

air outlet. Open beaker tests were therefore made instead. The glass beakers were slowly etched, indicating the presence of small traces of free hydrofluoric acid. Beakers were either paraffin-lined or Bakelite-coated when carrying out tests with hydrofluoric acid additions to c. p. acids.

The volume of solution used was 150 cc. With 300 cc. no appreciable difference in corrosion was observable with a copper alloy whose rate of corrosion was affected by the corrosion products, and was of the order of 30×10^{-5} cm. per day.

The specimens varied considerably in shape, but were approximately 10 sq. cm. in area. The usual dimensions were about $0.5 \times 1 \times 3$ cm., and the weight was in the neighborhood of 10 grams. Surface oxides and pits were removed by grinding on an Aloxite wheel, grade 50-G.

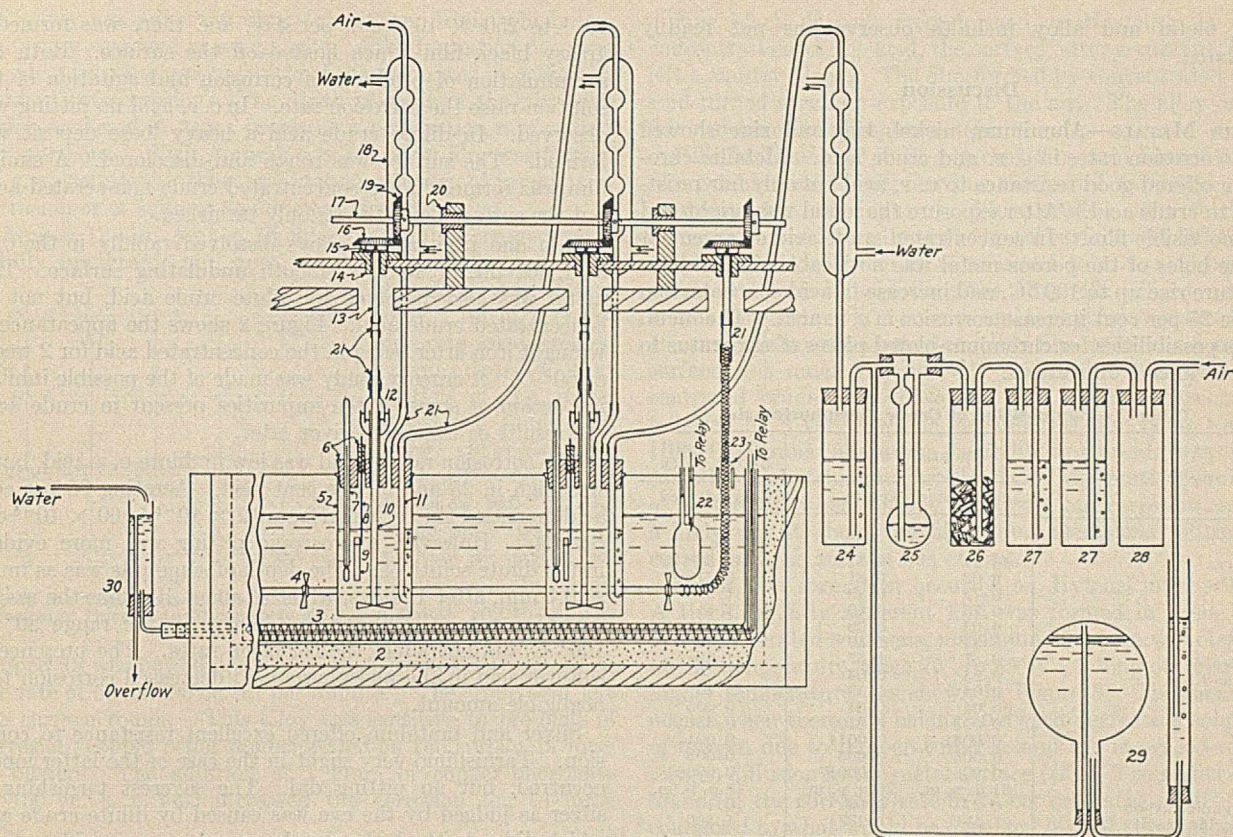


Figure 1—Apparatus for Corrosion Tests

- | | | |
|--------------------------------|------------------------------------|--|
| 1—Wooden container for bath | 11—Air inlet | 21—Rubber tubing |
| 2—Felt insulator | 12—Mercury seal | 22—Thermoregulator |
| 3—Heating coil in Pyrex tubing | 13—Brass shaft | 23—Spring coupling of nichrome through glass bushing |
| 4—Agitator | 14—Bronze bushing | 24—25 per cent phosphoric acid |
| 5—Straight-walled beaker | 15—Fiber washer | 25—Flowmeter |
| 6—Rubber stopper | 16—Brass bevel gear | 26—Caustic |
| 7—Thermometer | 17—Brass shaft | 27—Concentrated sulfuric acid |
| 8—Glass specimen holder | 18—12-inch condenser on air outlet | 28—Trap |
| 9—Specimen | 19—Fiber bevel gear | 29—Constant gas flow regulator |
| 10—Propeller | 20—Fiber bushing | 30—Constant water level device |

The weighed specimens, cleaned by scrubbing with a bristle brush using soap and hot water, and dried by dipping in alcohol and in ether, were suspended on glass hooks in the acid, and exposed for 24 hours or more. After the initial exposure the specimens were scrubbed, dried, weighed, and again exposed. This was repeated as often as necessary. The scrubbing did not remove any tarnishing that occurred. To restore the original metallic luster between exposures was considered not simulating plant conditions.

Results

The corrosion rates were combined with observed densities and calculated over to penetration figures expressed in centimeters per day, multiplied by 10^{-5} . Thus, from Table V, copper dissolved in 85 per cent c. p. acid at the rate of 3.2×10^{-5} cm. per day.

The results of the primary beaker tests and of the effects of aeration are given in Table V. Table VI shows the results obtained when air was bubbled through mechanically agitated solutions at the rate of 95 cc. per minute. In these two tables the maximum and minimum corrosion rates observed, as well as the average of all observations, are recorded. Film formation is distinguished from tarnishing or discoloring in that the film can be scrubbed off the specimen with a bristle brush. Non-adherent films wash off under running water, whereas adherent films must be brushed off.

In addition to the information to be gained from a study of these tables, the following discussion on the behavior of

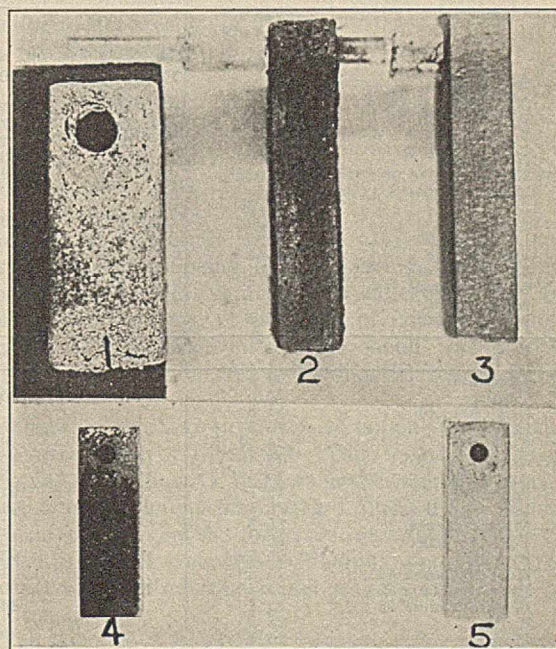


Figure 2—Effect of Crude Phosphoric Acid on Ferrous Alloys

(1) Wrought iron, (2) 18 Cr-8 Ni steel, (3) 28 Cr steel; all in concentrated Florida pebble acid for 2 weeks at 60° C., open beaker test. (4) 18 Cr-10 Ni steel in dilute Florida pebble acid for 2 weeks at 60° C. (5) 18 Cr-10 Ni steel in concentrated Florida pebble acid for 2 weeks at 60° C.

each metal and alloy includes observations not readily tabulated.

Discussion

THE METALS—Aluminum, nickel, tin, and zinc showed high corrosion rates in c. p. and crude acid. Metallic chromium offered good resistance to c. p. acid but only fair resistance to crude acid. After exposure the metal was bright and had no visible film. In concentrated crude acid enlargement of the holes of the porous metal was noticeable. Both temperature rise up to 100° C. and increase in acid concentration above 25 per cent increase corrosion in c. p. acid. The metal offers possibilities for chromium-plated pieces of apparatus to be used in cool dilute acid.

Table IV—Composition of Crude Phosphoric Acid

CONSTITUENT	FLORIDA PEBBLE		TENNESSEE BROWN ROCK
	Concentrated	Dilute	Concentrated
	%	%	%
P ₂ O ₅	44.14	19.87	41.38
SiO ₂	0.02	0.81	0.21
Al	0.77	0.38	1.59
Fe	0.73	0.40	1.41
Ca	0.03	0.06	0.01
SO ₂	5.32	2.49	1.46
Total F	0.57	1.57	1.98
F as F ⁻	0.53	0.04	1.58
F as SiF ₆ ²⁻	0.04	1.53	0.40
Cl	0.04	0.04	0.005
Mn	0.023	0.010	0.33
Cr	0.0031	0.0014	0.0012
Cu	0.005	0.006	0.008
Pb	0.006	0.00017	0.00062
As	31 p. p. m.	26 p. p. m.	46 p. p. m.
Organic carbon	0.27	0.09	0.13
Specific gravity (22° C.)	1.581	1.237	1.560

Copper was resistant to non-aerated concentrated c. p. acid. Aerating 25 per cent acid increased the corrosion from 12 ×

10⁻⁵ to 250 × 10⁻⁵ cm. per day, and there was formed a greasy black film which floated off the surface. Both the accumulation of products of corrosion and agitation of the solution raise the corrosion rate. In c. p. acid no pitting was observed. In dilute crude acid a heavy loose deposit was formed. The surface was rough and discolored. A similar film was formed in the concentrated crude non-aerated acid, but the surface beneath was only tarnished.

Iron and iron-carbon alloys dissolved rapidly in the c. p. acid, leaving, if steel, a smooth undulating surface. This metal was also dissolved by dilute crude acid, but not by concentrated crude acid. Figure 2 shows the appearance of wrought iron after being in the concentrated acid for 2 weeks at 60° C. A cursory study was made of the possible inhibiting action of some of the impurities present in crude acid, the results of which are given later.

The corrosion rate of lead was low in dilute c. p. acid, but it was high in 25 and 50 per cent acid. Aerating 25 per cent acid increased the corrosion from 12 × 10⁻⁵ to 60 × 10⁻⁵ cm. per day. However, microscopic pitting was more evident in the dilute solutions. The depth of some pits was as much as 0.1 mm. after 11 days, which is about 10 times the weight corrosion rate. Temperature changes in the range 80° to 100° C. did not affect the corrosion rates. The presence of sulfuric acid in the phosphoric acid decreased corrosion to a negligible amount.

Silver and tantalum offered excellent resistance to corrosion. Tarnishing, very slight in the case of the latter metal, occurred, but no pitting did. The severest tarnishing of silver as judged by the eye was caused by dilute crude acid which did not attack the metal as much as c. p. acid.

NON-FERROUS ALLOYS—Very few non-ferrous alloys exhibited low corrosion rates in c. p. or crude phosphoric acid.

Table V—Corrosion of Metals in Pure Phosphoric Acid

(Specimen ground to remove surface imperfections, washed in soap and water, dried in alcohol and in ether; totally immersed in 150 cc. of solution at 95° ± 3° C.)

SAMPLE	ACID STRENGTH	CORROSION RATE PER DAY				REMARKS	
		Max.	Min.	Average			
		BEAKER TESTS					
	%	Cm. × 10 ⁻⁴	Cm. × 10 ⁻⁵	Cm. × 10 ⁻⁵	In. × 10 ⁻⁵		
1	Aluminum	85	170,000	140,000	160,000	63,000	Film, pitting
3	Copper	85	3.5	2.9	3.2	1.3	
	Copper	25.5	13	12	12	4.7	Porous film
5	Lead	85	86	79	82	32	
	Lead	25.5 ^a	12	12	12	4.7	Bright, no adherent film
6	Nickel	85	380	360	370	150	Film, pitting
9	Tin	85	710	490	600	240	Film
10	Zinc	85			Very high		
	Zinc	25.5			Very high		
13	Alpax	25.5	12,000	12,000	12,000	4700	Severe pitting
19	Low brass B	85	4.8	2.8	3.7	1.5	
	Low brass B	25.5	1.9	1.9	1.9	0.74	Discolored
20	Machine brass	85	0.9	0.9	0.9	0.4	Discolored
	Machine brass	25.5	3.2	3.2	3.2	1.3	Copper-colored film
37	Monel metal	85	3.0	2.3	2.6	1.0	Discolored
	Monel metal	25.5	2.7	2.6	2.7	1.1	Discolored
AERATED TESTS							
2	Chromium	25.4	7.0	6.2	6.6	2.6	Bright
3	Copper	25.5	250	250	250	98	No adherent film
4	Iron (Armco)	50.8			Dissolved		
5	Lead	25.5 ^a	63	56	60	24	Film
12	Alcumite	25.5 ^a	230	180	200	79	Film
15	Ampeco 12	25.4 ^a	1000	150	600	240	Rough, pitting
16	Ampeco 18	25.4 ^a	33	30	32	13	Film, pitting
17	Barberite	25.7 ^a	940	910	930	370	Etched, pitting
19	Low brass B	25.5	18	16	17	6.7	Adherent film
20	Machine brass	25.5	24	17	20	7.9	Adherent film
21	Tobin bronze	25.7	55	50	52	20	Discolored
23	Everdur	25.5 ^a	1500	930	1100	430	Porous film, microscopic pitting
26	Hills McCanna 45	25.5 ^a	16	15	16	6.3	Discolored
27	Hills McCanna 52	25.5 ^a	1300	1300	1300	510	Etched
28	Hills McCanna 55	25.5	190	140	160	63	Etched
29	Hytensl	25.5	23	15	21	8.3	Film
37	Monel	25.5	34	32	33	13	Discolored
38	Nichrome IV	25.5	490	460	480	190	Severe pitting
39	Allegheny	25.5 ^{a,b}	1.5	0.06	0.6	0.2	No film, microscopic pitting
40	CrV ₃	25.5 ^a			80,000	30,000	Porous film, severe localized pitting
41	CrV ₄	25.5 ^a	210	200	200	79	Adherent film, severe localized pitting
44	Enduro (C. L. P.)	25.5 ^{a,b}	0.4	0.2	0.3	0.1	No film, bright
52	Uniloy 2825	25.5 ^{a,b}	0.9	0.1	0.4	0.2	No film, bright

^a Partially immersed.

^b Very high corrosion rate upon initial exposure.

Brownish non-adherent films formed on Adnic which was uniformly corroded at a high rate. Film formation occurred on Alcumite G whose high rate of corrosion was increased by products of corrosion. The depth of some of the pin holes which occurred in Alpac indicated a penetration rate of 0.03 cm. per hour. With Ambrac a loose yellow film was formed in c. p. solutions. The presence in solution of products of corrosion or of sulfuric acid increased its corrosion.

Ampeco 12 and Ampeco 18 were uniformly corroded when totally immersed, but were not when partially immersed,

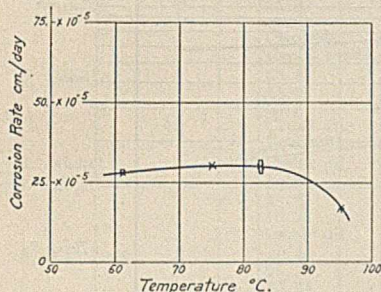


Figure 3—Temperature Effect on Corrosion of Hytensl in Phosphoric Acid

especially the former alloy. Its high corrosion rate was increased tremendously, that portion of the metal above the liquid line being attacked the most. The fairly low corrosion rate of the latter alloy was only doubled by partial immersion. In non-aerated solutions the rate of corrosion of Ampeco 18 was but 50 per cent of that in solutions aerated at the rate of 50 and 95 cc. air per minute. The crude acid left the surface rough. This alloy was sensitive to products of corrosion, copper being reprecipitated on the surface in form of blisters. The addition of 1 gram of copper phosphate to 150 cc. c. p. acid increased the corrosion ten to forty fold.

Barberite was badly corroded when partially immersed, the area above the liquid line being affected the most. The metal was etched and microscopically pitted. The depth of some pits corresponded to a penetration rate of but 30×10^{-5} cm. per day. The corrosion rate at room temperature was found to be 2.5×10^{-5} cm. per day in 25 per cent acid, as determined by a beaker test extending over 42 days.

Low brass A and Low brass B both have high corrosion rates. Non-adherent films were formed in c. p. acids. The presence of sulfuric acid and of products of corrosion increased the corrosion rate of the former. A thick adherent film formed on the latter alloy when in crude acid. After the initial exposure no loss in weight was observable in non-aerated non-agitated concentrated crude acid.

Little or no deposits were formed on Tobin bronze by c. p. acids, but the surfaces were part copper-colored and part blue-black. In 10 per cent acid there was microscopic pitting. Non-uniform tarnishing occurred in dilute crude, but in concentrated crude, on top of a uniform and adherent tarnish film was a loose gray outer deposit. The corrosion rates in 10 per cent c. p. and in the dilute crude acids were initially high, but decreased with each exposure, rapidly at first, and then more slowly; the corrosion rate indicated is probably near the true rate. Products of corrosion seemed to have little effect on the fairly low rates of corrosion.

Yellow brass corroded uniformly at a fairly low rate, little affected by the accumulation of the products of corrosion. A black adherent film forms in aerated solutions as compared to the copper-colored surface when under conditions of non-aeration. The addition of hydrofluoric acid to phosphoric acid at room temperature did not seem to affect the corrosion rate of a machine brass similar to the yellow brass.

Heavy crustations formed on the unexposed portion when Everdur was partially immersed in the acid, and microscopic pitting occurred. The depth of some pits indicated a pitting rate of 0.01 mm. per day. At room temperature the corrosion rate, as determined by a beaker test, was 2.7×10^{-5} cm. per day.

Fine black deposits were formed on Hastelloy D in all concentrations of the acid, the surface, after scrubbing, being left a smutty black. The film formed by concentrated crude acid turned green on exposure to the air. The alloy offered fair resistance to phosphoric acid.

Hills McCanna 42 in 25 per cent c. p. acid formed a light film which washed off, leaving the metal tarnished. The corrosion rate was high. In dilute crude acid a thick adherent film was formed and the metal surface was left rough. Hills McCanna 45 was more resistant to c. p. acid but less resistant to crude acid than the alloy 42. Slight non-adherent films formed in c. p. acids and the surface was tarnished. In crude dilute acid a heavy crumbly film was formed and the surface was much roughened. The beaker test with concentrated crude acid showed a high initial corrosion rate followed by a very low one, an adherent film being formed. Hills McCanna 52, when partially immersed, was badly corroded and etching occurred. Hills McCanna 55 corroded at a slow rate when initially immersed, but corrosion reached a high rate at about the fifth day. Occasional pitting occurred and the surface was etched.

Slight film formation occurred on Hytensl in c. p. acids. A thick, slightly adherent film was formed in crude acid. When in aerated solutions, maximum corrosion was observed in the temperature range 75° to 85° C., falling off rapidly at higher temperatures, as shown in Figure 3. The maximum occurs when there is a balance between decreasing solubility of oxygen due to temperature rise and the increased rate of oxygen diffusion to the metal surface (45). The higher value found for the corrosion rate in 25 per cent acid at 80° C., as compared to what would be expected in 25.2 per cent acid as read from the curve in Figure 3, shows the degree of reproducibility between two workers working with the same alloy and apparatus. The preparation of the surface before weighing was a controlling factor.

Illium G showed very good resistance to c. p. phosphoric acids of all concentrations up to 50 per cent and at temperatures up to at least 95° C. There was no film formation nor pitting, and the metallic luster was not dimmed. The corrosion rate in the crude acids was also very low, a slight non-adherent film being formed leaving the surface dull. No pitting occurred. Sulfuric acid additions to c. p. acid, as well as the presence of products of corrosion, tended to increase the corrosion rate. The metal was porous and difficulty was encountered in drying the test specimens to constant weight.

Somewhat erratic results were obtained when determining the corrodibility of Illium 50. This metal was much less resistant than Illium G, being etched deeper and deeper with time, a non-adherent film being formed. The addition of sulfuric acid caused the formation of an adherent film, yet tended to increase corrosion. Products of corrosion increased the corrosion rate. The metal was severely attacked by crude acid.

The lead alloy, A, with 9.4 per cent antimony, was much more corrodible than lead, especially in the more dilute solutions. The corrosion rate was highest in 25 per cent c. p. acid, and a loosely adherent film was formed. At other concentrations the films formed were much more adherent. The low corrosion rate in crude acid was undoubtedly due to

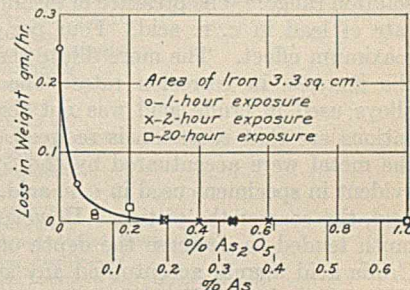


Figure 4—Effect of Arsenic on Corrosion of Iron by Phosphoric Acid

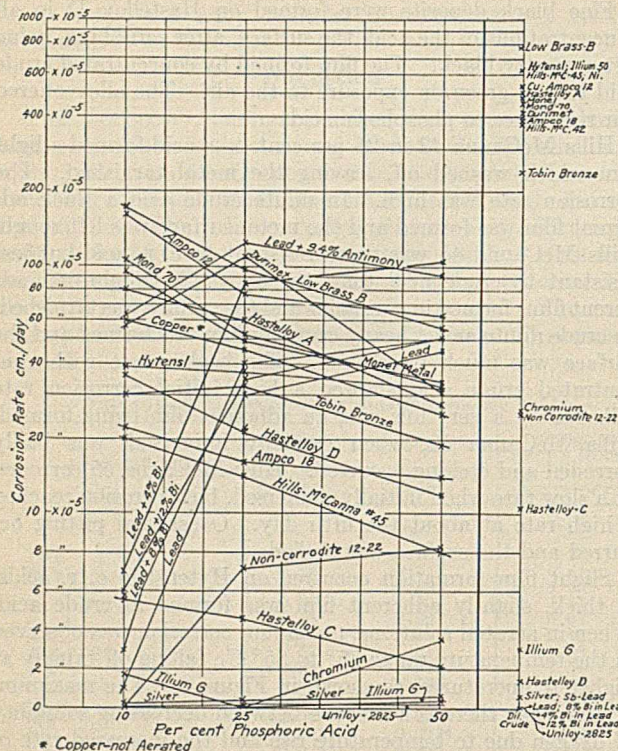


Figure 5—Corrosion of Metals in Aerated Phosphoric Acid at 80° C.

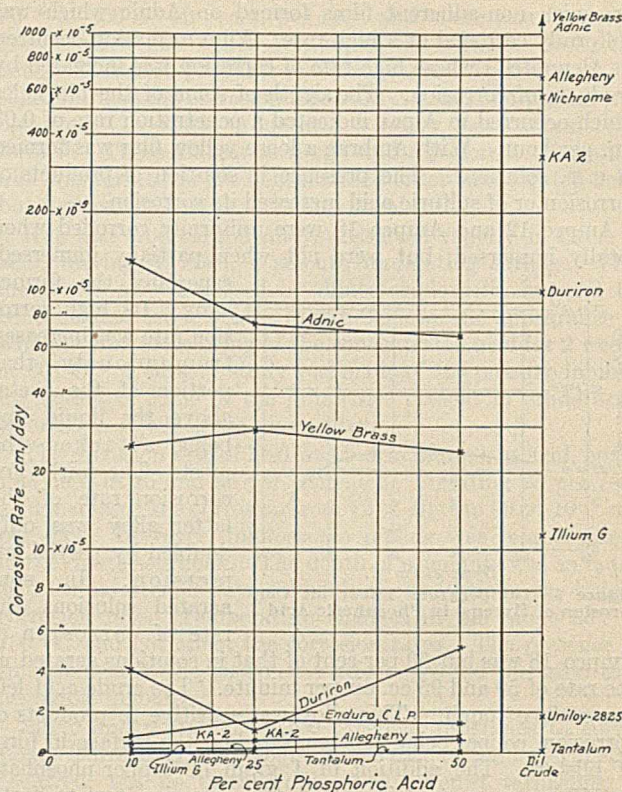


Figure 6—Corrosion of Metals in Aerated Phosphoric Acid at 95° C.

the protective action of the film. There was no evidence of pitting.

To be compared with the lead-antimony alloy are the lead-bismuth alloys, B, C, and D, all of which are in the solid solution range. The presence of bismuth raised the corrosion rate of lead in c. p. acid. Four per cent bismuth had the maximum effect. The more dilute the solution the less was the increase in corrosion rate. The effect of bismuth in alloys used in crude acid was not readily apparent. Indications are that corrosion is reduced. Any indentations in the metal were accentuated by the corrosion. Pitting was evident in specimens used in c. p. acid. The more dilute the acid, the coarser the pitting. However, the presence of bismuth tended to decrease the depth of pitting in pure lead. Crude acid merely accentuated any surface indentations in the same period of time.

Mond 70 and monel metal behaved quite similarly as regards their high corrosion rates, film formations, and pitting. The former alloy pitted deeper than the latter and pitting was most noticeable in the c. p. dilute acid. It was very evident on both metals when in dilute crude acid. The direction of pitting was perpendicular to the face of the sheet. Cuts from the grind wheel were widened and deepened.

Nichrome IV and nichrome ribbon offered very little resistance to phosphoric acid and were deeply pitted.

FERROUS ALLOYS—CrV₃ and CrV₄, steels containing 7.7 and 14.4 per cent chromium, respectively, were both badly pitted by c. p. acid. It is believed that if CrV₄ were heat-treated to keep the carbon in solution the corrosion resistance would be considerably improved.

The Durimet alloy that was tested was not particularly resistant to phosphoric acid. A black non-adherent film formed in c. p. acid, while in crude acid the film formed was adherent.

Duriron was very resistant to c. p. acid, even though etched, and offered fair resistance to crude acid. It is believed that the corrosion in crude acid is considerably affected by the presence of hydrofluoric acid. The discrepancy between these values and those shown in Table I is due to the

shortness of these tests. Corrosion rates were highest during the first immersion period, and slowly decreased with time.

Enduro (C.L.P.-18 Cr) offered slightly less resistance than 18-8 metal. Partial immersion did not affect the corrosion rate. The crude acid attacked this alloy at a very rapid rate, and the more concentrated the acid, the more severe the attack.

Fahrite, a high carbon steel alloyed with nickel and chromium, was very deeply pitted by c. p. acid.

Hastelloy A corroded at a high rate, forming non-adherent black films in c. p. acid, and pitting slightly. Both the film formation and pitting were the most severe in 10 per cent acid. In dilute crude, a non-uniform adherent film was formed, and the surface was discolored and roughened. Tarnishing and pitting occurred in concentrated crude acid with no film formation.

Hastelloy C appeared to be highly resistant to all concentrations of the acid. In the c. p. acids there was no film formed, no pitting, and the metallic luster was not dulled. In the dilute crude a slightly crumbly film was formed, and in both the dilute and concentrated crude the luster of the metal was dulled, but no pitting occurred.

Allegheny metal, when totally immersed, offered excellent resistance to c. p. acids, but a considerable attack, accompanied by film formation, occurred in crude acid, as shown in Figure 2. When hydrochloric acid was added to c. p. acid, a thin non-adherent black film was formed and the corrosion rate was increased. KA-2 was similar in behavior. The difference in nickel content might explain the slight differences in corrosion rates. Pitting occurred along the edge of the plate and was most noticeable after treatment in crude acid. Figure 2 shows the appearance of the metal after being in crude acid for two weeks. Non-corrodite 12-22 showed very good resistance to c. p. acid, no film being formed and the surface remaining bright. In dilute crude acid a slight film formed and the surface was etched. No film was formed in the concentrated crude acid.

Table VI—Corrosion of Metals in Pure and Crude Phosphoric Acid^a

SAMPLE	ACID STRENGTH TEMP.		CORROSION RATE PER DAY				REMARKS
			Max.	Min.	Average		
	%	° C.	$\text{Cm.} \times 10^{-5}$	$\text{Cm.} \times 10^{-5}$	$\text{Cm.} \times 10^{-5}$	$\text{In.} \times 10^{-5}$	
METALS							
2 Chromium	50.8	81			3.5	1.4	Bright
	25.0	81			0.0	0.0	Bright
	10.3	81			0.0	0.0	Bright
	Crude dil.	81			26	10	Bright
	Crude concd. ^e	80			10	3.9	Bright, pitting
3 Copper (electrolytic)	50.0 ^c	80	26	24	25	9.8	No film
	25.0 ^c	80	51	38	45	18	No film
	10.0 ^c	80	62	56	59	23	Film
	Crude dil.	80	540	530	535	210	Porous film, rough surface
	Crude concd. ^{d,e}	79	250	240	245	96	Porous film, discolored
5 Lead	50.8	81	48	42	45	18	Film
	25.5	81	34	26	30	12	Microscopic pitting, rough surface
	10.3	81	1	0.0	1	0.4	Microscopic pitting, discolored
	Crude dil.	81	Gain	Gain	0.0	0.0	Discolored
	Crude concd. ^e	80	0.4	Gain	0.4	0.2	Discolored
6 Nickel	Crude dil.	80			560	220	Film, pitting/
7 Silver	50.0	80	0.7	0.5	0.6	0.24	Discolored/
	25.0	80	0.5	0.2	0.35	0.14	Discolored/
	10.3	80	0.4	0.0	0.2	0.08	Discolored/
	Crude dil.	80	0.1	0.0	0.1	0.04	Discolored/
8 Tantalum	50.8 ^b	98			0.0	0.0	Discolored/
	25.7 ^b	98			0.0	0.0	Discolored/
	10.8 ^b	98			0.0	0.0	Discolored/
	Crude dil.	98			0.0	0.0	Discolored/
9 Tin	Crude concd. ^e	98			800	310	Etched
NON-FERROUS ALLOYS							
11 Admic	50.8	98			68	27	Film, discolored/
	25.7	98			75	30	Film, discolored/
	10.3	97			130	51	Non-adherent film, discolored/
	Crude dil.	98			1300	510	Porous film, discolored/
14 Ambrac	50.8	98	38	38	38	15	Porous film, microscopic pitting
15 Ampco 12	50.8	81	67	58	63	25	Discolored/
	25.7	81	77	77	77	30	Discolored/
	10.3	81	160	160	160	63	Film, etched
	Crude dil.	80	590	460	530	210	Porous film, localized pitting
	Crude concd. ^e	79	11	1.0	6	2.4	Porous film
16 Ampco 18	50.8	81	16	13	14	5.5	Discolored/
	25.7	81	16	15	16	6.3	Discolored/
	10.3	81	24	21	22	8.7	Discolored/
	Crude dil.	81	390	390	390	150	Porous film, rough surface, localized pitting
	Crude concd. ^e	79	95	14	25	9.8	Film, pitting, discolored/
18 Low brass A	50.8	95	160	150	155	61	Film, microscopic pitting, bright/
19 Low brass B	50.0	80			56	22	Film, discolored/
	25.0	80			98	39	Film, dull/
	10.0	80			170	67	Film, discolored/
	Crude dil.	79			790	310	Discolored/
	Crude concd. ^e	79			0.0	0.0	Discolored/
21 Tobin bronze	50.8	80	19	18	19	7.5	Colored
	25.0	80	35	32	34	13	Discolored/
	10.3	80	40	29	30	12	Microscopic pitting, discolored/
	Crude dil.	80	350	230	240	94	Discolored/
	Crude concd. ^e	79	31	19	25	19.8	Discolored/
22 Yellow brass	50.8	97	25	23	24	9.4	Discolored/
	25.7	97	38	19	29	11	Discolored/
	10.3	96	26	24	25	9.6	Discolored/
	Crude dil.	95			1400	550	Copper-colored, porous film
24 Hastelloy D	50.0	80	13	11	12	4.7	Film, discolored/
	25.0	80	25	18	22	8.7	Film, localized pitting, discolored/
	10.0	80	39	32	35	14	Film, localized pitting, discolored/
	Crude dil.	80	2.7	0.0	1.4	0.6	Porous film, discolored/
	Crude concd. ^e	79	56	55	56	22	Adherent film, localized pitting/
25 Hills McCanna 42	25.0	81			60	24	Non-adherent film, discolored/
	Crude dil.	81			380	150	Adherent film, rough surface, discolored/
26 Hills McCanna 45	50.8	81			8	3.1	Discolored/
	25.0	80			14	5.5	Film, discolored/
	10.3	80			20	7.9	Film, discolored/
	Crude dil.	80			580	230	Porous film, rough surface, discolored/
	Crude concd. ^e	79	3	Gain	3	1.2	Porous film, discolored/
29 Hytensl	50.8	80	34	30	32	13	Film, discolored/
	25.2	81	29	28	28.5	11	Film, discolored/
	25.2	75	30	30	30	12	Film, discolored/
	25.0	80	38	37	37.5	15	Film, discolored/
	25.2	83	32	28	30	12	Film, discolored/
	25.2	95	22	17	20	7.9	Film, discolored/
	10.3	80	40	38	39	15	Film, discolored/
	Crude dil.	79	660	570	615	240	Film, rough surface/
	Crude concd. ^e	79	155	142	148	58	Film, discolored/
30 Illium G	50.8	98	16	0.4	8	3	Film
	50.0	80	1.1	Gain	0.4	0.16	Bright
	25.7	94			0.2	0.08	Bright
	25.0	80	0.19	Gain	0.0	0.0	Bright
	10.3	94	0.0	Gain	0.0	0.0	Bright
	10.0	80	2.2	Gain	1.7	0.7	Bright
	Crude dil.	94	15	9.4	13	5.1	Film, dull
	Crude dil.	80			3.0	1.2	Film, dull
	Crude concd. ^e	94			11	4.3	Film, dull
	Crude concd. ^{d,e}	80			3.4	1.3	Film, dull
31 Illium 50	50.8	97	53	51	52	20	Film, etched
	Crude dil.	81			600	240	Film, rough surface/
32 Lead A	50.0	80	106	77	92	36	Adherent film
	25.0	80	130	120	123	49	Film, discolored/
	10.0	80	64	63	63	25	Adherent film, discolored/
	Crude dil.	80	1.2	0.0	0.6	0.24	Black adherent film
	Crude concd. ^e	80	0.36	0.0	0.18	0.07	Black adherent film

Table VI—Corrosion of Metals in Pure and Crude Phosphoric Acid^a—(Continued)

SAMPLE	ACID STRENGTH	TEMP.	CORROSION RATE PER DAY				REMARKS
			Max.	Min.	Average		
	%	° C.	Cm. × 10 ⁻⁵	Cm. × 10 ⁻⁵	Cm. × 10 ⁻⁵	In. × 10 ⁻⁵	
METALS							
33 Lead B	50.8	81	116	47	106	42	Microscopic pitting
	25.7	82	89	81	85	33	Microscopic pitting
	10.3	81	7	Gain	7	3	Microscopic pitting
	Crude dil.	81	0.4	Gain	0.2	0.08	
	Crude concd. ^e	80	0.4	Gain	0.2	0.08	
34 Lead C	50.8	81	55	47	51	20	Microscopic pitting
	25.7	81	50	31	41	16	Pitting
	10.3	81	5	Gain	3	1.2	Localized pitting
	Crude dil.	81	Gain	Gain	0.0	0.0	
	Crude concd. ^e	80	0.2	Gain	0.2	0.08	
35 Lead D	50.8	81	62	49	56	22	Microscopic pitting
	25.7	81	36	34	35	14	Pitting
	10.3	81	7	5	6	2	Pitting
	Crude dil.	81	Gain	Gain	0.0	0.0	
	Crude concd. ^e	80	0.3	Gain	0.2	0.08	
36 Mond 70	50.8	80			34	13	Film, discolored/
	25.0	80			52	20	Film, discolored/
	10.3	80			105	41	Film, microscopic pitting
	Crude dil.	80			450	180	Porous film, severe microscopic pitting, discolored/
	Crude concd. ^e	79			74	29	Thick film, discolored/
37 Monel	50.8	80			34	13	Film
	25.0	80			49	19	Film
	10.3	80			95	37	Film
	Crude dil.	80			480	190	Film, pitting, discolored/
	Crude concd. ^e	79			70	28	Film, discolored/
38 Nichrome IV	Crude dil.	97			560	220	Severe localized pitting
FERROUS ALLOYS							
39 Allegheny	50.8	97			0.7	0.3	Bright/
	25.7	97			0.2	0.08	Bright/
	10.3	95			0.2	0.08	Bright/
	Crude dil.	97			680	270	Non-adherent film
42 Durimet	50.8	80			31	12	Film, discolored/
	25.0	80			110	43	Non-adherent film, bright/
	10.3	80			57	22	Non-adherent film
	Crude dil.	80			410	160	Porous film, rough surface/
	Crude concd. ^e	80			140	55	Film, discolored/
43 Duriron	50.8	97			5.2	2.0	Etched, bright/
	25.7	97			1.1	0.4	Etched, bright/
	10.3	96			4.1	1.6	Etched, bright/
	Crude dil.	98			100	39	Film, discolored/
44 Enduro (C. L. P.)	50.8	98	1.7	1.5	1.5	0.59	Bright/
	25.7	97	1.6	1.1	1.4	0.55	Bright/
	10.3	97	0.9	0.6	0.8	0.3	Bright/
	Crude dil.	98			8500	3700	Non-adherent film
45 Fahrite	50.8	98	350	230	280	110	Severe pitting, discolored/
46 Hastelloy A	50.0	81	30	25	28	11	Bright
	25.0	81	60	59	60	24	Dull
	10.0	80	85	76	80	32	Film, pitting/
	Crude dil.	80	540	470	505	195	Porous film, rough surface/
	Crude concd. ^{d,e}	80	230	230	230	91	Film, pitting/
47 Hastelloy C	50.0	81	3.4	0.8	2.1	0.8	Bright
	25.0	81	4.7	4.5	4.6	1.8	Bright
	10.0	81	5.8	5.2	5.5	2.2	Bright
	Crude dil.	80	11	10	10.5	4.1	Dull
	Crude concd. ^{d,e}	80	7.8	6.9	7.4	2.9	Dull
48 KA-2	50.8	98	0.7	0.7	0.7	0.3	Bright, pitting
	25.7	98			0.5	0.2	Bright, pitting
	10.3	98			0.4	0.2	Bright
	Crude dil.	97	440	220	330	130	Film, pitting
49 Non-corrodite—12-22	50.0	80	0.82	Gain	0.82	0.32	Bright/
	25.0	80	0.72	Gain	0.72	0.28	Bright/
	10.3	80	0.0	0.0	0.0	0.0	Bright
	Crude dil.	80			25	9.8	Film, etched
	Crude concd. ^e	78	3.0	2.0	2.5	0.98	Bright
50 Silchrome	50.8	98	1.5	1.1	1.3	0.51	Bright
51 Uniloy 1409	50.0	80			13000	5100	Rough surface
	25.0	80			6700	2600	Porous film, rough surface/
	10.0	80			1900	750	Porous film, rough surface/
	Crude dil.	80			9600	3800	Porous film, pitting
	Crude concd. ^e	79			8700	3400	Heavy porous film, rough surface/
52 Uniloy 2825	50.8	99	0.4	0.2	0.3	0.11	Bright/
	50.0	81	0.3	0.0	0.2	0.08	Bright/
	25.0	81	0.0	0.0	0.0	0.0	Bright/
	10.0	81	0.0	0.0	0.0	0.0	
	Crude dil.	99	3.6	0.0	1.8	0.7	Dull
	Crude dil.	80	0.0	0.0	0.0	0.0	Bright
	Crude concd. ^e	80	1.7	1.4	1.6	0.6	

^a Crude H₃PO₄ made from Florida pebble phosphate.^b Partially immersed.^c Not aerated.^d Concentrated crude from Tennessee brown rock not agitated.^e Beaker test—totally immersed, not aerated.^f After scrubbing with bristle brush, soap, and water.

Silchrome, an alloy with 19 per cent chromium, but high in silicon, was resistant to c. p. acid.

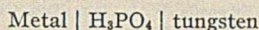
Uniloy 1409 showed very high corrosion rates. Film formation occurred, and the metal was pitted along the edge of the plate. But Uniloy 2825 was extremely resistant to phosphoric acid corrosion. No films were formed in any concentration of acid and the metallic luster was dulled only in the dilute crude.

Observations on Passivity

When stainless irons and steels were first placed in c. p. phosphoric acid, the rate of corrosion was very high, but slowly fell off to a very low figure. The difference in rates was as much as 1000×10^{-5} cm. per day. If 18 per cent chrome iron was dipped in nitric acid, then placed in phosphoric acid, no reaction was noticeable, and the corrosion was low. But if it was dipped in hydrochloric acid before

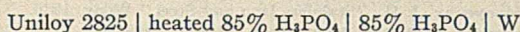
being placed in phosphoric acid, rapid reaction occurred, even with air bubbling through the solution; if left over night, passivation ensued. Halides are well-known de-passivating reagents. They caused film formation. The presence of hydrofluoric acid brought about an etching of the surface.

The behavior of some of these ferrous alloys when placed in hot acid was studied by watching the voltage changes of the cell,



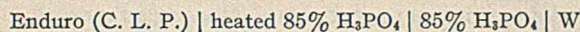
Phosphoric acid was placed in two beakers connected by a siphon. One beaker was on a hot plate and the other was heat-insulated and placed near by. A strip of metal was placed in the former beaker, and an electrode of tungsten, which offers excellent resistance to c. p. acid, was placed in the latter. The electrode was made of a thick piece of tungsten wire, one end of which was fused to a glass tube. Mercury was used to make electrical connection between the tungsten and the lead wire from the potentiometer used to determine the e. m. f. of the cell. If the metal was passive it was cathodic—i. e., current flowed within the cell from anodic tungsten to cathodic metal.

Simultaneous readings of temperature and voltage of the cell



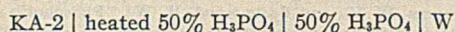
were taken. Around 80° C. there were fluctuations of the voltage, but Uniloy 2825 remained cathodic; around 130° C. the voltage was 0; at 140° C. Uniloy became anodic and rapid reaction took place, the voltage being around 0.25 volt. On cooling a hysteresis was noticed, the voltage not reaching 0 till 100° C., which showed that passivation of the metal was a slow process in phosphoric acid.

The voltage of the cell



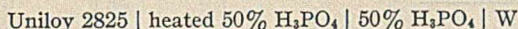
had reduced to 0 at 80° C. and at 135° C. vigorous reaction was noticeable, Enduro being anodic.

The cell



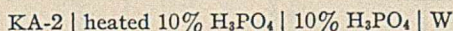
at the boiling point developed only 0.05 volt (KA-2 anodic).

The cell



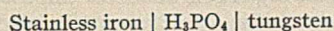
developed 0.05 volt (Uniloy 2825 cathodic) at the boiling point of the acid.

The cell



increased in voltage as the acid was heated, KA-2 remaining cathodic. When a drop of hydrochloric acid was added to the boiling phosphoric acid, the polarity of the cell reversed, KA-2 becoming anodic with rapid reaction occurring. The voltage was 0.5 volt.

This data, in correlation with information in Table I, indicates a quick way of determining the maximum temperature at which stainless irons may be used with phosphoric acid—namely, the determination of the temperature at which the stainless iron becomes the anode of the cell



Inhibitors of the Attack of Phosphoric Acid on Iron

There is present in concentrated crude acid made by the sulfuric acid method, some inhibitor of the action of phosphoric acid on iron. In an effort to determine what the inhibitor is, Armco iron disks $\frac{1}{2}$ inch (1.27 cm.) in diameter by

$\frac{3}{8}$ inch (0.95 cm.) thick were suspended in 50 per cent c. p. acid to which was added a small quantity of a possible inhibitor. The loss in weight was determined after the disks had been in solution for 1 hour at 80° C. Table VII lists the results.

Table VII—Effect of Inhibitors on Armco Iron in Phosphoric Acid
100 cc. solution; 50 per cent H_3PO_4 ; 80° C.; 1 hour

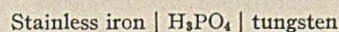
ADDITION		SURFACE	LOSS IN WEIGHT
	%		Gram
None		Pitting, film	0.13
As ⁺⁺⁺	0.49	Bright	0.00
HCl	0.75	Film	0.04
Pine oil	1 cc.	Film	0.05
Mucilage	1 cc.	Film	0.06 ^a
Pyridine	0.75	Film	0.10
HF	0.45	Film	0.14
H ₂ SiF ₆	0.27	Film	0.14
H ₂ SO ₄	0.75	Film	0.18

^a Frothing.

The presence of sulfuric acid, fluosilicic acid, and hydrogen fluoride tended to increase the corrosion of iron in phosphoric acid. Pine oil, mucilage, and pyridine inhibited the reaction of iron with phosphoric acid. It is quite possible that other types of organic material also inhibit the reaction. The inhibiting effect of hydrochloric acid was also noticed at room temperature. It was because of the sluggishness of the reaction and the unexpected result that the experiment was carried out at 80° C., as recorded above. Arsenic is an efficient inhibiting agent. Figure 4 shows the effect of various quantities of arsenic pentoxide on the corrosion of iron in 85 per cent c. p. acid at 80° C. Indications are that in 50 per cent acid slightly more arsenic is required to prevent corrosion, about 1400 p. p. m. This is much more than is found in the crude acid, so there must be present in the crude phosphoric acid other materials which inhibit corrosion.

Conclusions

This work has indicated that 18 per cent chromium should be present in stainless irons used to resist c. p. acids; that the presence of 8 per cent nickel with 18 per cent chromium is beneficial, and that more nickel is detrimental for use in c. p. acid and very beneficial for use in crude acid (35); that corrosion resistance increases with the chromium content; that concentrated acid attacks stainless irons more than dilute acids; that there is a maximum temperature for each alloy above which it should not be used in concentrated acid; that this maximum temperature is the temperature at which the stainless iron becomes the anode of the cell



Only a few of the non-ferrous alloys can be compared to show relationships between composition and corrosion resistance to phosphoric acid. For instance, the higher the aluminum content of copper-aluminum-iron alloys, the better the corrosion resistance to c. p. acid. The corrosion resistance to c. p. acid is decreased, but to crude acid increased by the presence of iron. Nickel is very detrimental to the corrosion resistance of these alloys.

Figures 5 and 6 show the corrosion rates of alloys tested in mechanically agitated solutions through which air bubbled at the rate of 95 cc. per minute. The corrosion rates in both c. p. and dilute crude acids are indicated. There are very few cases where alloys show equal or better resistance to crude acid than to c. p. acid.

A corrosion rate of 1×10^{-5} cm. per day may be regarded as indicative of a resistant material. Those alloys whose corrosion rate is 10×10^{-5} cm. per day may be regarded as of doubtful use. Thus in c. p. acids, the stainless irons and steels, Illium G, Tantalum, Duriron, silver, chromium,

Hastelloy C, and Hills McCanna 45 (concentrated acid) are possible resistant metals, and in dilute crude, 28 per cent chromium steel, Tantalum, lead and its alloys, Hastelloy D, and Illium G. If Duriron be taken as a standard for crude acid, then Hastelloy C, high nickel 18 per cent chromium steels, and chromium may be also considered.

It must not be construed that other metals, like copper, cannot be used on certain occasions. Before using any metal in large quantities, preliminary trials should be made. Such trial should be under actual working conditions and should involve checking up totality of immersion, concentration changes, composition of the acid, relative velocity between specimen and acid, the possibility of the metal surface being rubbed, temperature, degree of aeration, and metallic contacts.

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Limitations of Phenol Coefficients of Coal-Tar Disinfectants¹

C. M. Brewer and G. L. A. Ruehle

FOOD AND DRUG ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

THE aim of many researches since disinfectants were first studied has been to devise a simple laboratory test for indicating the value of a germicide under practical conditions of use. As a result of this effort, the idea of the phenol coefficient has been conceived, and today an integral part of the bacteriological examination of a disinfectant consists in the determination of its phenol coefficient. Its value lies in its convenience and reliability when carried out under strictly standardized laboratory conditions. Unfortunately, the phenol coefficient test does not duplicate accurately the many diversified conditions met with in the fields in which disinfectants are used. In fact, it is too much to expect a single laboratory test to accomplish this. However, there seems to be a tendency, even among experi-

enced workers, to place too much reliance upon the phenol coefficient. Attempts have been made with the usual types of disinfectants to establish a ratio between the killing dilutions for *B. typhosus* (*Eb. typhi*) and those for the other common pathogens, and thus from the *B. typhosus* phenol coefficient to specify the desirable dilutions to be used for certain pathogenic organisms under certain conditions. This, of course, would result in a great saving in time and labor.

Philbrick (1) has recently tested four coal-tar disinfectants against several pathogenic organisms, and concludes from his experiments that if the *B. typhosus* phenol coefficient of a coal-tar disinfectant is known, it is possible to calculate the approximate efficiency of the preparation against *Staphylococcus aureus*, *B. diphtheriae*, *Streptococcus hemolyticus*, and *Pneumococcus*. Such a statement, however, must be closely

¹ Received October 20, 1930.

Table I—Coal-Tar Disinfectants Giving Milky Solutions

PHENOL COEFFICIENTS		APPROX. RATIO OF COEFFICIENTS	PHENOL COEFFICIENTS		APPROX. RATIO OF COEFFICIENTS
<i>B. typhosus</i>	<i>Staph. aureus</i>		<i>B. typhosus</i>	<i>Staph. aureus</i>	
0.66	0.25	3:1	3.3	1.0	3:1
0.8	0.04	20:1	3.6	0.33	11:1
0.8	0.4	2:1	3.6	0.67	5:1
0.9	0.17	5:1	3.6	0.67	5:1
1.4	0.1	14:1	3.6	0.75	5:1
1.55	0.12	12:1	3.9	0.25	16:1
1.55	0.15	10:1	3.9	0.33	12:1
1.7	0.12	14:1	3.9	0.33	12:1
1.7	0.17	10:1	3.9	0.33	12:1
1.7	0.25	7:1	3.9	0.33	12:1
1.7	0.5	3:1	3.9	0.4	10:1
1.7	0.66	3:1	3.9	0.4	10:1
1.7	0.66	3:1	3.9	0.4	10:1
1.8	0.33	5:1	3.9	0.5	8:1
2.0	0.12	16:1	3.9	0.5	8:1
2.0	0.15	13:1	3.9	0.5	8:1
2.0	0.25	8:1	3.9	0.5	8:1
2.0	0.25	8:1	3.9	0.5	8:1
2.0	0.33	6:1	3.9	0.6	7:1
2.0	0.33	6:1	2.9	0.6	7:1
2.0	0.33	6:1	3.9	0.67	6:1
2.1	0.33	6:1	3.9	0.67	6:1
2.2	0.12	18:1	3.9	0.67	6:1
2.2	0.17	13:1	3.9	0.67	6:1
2.2	0.17	13:1	4.2	0.33	13:1
2.2	0.17	13:1	4.2	0.8	5:1
2.2	0.20	11:1	4.4	0.33	13:1
2.2	0.25	9:1	4.4	0.4	11:1
2.2	0.25	9:1	4.4	0.5	9:1
2.2	0.25	9:1	4.4	0.5	9:1
2.2	0.25	9:1	4.4	0.5	9:1
2.2	0.25	9:1	4.4	0.5	9:1
2.2	0.33	7:1	4.4	0.5	9:1
2.2	0.33	7:1	4.4	0.5	9:1
2.2	0.33	7:1	4.4	0.6	7:1
2.2	0.33	7:1	4.4	0.6	7:1
2.2	0.33	7:1	4.4	0.67	7:1
2.2	0.33	7:1	4.4	0.67	7:1
2.5	0.12	20:1	4.4	0.67	7:1
2.5	0.33	8:1	4.4	0.67	7:1
2.5	0.33	8:1	4.4	0.67	7:1
2.7	0.33	8:1	4.4	0.67	7:1
2.8	0.17	17:1	4.4	0.67	7:1
2.8	0.17	17:1	4.4	0.67	7:1
2.8	0.17	17:1	4.4	0.67	7:1
2.8	0.25	11:1	4.4	0.75	6:1
2.8	0.25	11:1	4.4	0.83	5:1
2.8	0.25	11:1	4.4	1.0	4:1
2.8	0.25	11:1	4.4	1.0	4:1
2.8	0.30	9:1	4.7	0.83	6:1
2.8	0.33	8:1	5.0	0.33	15:1
2.8	0.33	8:1	5.0	0.5	10:1
2.8	0.33	8:1	5.0	0.67	8:1
2.8	0.33	8:1	5.0	0.67	8:1
2.8	0.4	7:1	5.0	0.75	7:1
2.8	0.4	7:1	5.0	0.75	7:1
2.8	0.4	7:1	5.0	0.75	7:1
2.8	0.5	6:1	5.0	0.83	6:1
2.8	0.6	5:1	5.0	1.0	5:1
2.8	0.67	4:1	5.0	1.0	5:1
2.8	0.83	3:1	5.0	1.17	4:1
3.0	0.25	12:1	5.0	1.17	4:1
3.0	0.33	9:1	5.3	0.5	11:1
3.0	0.33	9:1	5.5	0.67	8:1
3.0	0.5	6:1	5.5	0.67	8:1
3.0	0.5	6:1	5.5	0.67	8:1
3.3	0.25	13:1	5.5	0.83	7:1
3.3	0.25	13:1	6.1	0.5	12:1
3.3	0.25	13:1	6.1	0.83	7:1
3.3	0.25	13:1	6.1	0.9	7:1
3.3	0.3	11:1	6.1	1.5	4:1
3.3	0.33	10:1	6.6	0.83	8:1
3.3	0.33	10:1	6.6	0.83	8:1
3.3	0.33	10:1	7.2	1.1	6:1
3.3	0.33	10:1	7.7	1.7	5:1
3.3	0.33	10:1	8.0	1.17	7:1
3.3	0.4	8:1	8.8	1.25	7:1
3.3	0.5	7:1	12.2	5.0	2:1
3.3	0.5	7:1	12.5	2.5	5:1
3.3	0.5	7:1	15.0	2.5	6:1
3.3	0.5	7:1	16.6	5.0	3:1
3.3	0.6	6:1	17.7	10.0	2:1
3.3	0.6	6:1	19.5	4.1	5:1
3.3	0.67	5:1			
3.3	0.67	5:1			

examined, since numerous considerations and difficulties underlie all attempts to make generalizations in this field. At present sufficient work has not been done to determine a criterion of resistance for the great bulk of the pathogenic species. For instance, any figure purporting to give the *Strep. hemolyticus* phenol coefficient of a certain disinfectant is likely to be grossly misleading in the absence of work on the resistance to disinfectants of a large number of strains of this organism. In general, it may be said that for every different germicide there is a different ratio between the *B. typhosus*

phenol coefficient and the phenol coefficient for other organisms. Thus, a chlorine disinfectant having a *B. typhosus* phenol coefficient of 6.0 might also have a *Staph. aureus* phenol coefficient of 6.0, whereas a mercury compound having a *B. typhosus* phenol coefficient of 6.0 (or even 20.0) would in all probability have a *Staph. aureus* phenol coefficient far below 1.

It is true that the ingredients of the coal-tar disinfectants do not present such extreme variations as the examples noted, but nevertheless the complex nature of these disinfectants necessitates consideration of this difference in behavior toward different organisms.

Table II—Cresol Compounds and Compounds Forming Clear Solutions

PHENOL COEFFICIENTS		RATIO OF COEFFICIENTS
<i>B. typhosus</i>	<i>Staph. aureus</i>	
0.66	0.33	2.0:1
1.7	0.83	2.0:1
1.7	1.0	1.7:1
1.7	1.0	1.7:1
1.7	1.0	1.7:1
1.7	1.0	1.7:1
1.7	1.0	1.7:1
1.7	1.17	1.5:1
1.7	1.17	1.5:1
1.7	1.17	1.5:1
1.7	1.33	1.3:1
1.8	1.0	1.8:1
1.8	1.33	1.3:1
2.0	0.83	2.4:1
2.0	0.83	2.4:1
2.0	1.0	2.0:1
2.2	1.17	1.9:1
2.2	1.25	1.8:1
2.2	1.25	1.8:1
2.2	1.5	1.5:1
2.2	1.5	1.5:1
2.8	1.67	1.7:1
2.8	1.67	1.7:1
2.8	2.25	1.2:1
2.8	2.3	1.2:1
2.8	2.67	1.1:1
3.3	1.83	1.8:1
3.3	2.0	1.7:1
3.3	2.1	1.6:1
3.3	2.1	1.6:1
3.3	2.5	1.3:1
3.9	2.5	1.6:1
4.4	2.1	2.1:1
5.0	2.9	1.7:1

In view of the fact that Philbrick reported on the results of only four disinfectants of this type, it seemed desirable to collect data on a much larger number of such preparations before accepting his conclusions as final. We have used the same type of disinfectant² (coal-tar disinfectant) as that used by Philbrick and have compared the *B. typhosus* and *Staph. aureus* phenol coefficients. Our work was limited to an organism whose resistance to phenol has been pretty well established and accepted, the Department of Agriculture strain of *Staphylococcus aureus*.

The *B. typhosus* and *Staph. aureus* phenol coefficients were obtained from 206 samples recently received at this laboratory. The results shown on the cloudy emulsifying type of disinfectants are given in Table I, and those of the clear solution type, similar to liquor *Cresolis Compositus* in Table II. Both the *Staph. aureus* and *B. typhosus* coefficients were determined by the R. W. modified method (2) in use for some years at the Department of Agriculture and used by Philbrick. It will be noted that the list includes preparations having *B. typhosus* phenol coefficients ranging all the way from 0.66 to 19.5, which covers the usual range of products offered in the market. The ratio of the two coefficients is given in the third column. It is realized, of course, that calculating the phenol coefficients to the second decimal place may seem

² The coal-tar disinfectant, as stated above, is not a specific compound. The proportions and kinds of phenols, neutral oils, or other ingredients may vary widely, but if it be necessary to limit the disinfectant to a single compound of known concentration before we can use the phenol coefficient to calculate the desired information, such knowledge would be of little practical use.

to give a false inference as to the accuracy of the method employed, and for this reason only one decimal place is customarily given. In this case, however, such a large proportion of the *Staph. aureus* phenol coefficients are below unity that a wide disparity from the true ratio would result by eliminating the second decimal place. If Philbrick were correct in his conclusion, a fairly constant ratio between the two coefficients should be maintained, since his figures indicate a ratio of approximately 4 or 5 to 1.

The data in the tables need very little discussion. The lack of any definite or reasonably fixed relation between the first two columns is quite apparent. It may be seen that the ratio between the two coefficients varies from 2.0 to 20.0, a discrepancy of 1000 per cent. In the case of the phenol and cresol preparations which form clear solutions, one might expect to find a very close comparison to phenol itself—i. e., a ratio between coefficients of 1 to 1. However, in the coefficients of the 34 preparations given in Table II, deviations of 100 per cent are noted, although in general the ratios are much more consistent than in the other type of preparations.

From these figures we may conclude that it is impossible to calculate the *Staph. aureus* phenol coefficient from the *B. typhosus* coefficient, at least in the case of coal-tar phenol disinfectants, and that the phenol coefficient is limited in usefulness to interpretations based on comparisons of different disinfectants against the test organisms alone and only under the prescribed conditions of the tests.

Noting the absence of a constant ratio of the phenol coefficients of a single type of disinfectant when tested against two organisms of standardized resistance, and having in mind the lack of standardization among other species of pathogenic bacteria and the fact that the resistance among individual strains of any one species varies widely, it seems reasonable in the present state of our knowledge to conclude that any attempt to estimate the efficiency of a disinfectant against other species of pathogenic bacteria from the *B. typhosus* phenol coefficient is unreliable and unsafe.

Literature Cited

- (1) Philbrick, *IND. ENG. CHEM.*, **22**, 618 (1930).
- (2) Reddish, *J. Am. Public Health Assoc.*, **17**, 320 (April, 1927).

Aluminum Chloride and the Friedel-Crafts Reaction^{1,2}

P. H. Groggins

COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

THE utilization of anhydrous aluminum chloride as a reagent for chemical reactions has increased tremendously during the past decade. The recent marked decline in the price of this chemical has stimulated widespread interest in further uses for it and the expansion of existing processes. A discussion of aluminum chloride and the Friedel-Crafts reaction is therefore distinctly appropriate at this time. This synthesis is the foundation of the vat-dye industry in the United States. The statistics in Table I, furnished by the U. S. Tariff Commission, give evidence of the rapid growth of this industry.

It is difficult to estimate the quantity of aluminum chloride required for the preparation of these vat colors, since aluminum chloride may be used, not only in the preliminary synthesis of anthraquinone and its derivatives, but also in many of the subsequent steps of manufacture. Furthermore, and unfortunately so, the data in Table I are not based on simple strength dyestuff. The poundage represents commercial pastes having an actual dyestuffs content ranging from 8 to 25 per cent. It is estimated that the consumption of anhydrous aluminum chloride will be approximately equal to the production of actual net dyestuffs.

In the field of petroleum technology the quantities of

The recent marked decline in the price of anhydrous aluminum chloride has stimulated widespread interest in further uses for it. It is estimated that almost 2 million pounds are used annually for the preparation of anthraquinone and its derivatives. The exceptional fastness of the vat colors made from these intermediates and the fact that they are being made available at progressively lower prices has resulted in an increase in vat dye production of 500 per cent in five years. The use of aluminum chloride in the production of saturated petroleum products, vat colors, and other useful compounds is certain to increase on account of the many important developments now receiving consideration.

aluminum chloride used are much greater. In 1929 McAfee (10) stated that the Gulf Refining Company manufactures aluminum chloride at the rate of 75,000 pounds per day, or about 25,000,000 pounds per annum. By examining the approximate production figures for the United States from all the available data and the figures submitted by McAfee of the Gulf Refining Company, it becomes apparent that

most of the anhydrous aluminum chloride produced in this country is manufactured and used by the Gulf Refining Company.

Table I—Domestic Consumption of Vat Dyes Other Than Indigo, 1924 to 1929

YEAR	DOMESTIC PRODUCTION Lbs.	IMPORT Lbs.
1924	1,821,319	1,493,851
1925	2,608,361	2,418,842
1926	2,815,241	1,845,208
1927	4,925,512	1,724,910
1928	6,514,132	2,301,761
1929	9,464,067	2,694,901 ^a

^a Constitutes 42 per cent of all dyestuffs imported.

Table II—Production of Aluminum Chloride in the United States, 1924 to 1929

YEAR	TOTAL PRODUCTION Lbs.	ANHYDROUS Al ₂ Cl ₆ Lbs.	CRYSTALS Al ₂ Cl ₆ · 12H ₂ O		ANHYDROUS Al ₂ Cl ₆ PRODUCED BY GULF REFINING CO Lbs.
			Lbs.	Lbs.	
1924	12,020,000				10,718,699
1925	26,665,000				21,386,530
1926	34,500,000				27,264,297
1927		29,200,000	540,000	5,520,000	26,550,186
1928		28,990,000	744,000	4,806,000	27,016,750
1929		28,574,000	730,000	4,798,000	26,840,146

¹ Received December 4, 1930. Part of paper presented before the meeting of the American Institute of Chemical Engineers, New Orleans, La., December 8 to 10, 1930.

² One hundred and eighty-sixth contribution from the Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

the anhydrous aluminum chloride was agitated, there was a progressive loss in weight, owing to the formation of aluminum hydroxide. The data in Table IV show that the reactivity of both products under such conditions was similar. On allowing these experiments to stand quiescent after these tests, there was a distinct increase in weight owing to the formation of hydrated aluminum chloride.

Table III—Comparative Flow of Anhydrous Aluminum Chloride on Inclined Plane

Length of chute, 18 inches (46 cm.); width of chute, 4 inches (10 cm.); sample, 50 grams; temperature, 29° C.; relative humidity, 50 per cent.

	30° SLOPE Grams	45° SLOPE Grams	60° SLOPE Grams
SCREENED C. P. ANHYDROUS ALUMINUM CHLORIDE			
Left on feeder	48.0	7.5	6.0
Discharged	2.0	42.5	44.0
	50.0	50.0	50.0
GULF REFINING CO. TECHNICAL ANHYDROUS ALUMINUM CHLORIDE			
Left on feeder	48.0	2.0	1.0
Discharged	2.0	48.0	49.0
	50.0	50.0	50.0

Table IV—Rate of Hydration and Hydrolysis of Anhydrous Aluminum Chloride

TIME Min.	TECH. AlCl ₃ INCREASE IN WEIGHT		SCREENED C. P. AlCl ₃ INCREASE IN WEIGHT	
	Gram		Gram	
HYDRATION—QUIESCENT CONDITION				
5	+0.05		+0.10	
10	+0.10		+0.15	
20	+0.11		+0.20	
30	+0.12		+0.25	
HYDROLYSIS—MANUAL AGITATION				
5	0.00		0.00	
10	-0.10		-0.10	
20	-0.25		-0.30	
30	-0.50		-0.55	
20 hours quiescent	+8.25		+8.50	
Ratio, weight in grams to exposed surface, sq. cm.	100 95	= 1.0526 grams per sq. cm.	100 97	= 1.0309 grams per sq. cm.

The loss in weight in the experiments with agitation is readily explained. Anhydrous aluminum chloride upon exposure to air containing water vapor is decomposed according to the following reversible reaction:



When the material is stirred the hydrogen chloride will escape. Since the molecular weight of the hydrogen chloride evolved is twice as great as the water of reaction, there will be a corresponding loss in weight. The equation above represents the limit of aluminum hydroxide formation. In fact, hydration and hydrolysis take place simultaneously. After 5 minutes the increase in weight due to hydration is just balanced by the loss due to hydrolysis.

When the mass is quiescent a crust forms on the exposed surface. This will offer resistance to the passage of water vapor and hydrogen chloride. The effusion of these two gases through the crust will follow roughly Graham's law as a limit; i. e., the passage will be inversely proportioned to the square roots of their densities. The tendency of gases to effuse through small apertures is a manifestation of the motion of their molecules. This activity may be represented by the following equation:

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{m_2}{m_1}}$$

where u_1 and u_2 denote the mean velocities of translation of the molecules of any two gases whose densities are d_1 and d_2 , respectively, and m_1 and m_2 denote the molecular weights of the two gases.

Since the molecular weight of hydrogen chloride is twice as great as that of water vapor, the flow of water vapor in-

ward will be $\sqrt{36.5/18}$, or 1.415 times as great as the effusion of hydrogen chloride outwards. The reversibility of the equation



holds only when no hydrogen chloride leaves the system. The hydrogen chloride then reacts with $\text{Al}_2(\text{OH})_6$, forming Al_2Cl_6 and $6\text{H}_2\text{O}$. The water thus formed unites with the aluminum chloride, forming $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$. In practical operations some hydrogen chloride escapes, and the end products are principally $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and $\text{Al}_2(\text{OH})_6$.

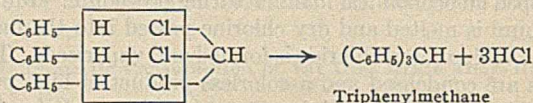
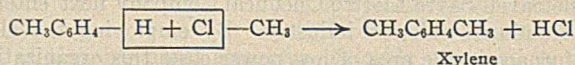
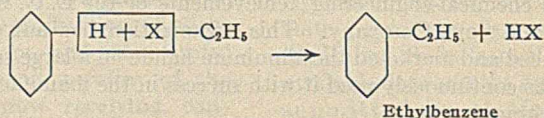
From the preceding discussion it is clear that the two types of anhydrous aluminum chloride exhibit differences in both physical characteristics and chemical composition. The effect of such differences when the aluminum halide is used in oil-cracking processes or in the preparation of aromatic hydrocarbons may be considered negligible. Here the metal halides do not accompany the volatile distillates. In the Friedel-Crafts synthesis of keto acids, however, the condensing agent must be separated from the reaction mass by hydrolysis.

The principal impurities in technical aluminum chloride are ferric chloride and titanium tetrachloride. These constituents are not inert. Both ferric chloride and titanium tetrachloride, as will be shown, are moderate condensing agents. Chemically these constituents behave like aluminum chloride and are removed with it during the course of operations.

Function of Anhydrous Aluminum Chloride

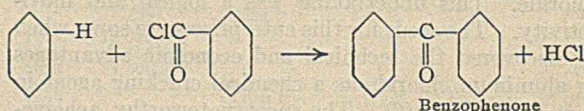
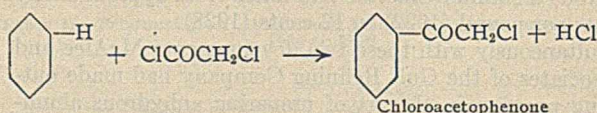
Anhydrous aluminum chloride can be used as a catalytic agent in the preparation of hydrocarbons, as a condensing agent in the synthesis of ketones and keto acids, and as a cracking agent in petroleum technology.

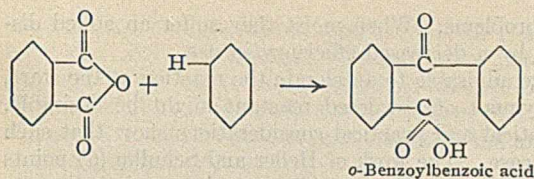
The following reactions illustrate the formation of hydrocarbons. The process involves the elimination of HX in the presence of aluminum chloride, the H (hydrogen) atom being linked to a carbon in a ring, while the X (halogen) atom must be linked to a carbon not in a ring.



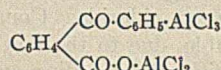
In the preceding reactions aluminum chloride behaves as a catalyst and less than the molecular quantity of halide considered as AlCl_3 can be used.

The formation of ketones and keto acids takes place as follows:

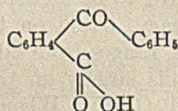




The synthesis of the ketones requires at least one molecular proportion of anhydrous aluminum chloride considered as AlCl_3 , whereas the preparation of keto acids necessitates its presence as 2AlCl_3 , or Al_2Cl_6 . Here it functions as a condensing agent and is not regenerated during the reaction. Instead, it forms a stable and inactive aluminum addition complex of the newly formed ketonic or acyclic groups. In the preparation of *o*-benzoylbenzoic acid from phthalic anhydride and benzene, the aluminum addition compound would probably best be represented as follows:



In order to obtain the keto acid it is necessary to hydrolyze this addition compound. When dilute hydrochloric acid is used it results in the formation of the keto acid



and the regeneration of aluminum chloride. The former is precipitated out while the latter goes into solution.

Aluminum Chloride as a Cracking Agent in Petroleum Industry

When used in petroleum-cracking processes, aluminum chloride probably functions as a labilizing and catalytic condensing and polymerizing agent. That the halide exercises such properties is definitely established.

Note—The following references shed some light on the multitudinous reactions that take place when hydrocarbons are treated with aluminum chloride:

- Duval, *Compt. rend.*, **146**, 341-3 (1908), reports displacement of hydrocarbon radicals in Friedel-Crafts reaction.
- Gustavson, *Ibid.*, **146**, 640 (1908); fission and addition products obtained by treating benzene with aluminum chloride.
- Lavaux, *Ibid.*, **146**, 345 (1908); formation of dimethyl anthracenes from toluene and chloroform, acetylene tetrabromide, etc., shown.
- Boeseken, *Rec. trav. chim.*, **29**, 85-112 (1910), believes catalytic reactivity is due to atom or group of atoms being either (1) entirely eliminated from rest of molecule and reacting as such, or (2) activated without being separated from the rest of the molecule. Experimental evidence is cited.
- Copisarow and Long, *J. Chem. Soc.*, **119**, 442 (1921); condensation, migration, and pyrogenic fission takes place when AlCl_3 reacts on bromobenzene.
- Copisarow and Long, *Ibid.*, **119**, 1806 (1921), believe that action of AlCl_3 on benzene represents a reversible reaction in so far as migration of alkyl groups is concerned. Fission of benzene nucleus is facilitated by high temperature, AlCl_3 concentration, extent of alkylation of hydrocarbon, and prolongation of reaction. Experimental evidence is cited.
- Bastet, *Chem.-Ztg.*, **37**, 564 (1913), obtains numerous addition and polymerization products from addition of series C_2H_4 to C_2Cl_4 to benzene.
- Norris and Couch, *J. Am. Chem. Soc.*, **42**, 2329, (1920); unsaturated compounds containing double bond can replace aryl hydrocarbons in the Friedel-Crafts synthesis.
- Groggins, *IND. ENG. CHEM.*, **20**, 597 (1928); in preparing resins by chlorinating *p*-cymene, observed (1) chlorination in side chains in presence of aluminum, (2) condensation of side chains to form addition compounds, and (3) polymerization with formation of resins.
- Michel, U. S. Patent 1,667,214 (1929), re. 17,548; condensation products from olefins and hydrocarbons of the naphthalene series with AlCl_3 .
- Johnson, British Patent 306,437 (1929); manufacture and production of hydrocarbons of low boiling point using aluminum chloride and Borneo mineral oil, 55 per cent of original material are recovered as conversion products, 25 per cent of which consists of benzene and toluene.

From our knowledge of the composition of crude oils and the nature of the distillates after cracking, it is safe to assume that all three reactions proceed simultaneously. The result is the formation of the more stable saturated compounds. Large molecules are labilized and broken down; the fission of the larger nucleus with the formation of carbon being favored by extreme conditions of temperature and concentration of aluminum chloride. Side chains become chlorinated and either form addition compounds or migrate. These smaller migratory molecules then condense or polymerize, forming more stable compounds. Finally unsaturated compounds containing a double bond react according to the Friedel-Crafts reaction, producing new compounds, which become saturated in the presence of carbon under the conditions of operation.

McAfee (9) states:

With proper control of the vapors leaving the distilling system and entering the final condenser, and with sufficient time given the aluminum chloride, high boiling oils can be completely broken down into lower boiling oils, and no matter how unsaturated the high boiling hydrocarbons may be, the low boiling oils produced therefrom are sweet smelling, water-white, and saturated. The reaction gives little gas and only about the right amount of carbon to allow production of saturated products. The carbon is deposited, not in the form of a hard, baked-on carbon, but as a granular, coky mass, easily removed from the still.

When Texas crude oil (20 to 28° B \acute{e} .) was distilled until free from moisture and until the naturally occurring gasoline and kerosene had been distilled over and then cracked by employing 15 per cent by weight aluminum chloride, the following results were obtained by McAfee.

Products from AlCl_3 Process (Per Cent Crude Oil)

	GASO-LINE %	GAS NAPHTHA %	KERO- SENE %	GAS OIL %	LUBRI- CATING OIL %	TOTAL %
Distillate:						
Primary	0.30	0.18	2.79			82.17
Secondary	17.45	12.85	5.87	17.15	25.58	
Loss due to:						
Distilling primary distillate					1.60	17.83
Distilling with AlCl_3					14.60	
Redistillation of primary distillate					0.08	
Redistillation of secondary distillate					1.55	
Total						100.00

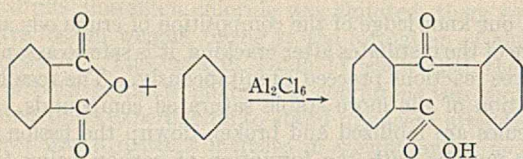
Comparison of AlCl_3 Process with Usual Process (Per Cent of Crude Oil)

	AlCl_3 PROCESS %	USUAL PROCESS %
Gasoline	17.75	0.00
Gas naphtha	13.03	0.10
Kerosenes	8.66	4.30
Gas oil	17.15	52.00
Lubricating oils	25.58	25.50
Asphaltic residual oil	...	12.00
Sum of products	82.17	93.90
Loss	17.83	6.10
Total	100.00	100.00

Chemical Engineering in Friedel-Crafts Reaction

There are a number of general chemical and chemical-engineering problems involved in the practical application of the Friedel-Crafts synthesis. The exact nature of the chemical-engineering problems can, of course, be forecast by a study of the theoretical and chemical aspects of the reaction. Efficient operation depends, therefore, on (1) proper preparation and handling of reacting materials, (2) scientific design of apparatus, and (3) control of the reaction so as to lead to the formation of the specific products desired.

Assuming, as a basis of discussion, that the synthesis relates to the preparation of *o*-benzoylbenzoic acid,



we may then expect to be confronted by the following considerations:

- I—Handling of materials
 - (A) Anhydrous aluminum chloride
 - (B) Phthalic anhydride
 - (C) Aromatic hydrocarbon
 - (1) Storage and transportation
 - (2) Effects of moisture
 - (3) Preparation for use in the reaction
- II—Design of apparatus
 - (A) For reactions using molecular proportions of the reactants
 - (B) For reactions using an inert solvent or an excess of liquid aromatic hydrocarbon
 - (1) Materials of construction
 - (2) Mechanical devices for feeding the charge
 - (3) Type of agitation
 - (a) Relation of size of charge to size of vessel
 - (b) Relation of size of charge to type of agitation
 - (4) Corrosion problems
 - (5) Discharging and hydrolyzing the reaction mass
- III—Control of Friedel-Crafts reaction
 - (1) Obtaining homogeneity
 - (2) Insuring formation of intermediate addition compounds without deleterious by-products
 - (3) Maintaining anhydrous operating conditions
 - (4) Removal of hydrogen chloride

Handling of Materials

When anhydrous aluminum chloride is packed in iron drums under conditions which insure the absence of appreciable moisture, it may be stored for long periods, or conveyed over long distances with safety. McAfee has stated that "hundreds of tons of the halide have been shipped in inter-refinery operations without any difficulty." At the Edgewood Arsenal this material has been stored in properly sealed iron drums over a period of years without deleterious effect either on the drum or the contents.

When, however, water is permitted to come in contact with anhydrous aluminum chloride, hydrogen chloride is certain to be formed. The quantity of hydrogen chloride will depend on the amount of water and the degree of agitation of the halide. If sufficient moisture is present, particularly in the free space in the container or reaction vessel or at the point of contact with the outside atmosphere, then hydrochloric acid is formed. The presence of this acid leads to problems of corrosion.

Phthalic anhydride and the aromatic hydrocarbons—benzene, toluene, naphthalene, etc.—offer no special corrosion problems. They may therefore be stored in any suitable containers. These compounds, furthermore, do not absorb atmospheric moisture with great avidity. Less attention is consequently paid to the storing and handling of these materials preparatory to their utilization in the Friedel-Crafts reaction. In fact, indifference in this matter often brings serious consequences. Substitution of fresh aluminum chloride, especially fused phthalic anhydride and dehydrated aromatic hydrocarbons, for materials that had been previously used, increased the yield from 2 to 6 per cent.

It has been shown that finely divided refined aluminum chloride absorbs atmospheric moisture more readily than the technical product. It is equally true that a powdered phthalic anhydride takes up moisture and forms *o*-phthalic acid more readily than does the crisp flaked product. Such powdered products are more difficult to handle either manually or mechanically. When dry they constitute unnecessary fume

and dust problems. When moist they suffer an added disadvantage by a decreased efficiency in use.

If it were advisable to accelerate the reaction at the start, the employment of powdered reactant might be desirable. But theoretical and practical considerations show that such is not the case. The work of Heller and Schulke (6) points to the necessity of a slow starting reaction, and the results obtained by Professor Allan and his students warn against the formation of undesirable phthalides. Moreover, plant experience relating to the delivery of the reactants to the reaction vessel demonstrates the inadvisability of using finely divided materials. To retard the reaction until all the materials are thoroughly mixed it is advisable to employ both granular phthalic anhydride and aluminum chloride. In conducting researches in this field at the Edgewood Arsenal, G. E. Miller concludes: "These results indicate clearly that the grinding has no effect on the catalytic activity of the aluminum chloride. Compact lumps of the material are preferable, due to the fact that it suffers very much less decomposition on handling and storage when it is in this condition."

The retardation of the initial reaction may also be accomplished by chemical means. Ferric chloride and titanium chloride are known to be moderate condensing agents. Their catalytic efficiency, based on the yields obtained in various condensations, ranges from 20 to 95 per cent of the theoretical and depends largely on the nature of the compounds being treated (1, 2). When small proportions of these milder condensing agents are present as constituents in anhydrous aluminum chloride, in reactions involving molecular proportions of the reactants, they cannot be considered deleterious.

Design of Apparatus

FLUID REACTIONS—Most of the early investigators of the Friedel-Crafts synthesis carried out the reactions in a liquid medium. This precaution insured a homogeneous reaction mass. By providing sufficient solvent, or liquid vehicle for the viscous intermediate reaction product, little difficulty was experienced in stirring the charge.

When aluminum chloride functions as a true catalyst, the reactants and final products are liquid and no problem in agitation is encountered. In the preparation of ketones and keto acids the formation of viscous intermediate addition compounds necessitates giving this subject consideration. The necessary fluidity is obtained consequently by utilizing either an excess of the liquid aromatic compound (benzene, toluene, chlorobenzene) or an extraneous inert solvent such as carbon disulfide or tetrachloroethane. In some instances where there is considerable variation in the reactivities of aromatic compounds at fixed temperatures, one can be used as a vehicle while the other enters into the reaction. Thus, Groggins and Newton (5) successfully employed *o*-dichlorobenzene as the inert solvent in the Friedel-Crafts preparation of α -naphthoylbenzoic acid by condensing naphthalene with phthalic anhydride.

Heller and Schulke (6) have pointed out that in the preparation of keto acids the reaction proceeds from the liquid stage to the viscous addition compound. During this transition it is difficult, if not impossible, to stir the charge with the usual vertical type agitators unless a solvent is employed to provide the necessary fluidity (3).

These considerations have led to the adoption of two types of apparatus for carrying out such syntheses. The older procedure involves the use of ordinary jacketed, agitated vessels, preferably enamel-lined. In these (Figure 1) the charge is kept fluid by the most desirable expedient, as previously indicated. Operations according to this system

are described in a number of reports from the Color Laboratory and also in numerous United States patents. The preparation of chloroacetophenone as carried out by the Edgewood Arsenal chemical division follows this procedure. Figures 1, 2, and 3 show diagrammatically the arrangement of the apparatus that is used.

It is obvious that the introduction of inert solvents or an excess of aromatic hydrocarbon entails an economic loss of considerable magnitude. It involves (1) cost of solvent recovery, (2) loss of solvent or equivalent, (3) increase in operating time, (4) more complex and more costly operating system, (5) additional problems regarding corrosion, and (6) deleterious effect on product.

A number of such drawbacks in the liquid-phase reactions are brought out in Table II of a previous article (4). The data show that with increasing economy in the use of solvent there is a proportional increase in the percentage lost. There is also a reduction in the yield when the chlorobenzene ratio is reduced from 3:1 to 2:1. When the solvent ratio is low difficulty is experienced in drawing off the charge for hydrolysis. Consequently this step must be carried out in the principal reaction vessel. Experience at this laboratory and at Edgewood Arsenal shows that sooner or later flaws will develop in the enamel lining, thus necessitating its replacement.

MOLECULAR REACTIONS IN IRON REACTOR—Appreciating the inherent deficiencies of the prior methods of operation, Stone and Jacobson, of the E. C. Klipstein & Sons Company, devised, patented, and utilized the apparatus which is shown in Figure 4. This is essentially a horizontal rotary ball mill which is provided with inlet and outlet connections for solids, liquids, and gases, so that it constitutes a closed reactor. The reacting materials may be introduced in any desired sequence and then mixed at a temperature so low that practically no reaction takes place.

When a reaction vessel of this type is used it is possible to employ approximately the molecular combining proportions of the reactant materials. This economical procedure now becomes feasible because homogeneity of the reaction mass is obtained by the grinding action of the balls or bars, in the reactor. The rotary effect and grinding action of the iron weights thoroughly mix the reactants, and with proper control of temperature a smooth and substantially complete reaction is obtained. The charge in the mill becomes viscous and porous during the intermediate stages of the reaction, even when all the reactants are solid (3). During this period the din of the crushing mechanism becomes deadened. If insufficient balls are present, they will be enmeshed in the viscous charge and no grinding action takes place. As the reaction progresses the anhydrous aluminum compound of the keto acid is formed and separates out as a fine colored powder.

That the aluminum complex of the keto acid may be obtained as a freely flowing dry powder is a matter of great importance. This fact makes possible a division of operations, such as condensation in the reactor followed immediately or subsequently by hydrolysis in any suitable covered agitated vessel. Since hydrolysis takes place in solutions that are weakly acid with mineral acid, it is advisable to use vessels of wood, silicon iron, or other suitable acid-resistant material for this operation. The dry, powdery, hygroscopic aluminum salt may be delivered to a dry, enclosed hopper, where it is cooled. It is then delivered in a regulated stream into the hydrolyzer, which contains cold, dilute mineral acid. The hydrolysis can therefore be easily controlled so that the maximum temperature does not rise above the optimum for condensation. This precaution leads to the formation of purer products.

By far the most important advantage in the use of the horizontal mill reactor is the practicability of using iron in its construction. When the necessary precautions have been observed, practically no free or combined moisture enters the reactor. Hydrogen chloride only is then liberated during the condensation. This will not attack iron to any appreciable extent. At the Color Laboratory a small iron reactor has been in use for more than three years and does not yet show any effects of corrosion. This is particularly remarkable because of its intermittent use for various investigations and failure to exercise continuously some of the known precautions against corrosion. Replacements were necessary only at the connection where the hydrogen chloride was exhausted.

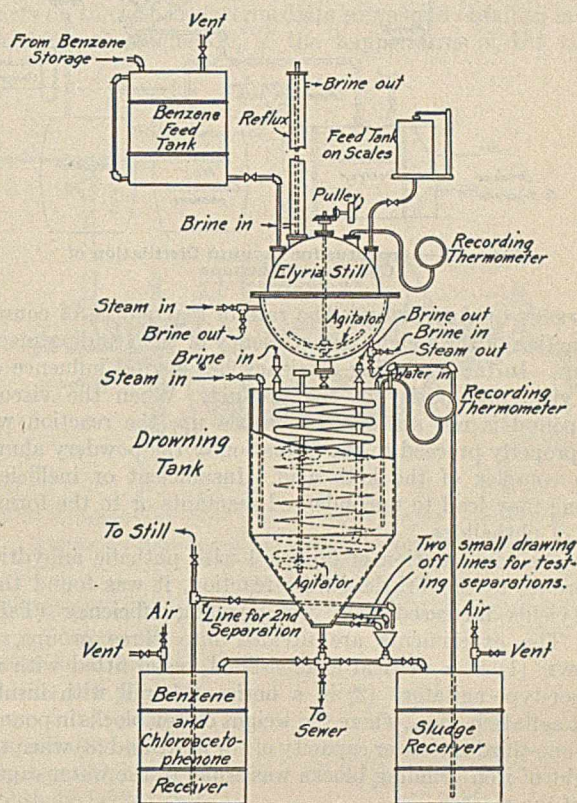


Figure 1—Apparatus for the Condensation and Drowning of Chloroacetophenone

The size of the horizontal reactor must be considerably out of proportion to the weight of the reacting materials. This precaution is necessary in spite of the fact that molecular proportions of the reactants are taken. During the transition from the liquid to the viscous stage the reaction mass becomes porous, owing to the liberation of hydrogen chloride. This spongy mass tends to fill the entire vessel. This phenomenon occurs even when the weight of the charge is only one-tenth the water capacity of the reactor. When pressure develops in the vessel, some of the spongy reaction mass oozes out into the hydrogen chloride exhaust line, which is at the horizontal axis of the reactor (Figure 4).

The formation of a spongy, viscous intermediate compound is a general characteristic of all the aluminum complexes in the synthesis of keto acids by the Friedel-Crafts reaction. The porosity of this mass appears to vary according to the nature of the aromatic compounds being condensed. The tendency of the viscous mass to exude is dependent upon the proportionality existing between the hydrogen chloride formed and the viscosity of the reaction mass. When it is difficult for the gas to escape, the charge becomes swollen and fills the reactor. An increase in the

reaction temperature produces a more fluid mass and gives the hydrogen chloride a better opportunity to escape. An increased reactivity induced by the use of a larger quantity of grinding blocks at low temperatures produces a more swollen reaction mass.

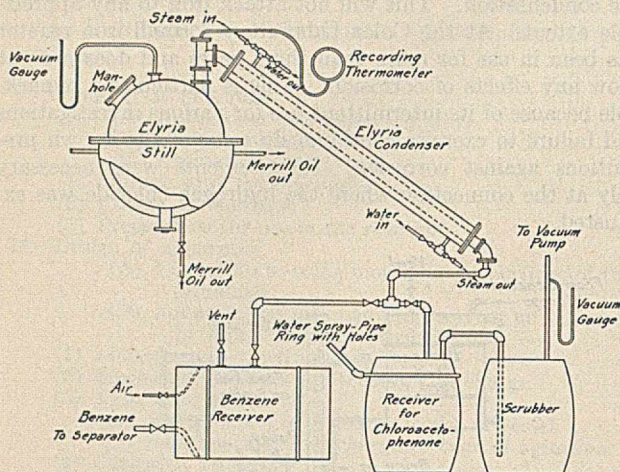


Figure 2—Apparatus for Vacuum Distillation of Chloroacetophenone

EFFECT OF AGITATION—The rate of reaction is, of course, a function of the weight and efficiency of the grinding mechanism. In fact, grinding efficiency has a vital influence on the yield and purity of the product. When the viscous compound is not stirred and broken up, the reaction will not properly proceed to the formation of the powdery aluminum complex of the keto acid. Insufficient or inefficient mixing may lead to uncondensed reactants or to the formation of phthalides.

In the condensation of diphenyl with phthalic anhydride according to the Friedel-Crafts reaction, it was found that the yields increased with the grinding efficiency (Table V). The experiments are divided into three groups, as follows: (1) in a vertical enamel-lined vessel fitted with an anchor-type agitator; (2) in a horizontal mill with insufficient agitation—i. e., where the weight of iron blocks in pounds was one-third the water capacity of the mill; and (3) when the weight of iron grinding blocks was equal to the water capacity of the reactor.

Table V—Effect of Type of Agitation in Preparation of 4'-Phenyl-2-Benzoylbenzoic Acid

Phthalic anhydride, 1 mol. = 148 grams; diphenyl, 1 mol. = 154 grams; aluminum chloride sublimed, 10 per cent excess = 293 grams; yield, theory = 302 grams.

TYPE OF AGITATION	TEMP. ° C.	TIME Hours	CRUDE Grams	YIELD %	PURITY %
Agitated kettle	55-60	18	244	80.8	97.4
Mill with insufficient agitation ^a	55-60	20	278	92.1	97.6
Mill with efficient agitation ^b	55-60	18	290	96.0	97.8
EXPERIMENT II					
Agitated kettle	60-65	12	208	68.9	97.5
Mill with insufficient agitation ^a	60-65	12	239	79.1	97.8
Mill with efficient agitation ^{a, b}	60-65	12	292	96.7	98.0

^a Ratio, weight of iron blocks in pounds to water capacity of mill = 1:3

^b Ratio, weight of iron blocks in pounds to water capacity of mill = 1:1.

Appreciating the intrinsic value of the horizontal iron reactor for the Friedel-Crafts synthesis, Müller and Apenzeller (13), of Germany, have evolved a modification of the operating process.² By way of example they state:

In an iron vessel provided with a stirrer 160 parts of monochlorobenzene, 200 parts of phthalic anhydride and 360 parts of anhydrous aluminum chloride are stirred at room temperature until a brown oily mass (liquid stage) is obtained. * * * The

² The German patent, 495,447, is practically identical with Stone and Jacobson's U. S. P. 1,656,575.

oily reaction product is drawn off onto drying plates and slowly heated to between 80° and 100° C. in a drier, while drawing off the hydrogen chloride by the aid of a vacuum or a current of gas, until the reaction is complete. A foamy, blown-up, brittle mass is obtained which, when introduced for instance into dilute acid, is converted into 4'-chloro-2-benzoylbenzoic acid.

It further states that "the reaction may also be carried out continuously for example on a moving band forming a long trough." This feature, however, does not appear in the claims allowed.

It is obvious that the mechanical or engineering merits of this procedure suffer in comparison with the process of Stone and Jacobson. As to the chemical aspects of this mode of operation, it is known from McMullen's work (12) that the oily liquid is not a homogeneous mass, but represents transitory stages of the reaction. By treating the clear oil incidental to the preparation of *o*-benzoylbenzoic with naphthalene, McMullen obtained 60 per cent benzoylbenzoic acid, 35 per cent naphthoylbenzoic acid, and 5 per cent naphthylphenyl phthalide.

DISCHARGING AND HYDROLYZING THE REACTION MASS—When the Friedel-Crafts synthesis is carried out in a solvent medium, the hydrolysis of the aluminum complex may take place either in the reaction vessel, or preferably, in a separate hydrolyzer. In either case, the vessel must be able to withstand the action of dilute mineral acids.

The recovery of the finished product may be effected by direct distillation with steam to remove the solvent, or by separating the oily layer containing the ketone or keto acid and subsequently treating this by suitable means to remove the solvent.

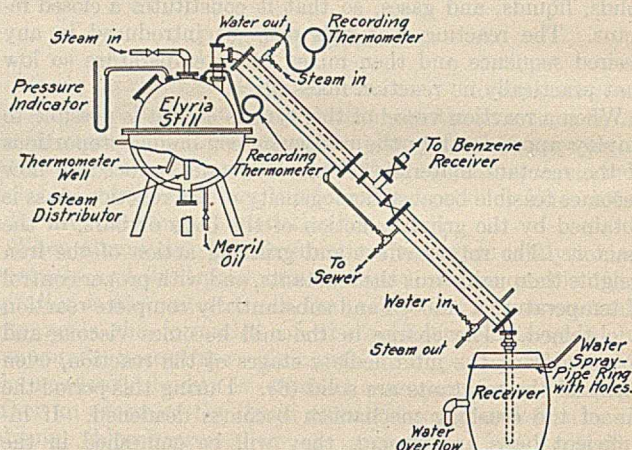


Figure 3—Apparatus for Steam Distillation of Chloroacetophenone

Murch (14) separates 4'-chloro-2-benzoylbenzoic acid in the following manner: The reaction mixture is slowly added, with stirring, to a solution of sodium carbonate in water at a temperature of about 90° C. Considerable heat and carbon dioxide are evolved, and large quantities of the excess chlorobenzene may distil off. The mixture is then heated with a current of steam, external heat being used if necessary, to keep the volume of the mixture approximately constant, until the excess chlorobenzene is removed by distillation. The remaining solution is then filtered, and the residue is washed free from alkali. The filtrate is made acid by the slow addition of sulfuric acid at 25° to 30° C. 4'-Chloro-2-benzoylbenzoic acid is precipitated and recovered by filtration.

Tinker and Gubelmann (17) in the preparation of the same product, treat the reaction mass as follows: The aluminum compound of 4'-chloro-2-benzoylbenzoic acid is charged into ice and water, sufficient ice being used to keep the tem-

perature of the final mixture at about 25° C. or below. A mineral acid is added to fix the aluminum as a soluble salt and to precipitate out the keto acid. Upon settling, a three-layer system is formed: The lower layer is chlorobenzene, the middle layer comprises the precipitated 4'-chloro-2-benzoylbenzoic acid, and the upper layer comprises the aqueous solution of the aluminum salt of the mineral acid. The aluminum salt layer is removed by decantation and washing. The solvent and keto acid layers are then made alkaline, and the excess of chlorobenzene is removed by distillation with steam. The alkaline solution of the keto acid is filtered to remove the final traces of aluminum and other insoluble impurities. By treatment with cold dilute mineral acid the 4'-chloro-2-benzoylbenzoic acid is reprecipitated.

When the horizontal reactor is employed, no solvent recovery problems arise. The powdery anhydrous aluminum complex that is obtained behaves in many respects like aluminum chloride. It is very hygroscopic, particularly when warm. It will flow readily on an inclined plane. When the aluminum complex is discharged it has a characteristic color, depending on the particular keto acid that is formed; but upon hydrolysis, the keto acid obtained is colorless.

The feeding and discharging devices for the horizontal reactor may be made of iron. It has already been shown (Table III) that the inclined plane should be set at an angle of 60 degrees. The chutes should be completely enclosed to minimize the absorption of moisture. The discharging chute coming in contact with the hydrolyzer will of necessity be subjected to the most severe service.

Control of Friedel-Crafts Reaction

What is probably the most important problem in the control of the Friedel-Crafts reaction may be expressed in one word—homogeneity. No other single factor appears to exert such a vital influence on the reaction. It is recognized that excessive heating will affect adversely the yields and quality of the product. But when an effort is made to control this factor, its deleterious effects are not of the same magnitude as may arise from insufficient or inefficient agitation.

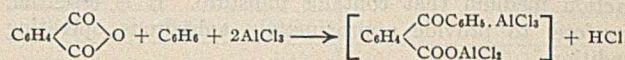
Table II of a previous article (4) shows that a decrease of approximately 10 per cent in yield of 4'-chloro-2-benzoylbenzoic acid results when the temperature is raised from 50° to 90° C., whereas it is approximately 35 per cent in experiment 6, in which there was no agitation. Similar results are obtained in the preparation of α -naphthoylbenzoic acid. The data in Table VI show a lower yield and inferior product when a less efficient solvent or a smaller quantity of solvent is employed. The solvent functions here merely as an inert chemical agent for producing homogeneity.

Table VI—Comparison of Solvents in Preparation of α -Naphthoylbenzoic Acid

EXPT.	RE-ACTION TIME Hours	RE-ACTION TEMP. ° C.	SOLVENT	SOLVENT RATIO	SOLVENT RECOVERY %	YIELD N.B.A. %	MELTING POINT ° C.
1	2	15	C ₆ H ₆	12:1	97	97.6	165-168
2	4	5	C ₆ H ₆	6:1	97	95.0	150-160
3	5	0	C ₆ H ₆	3:1	97	92.0	140-155
4	2	15	CS ₂	12:1	90	95.0	145-155
5	4	5	CS ₂	6:1	90	93.0	140-150
6	5	0	CS ₂	3:1	90	92.0	135-145
7	2	15	C ₆ H ₄ Cl ₂ (1,2)	12:1	99	97.5	167-170
8	4	5	C ₆ H ₄ Cl ₂ (1,2)	6:1	99	97.0	168-171
9	5	0	C ₆ H ₄ Cl ₂ (1,2)	3:1	99	97.5	170-172

To control the Friedel-Crafts synthesis successfully homogeneity must be obtained at the beginning of the operation. Homogeneity depends on the efficiency of the mixing or grinding mechanism and the time of agitation, provided no

appreciable reaction takes place before the batch becomes uniform. If the reaction is permitted to proceed prematurely, the main synthesis suffers interference. Thus, in the preparation of *o*-benzoylbenzoic acid it is necessary to have one molecule each of the reactants intimately associated; for example,



Heller and Schulke (6) and Rubidge and Qua (15) have shown that the yield drops off when insufficient aluminum chloride is present. McMullen (11), Laurance and Oddy (8), and numerous other investigators have shown that phthalides are formed when phthalic anhydride (or other anhydrides) reacts on the viscous intermediate compound obtained in this reaction. Consequently, if the temperature of the batch

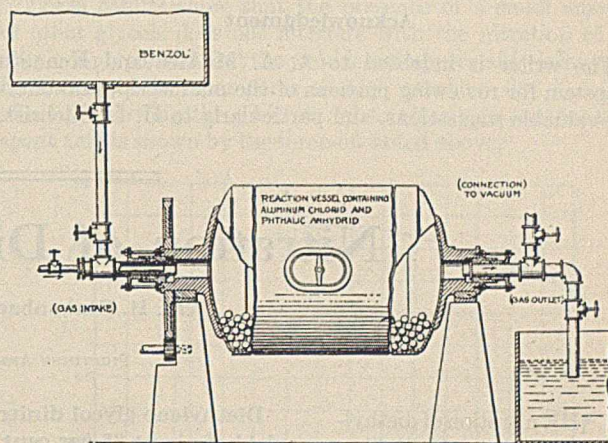


Figure 4—Manufacture of Useful Products by Means of Friedel-Crafts Reaction

is permitted to rise prematurely to the active reaction point, various stages of the synthesis will be present at one time. Under such circumstances some uncombined phthalic anhydride will probably exert an influence toward the formation of phthalides. When phthalides are formed, more benzene than phthalic anhydride from the charge is used up. Consequently the hydrolyzed reaction mass will contain both *o*-phthalic acid, which separates out from the hot acid filtrate, and phthalides, which remain insoluble when the keto acid is treated with dilute alkaline solutions. These observations can be confirmed by accelerating the reaction at the start and then regulating the subsequent temperature at any desired point.

The preceding discussion brings up the question of the order of feeding the reactants to the reaction vessel. Most of the German references indicate a preference for adding the aluminum chloride as a final constituent. Some of these investigators add the halide in small portions, whereas others prefer to incorporate it all at once. Stone and Jacobson (16) first mix the aluminum chloride with phthalic anhydride and then add the benzene to the finely divided mixture. This procedure unquestionably facilitates the mechanical and operating phases of the reaction and reduces fume problems to the minimum. When aluminum chloride is added intermittently to a charge that is reacting, it may reasonably be expected that the excess of phthalic anhydride present will react on some of the oily or viscous intermediate products already formed, leading to the formation of phthalides. The safest way to insure the formation of the desired product is to put all the ingredients in the reactor and mix thoroughly at a temperature below that required for promoting the reaction. A homogeneous charge is thus obtained. After

this there should be a slow and gradual increase of temperature up to the optimum range.

It is obvious that satisfactory results in the Friedel-Crafts synthesis cannot be obtained when the delivery of the reacting materials takes place in a moist atmosphere. Maximum efficiency cannot be expected in a reactor or reaction medium that contains moisture. It is essential, therefore, to provide approximately anhydrous operating conditions.

In small-scale work this is simpler than in factory practice. It is feasible, however, to provide a separate dehumidified room for the reactor. All connections to the reaction vessel should be closed after each run to prevent the absorption of moisture by the hygroscopic residual material. It is furthermore desirable to sweep the reactor with hot, dry air or gases before each run. These precautions are simple and inexpensive steps in the right direction.

Acknowledgment

The writer is indebted to A. A. McAfee and Kenneth Klipstein for reviewing portions of the manuscript and offering valuable suggestions, and particularly to H. L. Gilchrist,

chief of the Chemical Warfare Service, for information regarding the work done at Edgewood Arsenal. Acknowledgment is also made of the courtesy shown him by the chemical personnel at Edgewood Arsenal, from whom much information of practical value in this field was obtained.

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Nitration of Diethylene Glycol¹

Wm. H. Rinckenbach and H. A. Aaronson

PICATINNY ARSENAL, DOVER, N. J.

THE nitration of diethylene glycol (β,β' -dihydroxyethyl ether) was first studied by Wurtz (3), who showed that nitric acid caused the formation of glycolic, oxalic, and an unnamed acid by oxidation, but found no evidence of the formation of nitrate or nitro derivatives. He made no effort to use mixed acids for the purpose of bringing about substitution.

The preparation of the dinitric ester, $CH_2(NO_2).CH_2O.CH_2.CH_2(NO_2)$, was first reported by one of the writers (2), who obtained it by the use of several mixtures of nitric and sulfuric acids. Little effort was made to determine the optimum conditions of nitration with respect to the composition of the nitrating acid, as the yields obtained were considered sufficiently satisfactory for the purpose of preparation and study.

Diethylene glycol dinitrate was found to possess properties which suggested its application in the manufacture of explosives, and an increasing interest in the compound has made it desirable that a study be made of the mechanism of the nitration and the determination of the conditions giving the maximum yield. This paper gives the results of such a study and adds to the existing data concerning the properties of the compound.

Commercial diethylene glycol usually contains about 5 per cent of ethylene glycol, which gives a high yield of ethylene glycol dinitrate when treated with mixtures of nitric and sulfuric acids. Because of this, commercial diethylene glycol was purified by fractional distillation and freezing before nitration. A number of nitrations of the commercial material were also made for purposes of comparison.

Diethylene glycol dinitrate has been prepared with a yield of about 85 per cent of the theoretical by the use of a mixed acid differing radically in composition from those used in nitrating other compounds.

The pure diethylene glycol dinitrate obtained is toxic when absorbed through the skin, or its vapors are inhaled. The symptoms are similar to those produced by nitroglycerin.

It was recognized that a complete study should evaluate the following variables with respect to maximum yield:

- (1) Ratio of nitric to sulfuric acid in nitrating acid
- (2) Percentage of water in nitrating acid
- (3) Ratio of nitric acid to diethylene glycol
- (4) Solubility of dinitrate in spent acid
- (5) Effect of temperature
- (6) Loss by oxidation
- (7) Losses during purification

In addition, it was considered desirable to study the stability of the purified product, the nature of the spent acid from the nitration, and the toxicity of pure diethylene glycol dinitrate.

Purification of Diethylene Glycol

Commercial diethylene glycol was distilled under a pressure of 120 mm. and the fraction boiling at 184–187° C. was separated. This was further fractionated by freezing. The pure compound so obtained was found to have a freezing point of -11.5° C. as compared with -11.3° C. reported previously (2).

Water in Nitrating Acid

The efficiency of a nitrating system, given the theoretical requirement of nitric acid and constant temperature and pressure conditions, is largely dependent upon the dehydrating value of the sulfuric acid present (DVS). This is best expressed as the quotient obtained by dividing the actual sulfuric acid content by the total water present when the reaction is completed (1).

A number of nitrations were made by adding 25.0 grams of pure diethylene glycol to 91.7 grams of mixed acid main-

¹ Received September 20, 1930. Published by permission of the Chief of Ordnance, U. S. War Department.

tained at 5–10° C. As the amount of nitric acid, representing an excess of 54.4 per cent over that required by theory, was the same in each case, the nitric acid ratio was a constant in this series. The results are given in Table I.

Table I—Effect of Water in Nitrating Bath on Yield of Diethylene Glycol Dinitrate

COMPOSITION OF MIXED ACID			DVS OF MIXED ACID	YIELD
HNO ₃	H ₂ SO ₄	H ₂ O		
%	%	%		%
50.0	30.0	20.0	1.02	0.5
50.0	35.0	15.0	1.44	21.5
50.0	40.0	10.0	2.07	78.3
50.0	42.35	7.65	2.50	81.0
50.0	45.0	5.0	3.15	83.9
50.0	50.0	0.0	5.39	75.2

When these results are plotted (Figure 1), it is seen that a nitrating acid having a DVS value of 3.15 represents an optimum with respect to yield of the dinitrate. It is believed that the reduction in yield when a mixed acid of higher DVS value is used is due to the tendency of strong sulfuric acid to dehydrate diethylene glycol. Such dehydration would result in the formation of polyethylene glycols (di-hydroxy polyethers), which give lower yields of dinitrates on subsequent nitration.

Nitric Acid Ratio

Nitrations carried out with all the variables held constant except the ratio of nitric acid used to that theoretically necessary gave the results shown in Table II.

Table II—Effect of Nitric Acid Ratio on Yield of Diethylene Glycol Dinitrate

DIETHYLENE GLYCOL	MIXED ACID	TEMP.	COMPOSITION OF MIXED ACID			DVS OF MIXED ACID	RATIO HNO ₃ USED TO THEORY	YIELD
			HNO ₃	H ₂ SO ₄	H ₂ O			
Grams	Grams	° C.	%	%	%		%	
25.0	68.6	5–10	43.3	51.7	5.0	3.15	1.0	66.6
25.0	78.74	5–10	45.3	49.7	5.0	3.15	1.2	74.8
25.0	86.2	5–10	48.2	46.8	5.0	3.15	1.4	80.4
25.0	91.7	5–10	50.0	45.0	5.0	3.15	1.54	83.9
25.0	95.6	5–10	51.2	43.8	5.0	3.15	1.65	85.4

When these results are plotted as shown by Figure 2, it is seen that the yield increases almost directly with the excess of nitric acid. The limit approached, however, is not 100 per cent, but about 89 per cent, because of the solubility of the dinitrate in spent acid and in water. The maximum yield recorded is therefore within 3.5 per cent of the practical maximum, and the curve indicates that this discrepancy could be reduced by increasing further the nitric acid ratio.

In view of the nature of the curve given in Figure 2, it is evident that the choice of a nitric ratio to be used in a mixed acid which is to be economically optimum must depend upon the relative values of nitric acid and the dinitrate produced. For experimental purposes a ratio of 1.55 was considered satisfactory.

Effect of Temperature

In order to determine the effect of temperature of nitration on the yield obtained, a number of nitrations were made with temperature as the only variable. In making these nitrations, 50 grams of diethylene glycol were added to 183.4 grams of mixed acid which was actually maintained within a narrower temperature range than indicated in each case. After the addition of the diethylene glycol was complete, the mixture was stirred for 1/2 hour, while cooling to about 5° C., before separating and washing the dinitrate. Nitration took place without difficulty. Allowed to stand at 30–35° C., the temperature of the two-layer system gradually rose, and the

whole fumed off in less than 2 hours. The results are given in Table III.

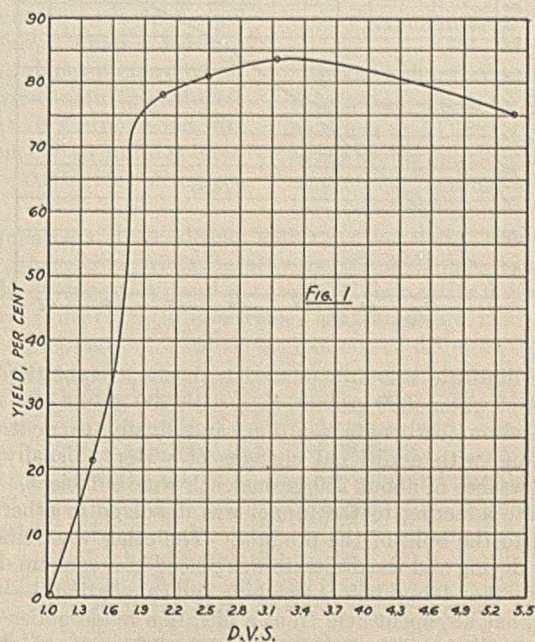
Table III—Effect of Temperature on Yield of Diethylene Glycol Dinitrate

COMPOSITION OF MIXED ACID			TEMP.	YIELD	TIME OF ADDITION OF DIETHYLENE GLYCOL
HNO ₃	H ₂ SO ₄	H ₂ O			
%	%	%	° C.	%	Min.
50.26	44.74	5.0	5–10	83.3 ^a	
50.26	44.74	5.0	5–10	84.6 ^b	
50.26	44.74	5.0	10–15	85.5 ^b	56
50.26	44.74	5.0	15–20	83.6 ^b	43
50.26	44.74	5.0	20–25	83.7 ^b	32
50.26	44.74	5.0	25–30	84.1 ^b	16
50.26	44.74	5.0	30–35	Note ^b	

^a Pure diethylene glycol used; nitrogen content of product, 14.26 per cent.

^b Commercial diethylene glycol used.

These results show that the presence of a small amount of other glycols does not interfere with the nitration of diethylene glycol and that the yield is not appreciably influenced by the use of temperatures as high as about 30° C. The effect of allowing the dinitrate oil to remain in contact with spent acid is shown by the fume-off noted above.



The temperature of nitration is of practical importance, however, if the time required is considered. Oxidation by the spent acid in the above experiments was prevented by cooling immediately after nitration, but on a large scale this would be less convenient. However, the time required for nitration might be reduced to a minimum by carrying out the nitration at 20–25° or 25–30° C. and then cooling.

Composition of Spent Acid

As the composition of the mixed acid found best for the nitration of diethylene glycol differs radically from those used for the nitration of other polyhydroxy derivatives and the benzene homologs, the spent acids from two such nitrations were analyzed and the results are recorded in Table IV.

Table IV—Composition of Spent Acid

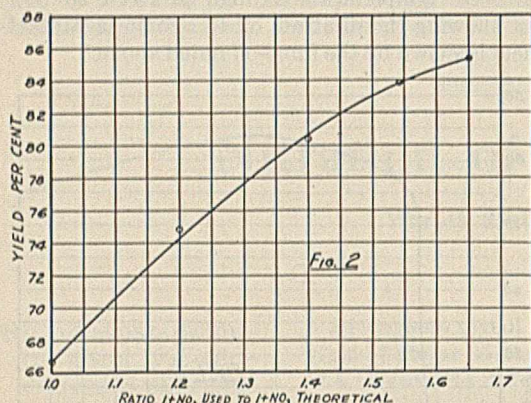
HNO ₃	H ₂ SO ₄	NO ₂	DINITRATE	H ₂ O ^a
%	%	%	%	%
10.58	60.76	1.13	3.50	24.03
10.93	60.81	0.63	3.17	24.46

^a By difference.

Losses

It will be noted that the maximum yields of acid-free dinitrate are only from 82 to 85.4 per cent of the theoretical. It was thought that this might be due to solubility of the dinitrate in the spent acid, oxidation of the raw material or product, and solubility of the dinitrate in the wash waters; and efforts were made to evaluate the effect of each of these possible factors.

In carrying out the nitrations the diethylene glycol was added slowly to the cooled and well-agitated mixed acid, the addition being made at such a rate that the temperature of the mixture would be maintained within the desired 5° C. range. Agitation was continued for 1/2 hour after all the diethylene glycol had been added, the temperature of the mixture being lowered to about 5° C. by means of an ice bath. The acid and dinitrate were allowed to form two layers and were separated by means of a separatory funnel. The acid was run into ice water and any dinitrate separating out was returned to the funnel.



The dinitrate was first washed with about eight times its weight of water (300 grams), then with 200 grams of a 2 per cent sodium carbonate solution, and finally to neutrality to litmus with additional changes of water. Usually two water washes of about 250 grams each were sufficient. Any dinitrate adhering to the funnel was dissolved in ether and added to the bulk of the product. The ether was removed by air-drying and the dinitrate was placed in a vacuum desiccator for 3 or 4 days before weighing and calculating the yield.

On analysis, spent acid from a nitration made under optimum conditions was found to contain 3.3 per cent of dissolved dinitrate. The solubility of the compound has been reported (2) as 4.1 grams per liter of water at 24° C.

On this basis it is possible to explain the losses encountered in nitration and purification. From 25.0 grams of diethylene glycol there should be obtained 46.2 grams of the dinitrate. With a yield of 85.4 per cent, 39.45 grams of purified material are obtained. The 1250 cc. of washes and spent acid dilution account for about 5.0 grams, or 11 per cent. This leaves 1.7 grams, or 3.6 per cent, to be accounted for. From Figure 2 it would appear that this unexplained loss is due to the fact that the maximum excess of nitric acid was not used and that nitration was not complete. It was thought that oxidation of some of the diethylene glycol by nitric acid might be responsible for this loss, but tests of spent acid for oxalic, formic, lactic, malic, citric, and tartaric acids gave negative results. No increase in the yield was noted when the time of nitration was increased, and it is uncertain whether the loss of 3.6 per cent unaccounted for is due to incomplete nitration or to complete oxidation of a portion of the diethylene glycol to carbon dioxide and water.

In view of the foregoing it does not appear that a yield

much greater than 80.5 per cent of that theoretically possible can be obtained on a practical production basis. Those reported above include the dinitrate recovered by drowning the spent acids, and this is not economical if the spent acid is to be recovered and concentrated. Furthermore, the dinitrate dissolved in spent acid is decomposed when the latter is heated or allowed to stand at ordinary temperatures.

The purification by washing is necessary, as diethylene glycol dinitrate is unstable in the presence of free acid; and this purification cannot be abbreviated if an acid-free product is to be obtained.

Stability

As stated above, diethylene glycol dinitrate is unstable in the presence of free acid. This is reflected by the fact that when spent acid having the composition 10.7 per cent nitric acid, 60.8 per cent sulfuric acid, 0.9 per cent oxides of nitrogen, 3.3 per cent diethylene glycol dinitrate, and 24.3 per cent water is allowed to stand at room temperature for about 2 hours, the dissolved dinitrate is oxidized and a fume-off takes place.

The diethylene glycol dinitrate prepared from pure diethylene glycol in the course of this work was of high purity, as shown by the nitrogen content of 14.26 per cent noted under Table III, while the theoretical value is 14.29 per cent. This material was used in studying the inherent stability of pure diethylene glycol dinitrate.

This compound is easily decomposed by the application of heat (2), and the empirical heat tests for stability are no more applicable to this than to nitroglycerin. Storage tests were made by placing a sample of pure, anhydrous neutral dinitrate in an unheated magazine for 1 year and another portion of the same sample was covered with an equal weight of water and placed in a small magazine for 3 months during the hottest part of the summer season. Each bottle was stoppered tightly so as to permit the acceleration of decomposition by the development of gas pressure incident to decomposition.

When tested at the end of the times noted, the dry sample was found to contain less than 0.005 per cent, and the wet sample not more than 0.004 per cent, of free acid calculated as nitric acid. These results indicate that pure diethylene glycol dinitrate is at least relatively stable when kept under storage conditions which are normal with respect to temperature.

Toxicity

It had previously been reported (2) that diethylene glycol dinitrate did not appear to be toxic. In the course of the first experiments made under the program reported in this paper the occurrence of headaches was noted. It was thought that these might be due to the formation of glycol dinitrate in the nitration of commercial diethylene glycol, but it was considered advisable to redetermine its toxicity with a larger number of subjects.

In making the test, 1 cc. of alcohol containing 0.02 gram of pure diethylene glycol dinitrate was placed on the wrist and forearm of each of twenty-seven people of both sexes. The results were definitely positive. Ten of the subjects were unaffected, five were only slightly affected, and twelve reported headaches during the next 12 hours. Those having nervous temperaments were much more affected than those classified as phlegmatic. The symptoms, similar to those produced by nitroglycerin, varied from a feeling of tenseness of the head, with some discomfort, to headache of extreme intensity, and considerable duration.

In the case of nitroglycerin many workers have developed

an immunity after experiencing the usual headaches, and the question might be raised as to possibility of their doing this when handling diethylene glycol dinitrate. Although data of sufficient scope are not available, it might be noted that severe headaches lasting from 2 to 4 hours were experienced by the worker after making the first two nitrations. In subsequent work no headaches were caused, but if the worker was feeling physically subnormal, a feeling of slight heaviness and tenseness about the head with general discomfort was experienced after making a nitration.

It would appear that diethylene glycol dinitrate is definitely toxic and that, since its structure and the symptoms produced

are similar to those of nitroglycerin, it affects the heart action and blood pressure in approximately the same ways.

Acknowledgment

The authors desire to express their appreciation of their associates who volunteered to submit to tests to determine the toxicity of diethylene glycol dinitrate.

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- (2) Rinckenbach, *IND. ENG. CHEM.*, **19**, 925 (1927).
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Cobalt Driers¹

E. Gebauer-Fuelnegg and Gottfried Konopatsch

DEPARTMENT OF RESEARCH BACTERIOLOGY, NORTHWESTERN UNIVERSITY MEDICAL SCHOOL, CHICAGO, ILL., AND LABORATORY OF CHEMICAL TECHNOLOGY UNIVERSITY OF VIENNA, VIENNA, AUSTRIA

WITH respect to the action of the siccatives on drying oils only the bare facts are known. The metal salts apparently have to be considered as catalysts, since comparatively small quantities speed up the drying process and film formation. Our present knowledge of the process indicates that the drying of the oil is a complex reaction, involving colloidal as well as chemical processes, polymerization, oxidation, and even loss of substance have been observed. Catalysts can be positive or negative, which in the case of drying oils means speeding up and retarding the process, respectively. It is probable that in the course of the present work both types have been encountered.

With the hope of getting an insight into the action of siccatives, an attempt was first made to simplify the driers, both as to the purity of the chemicals used and as to their constitution.

The metal resinsates or oleates that have been used have several obvious disadvantages. Since the metal part only is the carrier of the drying (catalytic) activity, the organic remainder, of high molecular weight, is largely ballast. The organic part, however, is considered indispensable for furnishing dispersibility of the siccatives in the oils. To decrease the molecular weight of the organic part should therefore prove advantageous. It is difficult to obtain metal resinsates and oleates of standard activity, no matter by what method they have been prepared, since they are chemically not uniform. As a result the quality of the products depends largely on the skill and experience of the manufacturer. The preparation of siccatives of well-defined chemical constitution was therefore attempted.

The literature shows that attempts have already been made in that direction. For example, the use of metal oxalates, benzoates, succinates, palmitates, and naphthenates as siccatives has been patented. All but the last two are of comparatively small molecular weight and, except for the last, it should be easy to prepare them in sufficient purity to insure products of definite standard. The naphthenates alone, however, are sufficiently soluble in the oils to make an efficient drier.

Several cobalt compounds of known structure and purity have been tested as siccatives. Their solutions in organic solvents have been found to be efficient driers in most cases. Some such siccatives caused the formation of glass-clear films of China wood oil. Simple salts such as the anhydrous cobalt halides have also been tested and found to be satisfactory driers.

Experimental

In the writers' experiments cobalt compounds were used as driers and China wood oil as the drying oil. The former were chosen, because a larger variety of compounds could

be prepared and tested than with the other metal salts so far used as siccatives, while the latter was selected to save time during the drying process and on account of the relative uniformity of its chemical constitution (80 per cent eleostearic acid).

The preparation of cobalt compounds of definite structure and their use as siccatives were at first tackled from the viewpoint of their solubility or dispersion in the oil. Most of the simpler compounds of known structure were found to be either insoluble or soluble only with difficulty. To facilitate their solubility the use of an organic solvent,² miscible with the oil, was thought to be advantageous. The requirements of such a solvent and solution may be summarized thus: (1) It must dissolve the siccatives readily; (2) it must be easily miscible with the drying oil; (3) it should be non-aqueous and not miscible with water; (4) it must not appreciably retard the drying action of the siccatives, and (5) it must have no bad effect on the film to be formed.

Benzene and its homologs were first used, but since some of the cobalt compounds were found to be insoluble, benzonitrile, benzaldehyde, benzyl chloride, benzyl alcohol, benzyl cyanide, furfural, aniline, nitrobenzene, and amyl alcohol were also tested. Intensely colored solutions were obtained. Work on other solvents is in progress.

With the exception of furfural such siccatives solutions were found to be well miscible with China wood oil. Furfural as such was likewise found to be miscible with the oil, but in presence of the cobalt salts it separated out again.

Aniline and amyl alcohol were found to retard appreciably the catalytic action of the substances tested and the films formed were inadequate. Benzyl chloride had to be discarded on account of the possible formation of hydrochloric acid and its insufficient solvent action.

Benzonitrile, benzaldehyde, benzyl alcohol, benzyl cyanide, and nitrobenzene, therefore, must be considered the best

² The terms "solvent" and "solution" as used in this paper are not meant to imply definite statements as to whether the cobalt compounds are in true or (ultra) colloidal solution.

¹ Received October 15, 1930.

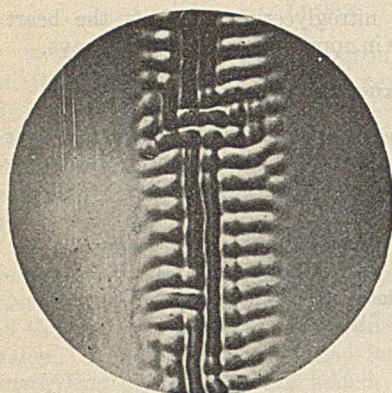


Figure 1—Benzaldehyde

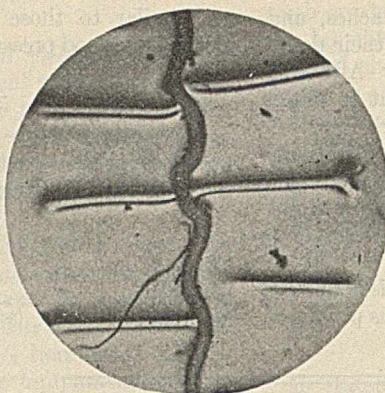


Figure 2—Benzyl Alcohol

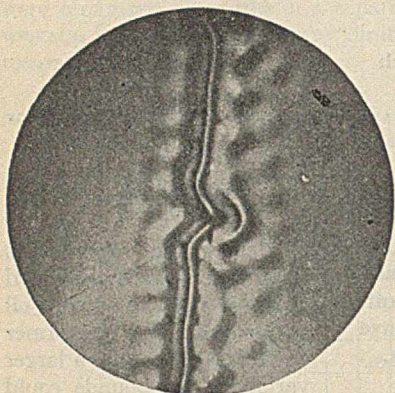


Figure 3—Benzyl Cyanide

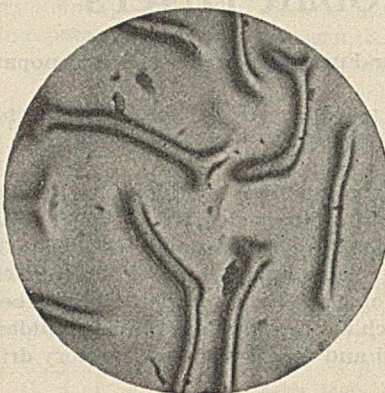


Figure 4—Benzonitrile

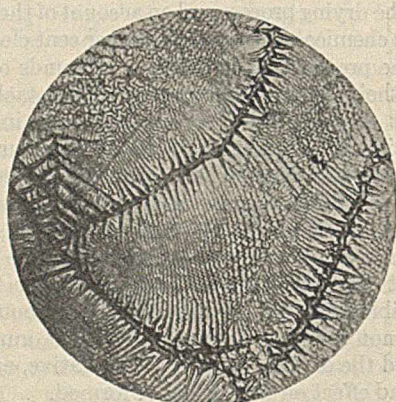


Figure 5—Control

Films Produced with Cobalt Driers in Various Solvents

solvents at the present time. In the case of benzaldehyde the formation of benzoic acid, catalytically hastened by the cobalt compounds can be disadvantageous both as a loss of solvent and as a danger for the film formed. Benzoic acid crystals embedded in the surface of the film could be washed out by water and so affect the resistance of the film "oxyn." As a matter of fact no such crystal formation can be seen under the microscope, so the use of benzaldehyde as a solvent was thought to be feasible.

The literature on the solubility of cobalt compounds which are soluble in the above solvents is rather scarce. The types of compounds which were found to be soluble were metal salts of tautomeric reacting substances (keto-enol tautomerism), salts and complex salts of both aliphatic and aromatic nitroso compounds, double salts of cobalt halides with bases or oximes, or double salts of cobalt compounds with tertiary bases such as pyridine, and anhydrous cobalt halides.

To test the drying action both 5 and 1 per cent solutions of the respective cobalt compounds in the above solvents were prepared. One part of the cobalt solution was mixed with five parts of China wood oil and a few drops poured over a glass plate, tilted to an angle of 45 degrees. Two controls were also made, one consisting of the same amounts of solvent and China wood oil without the cobalt compound, the other containing a cobalt resinatate siccative of high quality. The cobalt content of each was the same as in the solution to be tested.

Results

Table I shows the drying activity of the various solvents with several cobalt compounds. With the exception of cobalt nitrosonaphthol, cobalt acetylacetonate, and benzaldehyde plus mixtures in which metallic cobalt, lead, or manganese has been dissolved, all the substances tested showed a definite drying action on the oil. The substances listed as "good" compare favorably with commercial siccatives of the highest grade.

In these drying experiments two facts were noted especially: (1) Cobalt compounds having apparently the same solubility in the organic solvent and oil mixture did not show the same drying activity; (2) the character of the dried China wood oil film changed according to the solvent used. Especially on two pairs of cobalt compounds it was clearly seen that changes in the chemical constitution of the siccative greatly influenced its activity. Cobalt acetylacetonate and cobaltnitroso-naphthol were found to have practically no drying action, while their molecular compounds with pyridine were excellent catalysts. All four of the compounds are readily soluble in the solvents mentioned and such solutions mix equally well with China wood oil.

These facts are contrary to expectations, since according to prevalent conceptions the solubility or dispersion of a siccative in the oil was considered of primary importance. Furthermore, it was thought that substances with free residual valences would be superior as catalysts to the

same compounds after their valences have been taken care of by double-salt formation (acetylacetonate, acetylacetonate plus 2 pyridine).

Based on the above observation the following conception of the action of a siccative was put forward as a working basis:

In an efficient siccative the valences as well as the residual valences of the metal atom will be largely saturated. The saturation, however, will be of such an order that in contact with a non-hardened particle of the oil a reaction, or possibly a "double decomposition," between the catalyst and the oil will occur. This in turn hastens the polymerization and oxidation processes of the particle in question. Soon after these reactions have been started, the valence forces of the oil are taken care of by the changes in the oil itself. As a result the catalytically active metal or metal complex is again given off, possibly with restoration of the original complex. This in turn is again capable of inducing in other non-hardened oil particles a chain of reactions which lead finally to film formation.

Table I—Drying Action of Cobalt Compounds in Various Solvents

COBALT COMPOUNDS		SOLVENTS
(1) Benzonitrile	(6) Furfural	
(2) Benzaldehyde	(7) Aniline	
(3) Benzyl alcohol	(8) Benzyl chloride	
(4) Benzyl cyanide	(9) Amyl alcohol	
(5) Nitrobenzene	(10) Benzene	
GOOD DRYING ACTIVITY		
Cobalt chloride (anhydrous)		1 to 4
Cobalt sulfo cyanide (anhydrous)		1 to 9
Cobalt chloride (acetaldoxime) ^a		2, 3, 10
Cobalt nitrosoacetophenone ^b		1 to 4
Cobalt benzyldioxime pyridine ^c		2, 3
Cobalt-2-nitroso-1-naphthol pyridine ^d		10
Cobalt acetylacetone (pyridine) ^e		1-4, 10
MEDIUM DRYING ACTIVITY		
Cobalt chloride (benzaldoxime) ^a		10, 2, 3
Cobalt acetylacetone (quinoline) ^g		1 to 4
Cobalt sulfo cyanide hexamethylenetetraminepyridine ^c		10
Cobalt chloride (anilinehydrochloride) ^d		7
INSUFFICIENT DRYING ACTIVITY		
Cobalt-2-nitroso-1-naphthol		10
Cobalt-1-nitroso-2-naphthol		10
Cobalt acetylacetone ^e		10
Cobalt, manganese, lead in benzaldehyde plus toluene ^f		

^a Hieber, W., and Leutert, F., *Ber.*, **60**, 2296 (1927).

^b Biltz, W., and Clinch, J. A., *Z. anorg. Chem.*, **40**, 223 (1904).

^c Gmelin Friedheim, *Handbuch der anorganischen Chemie*, Band V, I, p. 295.

^d Byrkit, G. O., and Dehn, W. M., *J. Am. Chem. Soc.*, **51**, 1167 (1929).

^e Urbaine and Debiere, *Compt. rend.*, **129**, 304 (1899).

^f Bernoulli, A. L., and Schaaf, Fritz, *Helv. Chim. Acta*, **5**, 721 (1922).

^g Prepared in course of present study; methods will be published later.

A cracked and wrinkled surface is characteristic of the dried China wood oil film. However, when benzonitrile, benzaldehyde, benzyl alcohol, or benzyl cyanide was used as a solvent for the cobalt compound, smooth and glass-clear sur-

faces were obtained. Under the microscope only the thickest parts of the film were found to be of a wavy appearance when dried on tilted glass (Figures 1 to 4). The accompanying photomicrographs are characteristic of each of the solvents used: benzaldehyde (Figure 1), a comparatively large number of short waves starting in a right angle from several middle lines; benzyl alcohol (Figure 2), a few wavy wrinkles starting in a right angle from a single middle line; benzyl cyanide (Figure 3) somewhat like Figure 1 but with still smaller wrinkles; benzonitrile (Figure 4), wrinkles with no direction; finally in Figure 5 we see a typical China wood oil film as a control.

It was previously known that the China wood oil effect (wrinkles and cracks) can be restricted by the addition of phenols or old turpentine to the oil. To explain this fact it was assumed that these substances act as diluents and thus make possible a more uniform oxidation. The high absorption of the phenols in the ultra-violet possibly cuts out light catalysis of the oil and as such adds to the uniformity of the hardening process. If these substances mentioned as well as the solvents used in the present experiments actually produce smooth films through light absorption in the ultra-violet, and so cut down light catalysis, they would have to be considered as negative catalysts, or possibly as compounded catalysts, the positive action being due to the cobalt-containing substance, while the solvent and solution would be responsible for the retardation.

Solubilities of Salts in Ethylene Glycol and in Its Mixtures with Water¹

H. M. Trimble

OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE, STILLWATER, OKLA.

ETHYLENE glycol for this study was prepared from Prestone or from dynamite grade glycol. A slight unpleasant odor, somewhat resembling that of crude pyrolytic acid, was removed by drawing dried air through the material for 12 hours or more, holding it meanwhile at about 100° C. The glycol was then distilled at atmospheric pressure, saving the portion which came over within about 0.3 degree of 197.2° C. (corrected for pressure and emergent stem), the accepted boiling point. On redistilling this fraction most of the glycol came over at 197.2° C. (corrected). This portion was saved and used in the experiments. Its density and index of refraction were exactly those given for pure glycol in the literature.

The salts whose solubilities were determined were all of the highest obtainable purity. Some of the less common water-insoluble salts were prepared when wanted by precipitation from solution, using only the purest of reagents. The others were commercial products. All the salts were dried in an oven at 105-110° C. just prior to determining their solubilities when this could be done. Some salts whose water of crystallization would have been lost if subjected to

The solubilities of salts in ethylene glycol are, in general, less than in water. The relative order of solubilities is much the same, though certain salts which are readily soluble in water are nearly or quite insoluble in glycol. The solubilities of salts in glycol-water mixtures have been studied. Data and illustrative curves are given.

this treatment were not subjected to preliminary drying.

In a preliminary study, which was planned to furnish a basis for more detailed investigation, the solubilities of some hundred salts were determined in a semi-quantitative way. Roughly weighed quantities of the salts were placed in test tubes together with known volumes of glycol, and the test tubes were then rotated at room temperature for periods of 24 to 36 hours. In case a salt was seen to dissolve completely, more was added. The amount dissolved in a given experiment was estimated by weighing roughly the salt which remained undissolved at the end, after pressing it between filter papers to free it from most of the adsorbed glycol. In case the salt was only slightly soluble one or other of its ions was precipitated, after diluting the saturated solution with water, and the quantity of salt which had dissolved was estimated.

Those salts which are insoluble in water were found to be insoluble, or only slightly soluble, in pure glycol.

Of the anhydrous salts which are soluble in water, the halides proved to be, in general, readily soluble also in glycol. The order of increasing solubility of these salts for a given cation was, as with water, fluoride, chloride, bromide, iodide. The order of increasing solubility of salt for any one of the halide anions was generally the same as the order of increasing

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atomic weight of the cation. Those halides which show marked tendency to crystallize with water of crystallization, however, were very highly soluble in pure glycol. There is much evidence to show that these salts form solvates with glycol, which may account for their unusual solubilities.

Table I—Data on Ternary Systems, Ethylene Glycol-Water-Salt at 30° C.

GLYCOL %	WATER %	SALT %	DENSITY
Glycol-Water-KI			
0.00	39.49	60.31	1.7302
8.96	35.14	55.90	1.6655
19.26	29.76	50.98	1.6031
32.27	22.35	45.38	1.5395
51.57	10.16	38.27	1.4687
66.41	0.00	33.59	1.4272
Glycol-Water-KBr			
0.00	58.42	41.58	1.3876
12.73	51.45	35.82	1.3417
28.29	42.07	29.64	1.2995
46.08	30.34	23.58	1.2637
65.67	16.30	18.03	1.2338
86.32	0.00	13.68	1.2131
Glycol-Water-CuSO ₄ ·5H ₂ O			
0.00	72.35	27.65	1.2259
7.34	67.20	25.46	1.1941
22.26	59.72	18.02	1.1502
28.50	56.66	14.84	1.1363
50.25	40.49	9.26	1.1202
66.66	24.18	9.16	1.1406
71.61	4.77	23.62	1.2535
67.71	0.00	32.21	1.3267
Glycol-Water-K ₂ SO ₄			
0.00	88.86	11.14	1.0881
4.21	85.95	9.84	1.0812
9.01	82.88	8.11	1.0737
18.64	75.70	5.66	1.0651
28.90	67.43	3.67	1.0627
38.58	59.01	2.41	1.0646
49.75	48.80	1.45	1.0708
65.62	33.75	0.63	1.0823
100.00	0.00	0.00	1.1060
Glycol-Water-NaCl			
0.00	73.48	26.52	1.1960
14.93	62.93	22.14	1.1816
32.11	50.22	17.67	1.1694
51.13	35.42	13.45	1.1593
71.97	18.61	9.42	1.1518
93.38	0.00	6.62	1.1485
Glycol-Water-KCl			
0.00	72.90	27.10	1.1820
15.08	62.95	21.97	1.1648
33.47	50.00	16.53	1.1510
52.00	36.16	11.84	1.1424
73.27	18.98	7.75	1.1371
94.90	0.00	5.10	1.1368

Anhydrous salts whose anions contain oxygen exhibited different degrees of solubility. In some cases they were slightly soluble or insoluble in glycol. Anhydrous potassium sulfate and sodium sulfate, aluminum sulfate, chromic sulfate, and cadmium sulfate were so little soluble that their solutions, after diluting with water, gave barely perceptible precipitates of barium sulfate. These salts were prepared by dehydrating their hydrated forms by heating for several hours at temperatures slightly above their decomposition temperatures. Anhydrous cupric sulfate dissolved to the extent of 0.5 per cent at 30° C. The alkali hydrogen sulfates were somewhat more soluble. The alkali carbonates and bicarbonates were moderately soluble. The secondary and tertiary alkali phosphates were only slightly soluble. The anhydrous nitrates varied in solubility from potassium nitrate and sodium nitrate, which were only slightly soluble, through the moderately soluble lead nitrate, to silver nitrate, which proved to be highly soluble. Sodium, potassium, and ammonium arsenates were fairly soluble. Ammonium molybdate crystals were decomposed to a white powder, which was nearly completely insoluble. The alkali formates and acetates were very highly soluble. Some potassium salts of higher acids in this series proved less soluble. Roughly, the solubility of such a salt is less the higher its molecular weight.

The addition of water of crystallization to an anhydrous salt serves, in every case studied, to increase its solubility in glycol very markedly. Thus, CuSO₄·5H₂O, Na₂SO₄·

10H₂O, and Al₂(SO₄)₃·18H₂O are all highly soluble, though their anhydrous forms are very little soluble. Hydrated salts in general are highly soluble, the only exceptions found in this study being potassium citrate and tartrate and sodium tartrate. Usually a salt is more soluble the higher the number of molecules of water of crystallization it carries.

Glycol shows different solvent powers toward the components of mixed salt. Thus, K₂Al₂(SO₄)₄·24H₂O and K₂Cr₂(SO₄)₄·24H₂O are split up, potassium sulfate is separated out in the form of fine crystals, and the heavier metal sulfates which are left are dissolved to a great extent. The alums containing the ammonium radical, both of whose components are soluble when taken singly, are highly soluble.

As would be expected, the addition of water to glycol increased the solubilities of many salts, particularly the anhydrous ones. This effect decreases as the salts carry more molecules of water of crystallization, and may even be reversed for some of the salts which are highly hydrated. Thus, as will be seen, the solubility of CuSO₄·5H₂O in glycol is actually decreased throughout a certain range by adding water.

Most salts were found to dissolve in glycol with but little thermal effect. It was found, too, that the temperature coefficients of solubility for many salts dissolving in glycol at about room temperature are quite low; whence it may be inferred that thermal effects on solution are generally small. Potassium iodide and a few other anhydrous salts, however, showed a cooling effect, just as these same salts do on dis-

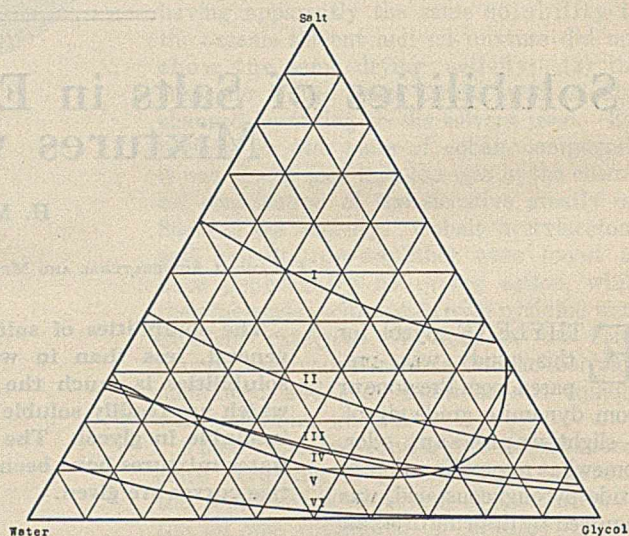


Figure 1—Ternary Systems, Glycol-Water-Salt at 30° C.

I—KI
II—KBr
III—NaCl
IV—KCl
V—CuSO₄·5H₂O
VI—K₂SO₄

solving in water. When anhydrous salts form solvates with glycol the quantity of heat evolved is often rather great. Anhydrous aluminum chloride and ferric chloride react violently with glycol, evolving much heat and copious fumes of hydrogen chloride. The more common acids and bases, together with strongly basic salts such as the alkali carbonates, also apparently enter into reaction with glycol—again with evolution of heat.

Comparisons were made between solubilities at room temperature and at the boiling point of ethylene glycol. Contrary to expectations, it was found that only in exceptional cases are salts very much more soluble at the higher temperature than at the lower. One such exceptional case is that of magnesium ammonium chloride, whose solubility change is so great that it might very readily be recrystallized from glycol if desired. A number of salts were found to show an in-

creased solubility at the boiling point momentarily. On holding these solutions at that high temperature for a short time, however, salts were again thrown down as amorphous precipitates. Mercuric chloride and mercuric acetate yielded gray precipitates which slowly turned black, presumably due to the formation of metallic mercury. Copper sulfate pentahydrate was dehydrated, forming a mixture of anhydrous CuSO_4 and of the monohydrate. The compositions of these precipitates were not investigated further. The alkali halides generally show but little greater solubility at high than at low temperatures, even in those cases where solvation seems to occur.

Table II—Solubilities of Salts in Ethylene Glycol-Water Mixtures

GLYCOL IN SOLVENT	SALT PER 100 GRAMS SOLVENT	GLYCOL IN SOLVENT	SALT PER 100 GRAMS SOLVENT	GLYCOL IN SOLVENT	SALT PER 100 GRAMS SOLVENT
%	Grams	%	Grams	%	Grams
Potassium Iodide		Sodium Chloride		$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	
0.00	153.20	0.00	36.09	0.00	38.22
20.30	126.80	19.17	28.44	9.85	34.16
39.30	104.00	38.99	21.46	27.15	21.98
59.08	83.08	59.07	15.54	33.47	17.43
83.41	62.00	79.45	10.40	55.38	10.20
100.00	50.58	100.00	7.09	73.38	10.08
				93.75	30.92
				100.00	46.88
Potassium Bromide		Potassium Chloride		Potassium Sulfate	
0.00	71.17	0.00	37.18	0.00	12.54
19.83	55.81	19.33	28.16	4.67	10.91
40.21	42.13	40.10	19.80	9.81	8.83
60.30	30.85	58.98	13.43	19.76	6.00
80.12	22.00	79.42	8.40	30.01	3.81
100.00	15.85	100.00	5.37	39.53	2.47
				50.48	1.47
				66.03	0.63
				100.00	0.00

Concentrated solutions of salts in glycol display high viscosities. Partly as a result of the viscosity of the solvent, saturation is reached slowly, quite high degrees of supersaturation may be attained in some cases, and the return to a state of saturation, even in the presence of added crystals, is slow compared with the same phenomenon in water solutions.

Salts in solution in glycol are ionized. Even when conditions are completely anhydrous, metathetical reactions occur readily. When precipitates insoluble in glycol are thus formed they are very finely colloidal; they remain suspended for long periods of time, and they show no tendency to grow larger either by growth of larger at the expense of smaller particles or by clumping together. Some of the colloidal precipitates formed seem worthy of careful study. Reactions in which one metal displaces another occur, too, just as in aqueous solutions, the relative activities in this regard being those indicated in the electromotive series of the metals. Cations may be separated from anhydrous solutions in glycol by electrodeposition just as from aqueous solutions, though the potential differences required are high. Conductance experiments in a few cases showed that under anhydrous conditions degrees of ionization are quite low. The addition of water to these solutions, of course, increases the degree of ionization of the salts, and with it the velocities of all the above-named accompanying effects.

Solubilities in Mixtures of Glycol and Water

Since it appears probable that solutions of salts in mixtures of glycol and water will prove of more importance than solutions in pure glycol, a careful study of solubility relations for some typical salts was made. Glycol for these determinations was prepared as before, the final distillation being carried out just before the glycol was wanted for experiments. The salts were of the highest obtainable purity.

Glycol-water mixtures were made up by weight for the experiments with the alkali halides. The mixtures were then sealed up in test tubes, together with excess of salt,

and rotated at 30° C. for 18 to 36 hours. Samples were then removed for analysis and for the determination of density. Densities were determined in the usual way, using Ostwald-Sprengel type pycnometers. The analysis was performed by precipitating silver halide from weighed portions of the saturated solution in the usual manner, after diluting largely with water, then heating and weighing. A number of tests showed that the presence of glycol in concentrations up to 10 per cent does not interfere with the analytical determination of the halide or sulfate ions. From the percentage of alkali halide found and the composition of the solvent the concentrations of each of the components of the solutions were calculated. Analysis of the undissolved salt showed that in every case unsolvated alkali halide was the solid phase at equilibrium.

The saturated solutions of copper sulfate were analyzed directly for both glycol and copper sulfate content. In determining glycol the method involving its oxidation in sulfuric acid solution with standard potassium dichromate followed by electrometric titration of the excess was used. As before, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was the solid phase in every case in which solubility determinations were made with this substance.

The solubility relations are set forth in the accompanying tables and graphs. As will be apparent from the curves, the solubilities of the alkali halides and of potassium sulfate decrease regularly with increasing concentration of ethylene glycol, the decrease for the halides being relatively more rapid

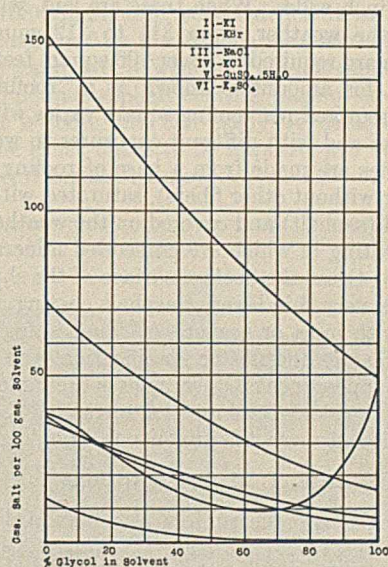


Figure 2—Solubilities in Glycol-Water Mixtures

the greater the solubility of the salt in water. Cupric sulfate pentahydrate shows a decrease to a minimum, followed by a rise to a maximum with increasing concentration of glycol. This salt is more soluble in pure ethylene glycol than in water. This seems to indicate that glycol forms a solvate of some kind with the salt at higher concentrations. No indication of the formation of a solvate in the solid phase was found with potassium sulfate.

Acknowledgment

The author wishes to express his thanks to the Carbide and Carbon Chemicals Corporation, who kindly furnished the glycol used in this investigation and furnished valuable information regarding properties and methods of analysis of glycol.

Asphalt Shingles¹

John Morris Weiss

WEISS AND DOWNS, INC., NEW YORK, N. Y.

ASPHALT shingles surfaced with mineral granules are an important material in the roofing industry. According to the statistics of the Department of Commerce, about 10,856,690 squares of asphalt shingles were sold in 1928 and 11,974,539 squares in 1929 by the forty-one producers who comprise the industry. About 90 per cent of the shingles sold are of the strip type. These consist of several units joined together in flat strips and are frequently called "multiple shingles." They can be laid more rapidly and with less labor than individual shingles and have "cut-outs" so as to give the same roof appearance as when individual shingles are used. Figure 1 shows a photograph of this type of roof.

A common type is a four-shingle strip with square butts 32 or 36 inches long, 12½ inches wide with cut-outs 4 inches deep and ¾ inch wide. When these are laid, with a 4-inch exposure to the weather, from 311 to 312 square feet of actual shingle are required to cover 100 square feet of roofing surface, and this amount is known as a "roofing square." The amount required per roofing square varies with different design shingles and with different exposures to weather.

Such shingles are made from a base of roofing felt (a rag paper with or without other fibers), saturated with a bituminous material (asphalt) and covered on the weather side with an asphalt coating in which are embedded mineral granules, usually slate. Often the bottom surface of the shingle is also treated with a very thin layer of asphalt coating and finished by dusting with mica or soapstone. Such shingles are sold under brand names and not on specification, and as the general outward appearance of all shingles is the same, except for the variation in color of the mineral surfacing, the purchaser cannot intelligently select between one brand and another.

A. S. T. M. Specifications

These shingles are the subject of a standard A. S. T. M. specification (D225-29) entitled "Standard Specifications for Asphalt Roll Roofing and Asphalt Shingles Surfaced with Mineral Granules." Their requirements as to composition of the finished product may be summarized as follows:

Weight per 108 sq. ft.	Minimum 80 lbs.
Saturation in felt.	Minimum 150%
Weight of felt per 108 sq. ft.	Minimum 10.8 lbs.
Ash in dry felt.	Maximum 10%
Mineral matter per 108 sq. ft.	Maximum 35 lbs. ^a

^a If above 35 pounds total weight must be equally above 80 pound limit.

Apart from the above, requirements are general and not specific in character, except for a heat test at 80° C. for 2 hours, which practically all commercial materials will pass.

All that these specifications really provide is that there shall be a certain minimum weight per unit area of shingle, a minimum weight of felt per unit area, a minimum percentage of saturation in the felt, a maximum of ash in the felt, and a maximum of mineral matter per unit area of shingle.

Asphalt shingles surfaced with mineral granules have become an important roofing material, and the published specifications now in use do not appear to be sufficient to secure adequate quality. The results of the examination of sixteen brands of asphalt shingles that are sold for roofing are presented, together with comments on the different compositions which are encountered. Certain recommendations as to the direction in which specifications should be changed are suggested.

Experimental Tests

In the last eight years the writer and his associates have had occasion to determine the composition of a number of grades of roofing.

These tests were made on samples submitted to them, and usually consisted of three strips supposedly chosen to represent the average of the material. The total weight of the strips submitted was determined in the laboratory and the pieces selected for actual test were selected so as to have the same average weight-area relationship as the average of the strips received. The methods used for examining the samples were variations of the methods suggested by Abraham (1). The fiber counts of the felts were made according to A. S. T. M. Tentative Standard (D272-29T).

Table I shows the result of representative tests of the proximate composition of sixteen brands of 36 inches long, 12½ inches wide strip shingles, with square butts. Shingle No. 8 represents an asbestos felt base shingle of a different class than the others, and is therefore not subject to direct comparison.

Only one of the brands tested is below the minimum weight of the A. S. T. M. requirements, which incidentally are substantially the same throughout as those of the Underwriters Laboratories, whose approval tag is usually on brand shingles of this type. This approval is, however, primarily from the standpoint of fire-retarding properties and not necessarily of durability and service. Two of the brands (Nos. 1 and 3) have used less felt than the requirements of the A. S. T. M. specification, while two others (Nos. 5 and 14) are above the maximum requirement for surface mineral matter. However, these will pass the specification since the excess over 35 pounds per 108 square feet is compensated by an excess in total weight over the 80 pound minimum.

Table I—Composition of Various Brands of Strip Asphalt Shingles

SHINGLE No.	TOTAL WEIGHT PER 108 SQ. FT.	WEIGHT OF COMPONENT PARTS PER 108 SQ. FT.					
		Felt	Saturant	Top coating	Mineral surfacing	Bottom coating	Bottom mineral
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
1	83.6	10.5	19.1	27.1	25.8	0.5	0.6
2	84.4	11.6	17.1	21.0	32.4	1.2	1.1
3	83.2	10.2	18.1	19.5	27.3	7.0	1.1
4	81.4	11.7	21.5	23.4	22.5	1.6	0.7
5	82.8	12.1	22.2	9.9	36.3	1.2	1.1
6	80.9	11.9	17.8	27.0	21.3	2.1	0.8
7	80.0	11.7	20.3	20.4	25.8	1.0	0.8
8	84.0	20.9	16.2	17.4	28.4	0.2	0.9
9	82.0	11.6	24.8	24.2	20.5	0.3	0.6
10	78.4	11.6	22.6	20.4	22.4	0.7	0.7
11	90.1	11.7	25.2	21.3	29.6	1.2	1.1
12	85.3	11.8	19.4	20.5	33.1	0.2	0.3
13	87.1	11.1	21.1	23.8	30.2	0.6	0.3
14	93.9	11.0	21.0	23.3	37.9	0.3	0.4
15	81.8	11.1	19.1	26.6	18.5	5.7	0.8
16	90.8	11.9	17.4	29.6	29.0	2.5	0.4
A. S. T. M. requirements	Min. 80	Min. 10.8			Max. 35.0		

From a material cost standpoint, felt is the most expensive item in shingle manufacture, saturant and coating come next,

and mineral surfacing is the cheapest. The raw material cost for No. 9 is about 25 cents more per roofing square than that for No. 1, although the finished weight per roofing square is considerably less in No. 9 than in No. 1.

Nos. 3 and 15 have a very heavy bottom protective coating, which differentiates them from the other brands tested.



Figure 1—Roof Covered with Multiple Asphalt Shingles

Table II shows the percentage saturation in the felt, and the tests of the dry felt. Excluding No. 8, the asbestos shingle, two (Nos. 2 and 16) are below the A. S. T. M. saturation limit and one (No. 6) is just on the limit. The last three (Nos. 14, 15, and 16) are too high in ash. Too light weight felt has been used in Nos. 1 and 3, as was indicated also in the tests of Table I. All of these represent considerable differences in cost of manufacture and probably in service. Those with low saturation in the felt usually show curling and blistering in service to a marked degree, although low saturation is not the only cause of such blistering. Figure 2 shows a roof on which curling has occurred and illustrates the undesirable appearance caused by this action.

As to the felts, a variation from a 45.5 to a 53.5 felt is quite considerable and represents a 17 per cent variation in the most expensive of the components.

Table II—Saturation Tests

SHINGLE No.	SATURATION	FELT		FIBER COUNT					
		No.	Ash	Wool	Cotton	Chemical wood	Mechanical wood	Jute-manila	Asbestos
	%	%	%	%	%	%	%	%	%
1	182	47.0	5.2
2	148	51.5	7.6
3	177	45.5	6.8
4	184	52.0	7.6
5	184	53.5	6.6	4.4	68.5	15.0	11.1	1.0	...
6	150	52.5	6.3	3.7	71.7	15.0	7.4	2.2	...
7	174	52.0	4.7	4.3	70.9	10.0	13.0	1.8	...
8	80	95.0	65.5	7.9	26.9	63.4
9	214	49.5	7.7	2.2	70.9	12.0	11.9	3.0	...
10	195	52.0	6.7	2.1	65.2	10.4	17.0	5.3	...
11	216	48.5	9.3	1.3	70.2	9.0	16.3	3.2	...
12	165	52.8	6.8	3.2	69.9	10.0	15.9	3.0	...
13	190	50.0	7.9	5.0	68.2	5.1	16.9	4.8	...
14	191	49.0	10.6	3.0	80.5	4.4	7.4	4.7	...
15	172	49.5	13.5	1.0	71.0	19.0	5.0	4.0	...
16	146	52.9	10.8	3.0	42.0	12.0	34.0	9.0	...

A. S. T. M. requirements

Min. 150
Min. 48
Max. 10

The character of the felts is also of interest. The extremes of 83.5 per cent rag fibers (cotton + wool) in No. 14 and 45 per cent in No. 16 is also of interest. Rags are far more expensive than wood fibers and, although it is a mooted

point as to how much wood can be used with safety, in the writer's opinion No. 16, with almost 50 per cent wood and a saturation of only 146 per cent, will give service results which are decidedly inferior to many of the others with much higher rag content and more complete saturation.

Discussion of Specification Requirements

The asphalt roofing industry has been very highly competitive in the last few years and there has been a tendency to reduce the material costs, often at the expense of real quality. More rigid purchase specifications are very desirable. The ideal specification, of course, would be a service test, but as yet no accelerated tests which have been so correlated with actual service records as to be reliable are available for general use.

Somewhat stricter limits than the A. S. T. M. requirements are necessary to assure real quality of product and prevent competition from further abstracting from the inherently necessary higher grade of raw materials. These requirements should place some upper limit on the wood-fiber content of the felt, increase the minimum allowable saturation, and prescribe a ratio between surface coating and mineral matter so that if the latter is increased the coating will be proportionately increased to insure there being enough to hold the grit to the surface. In general mineral-surfaced roofing lasts considerably longer than smooth-surfaced roofing where the asphaltic coating forms the wearing surface. There must be enough mineral matter to cover and protect the coating adequately. No. 15, with only 18.5 pounds of mineral surfacing per 108 square feet, seems deficient in this respect, and this is confirmed by the visual appearance of the sample. On the other hand, No. 5, with 36.3 pounds mineral surfacing and only 9.9 pounds asphalt coating, has not enough coating and the grit is loose and can easily be detached from the surface. The exact limits to be imposed will vary with the type of mineral surface employed.



Figure 2—Roof of Asphalt Shingles on Which Curling Has Occurred

On the saturation specification, the writer would be inclined to set a low limit of 170 per cent, which would exclude Nos. 2, 6, 8, 12, and 16 (see Table II), and would further give consideration to the ratio between actual saturation and saturating capacity of the felt used. Felts vary in their capacity to take saturation. Some makers control saturation by making a kerosene absorption test on dry felt and regulating the saturation to at least 90 per cent of that which the felt should theoretically absorb. This practice seems to be an excellent one to insure thorough saturation of the felt.

It must also be considered that improper manufacturing

methods can detract from values even if adequate amounts of suitable-quality raw materials are used. Analyses of the type given here will naturally not detect such differences which are to a certain extent evident by inspection of the roofing. However, in general, the higher the grades of materials used in the roofing the greater care will be taken by the makers. Tests of the kind outlined here will do much toward eliminating the lowest grades of product from con-

sideration and should give the consumer a better chance of obtaining service from the brand of roofing which he purchases. From time to time, based on experience, the limits of acceptable quality can be narrowed so as to insure more adequate service.

Literature Cited

- (1) Abraham, H., "Asphalt and Allied Substances," 1929.

Solubilities of Oils and Waxes in Organic Solvents—II¹

John Ward Poole and Collaborators

FUEL AND GAS ENGINEERING DEPARTMENT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

IN A previous article by the senior author in collaboration with R. K. Opper and A. K. Scott [IND. ENG. CHEM., 21, 1098 (1929)] there has been published qualitative data for twenty-eight organic solvents. In addition, quantitative data on the solubilities of oil and wax in acetone, in *n*-butyl alcohol, in *n*-butyl aldehyde, and in a "50-50" mixture of acetone and *n*-butyl alcohol were presented graphically as a function of temperature. Similar curves were given for the solubility of wax only, in butyl acetate, chlorobenzene, and toluene. With the last three solvents oil is completely miscible, at least over the temperature range in question.

The work reported in this article, however, did not finish the program for this group of solvents. Certain solvents not quantitatively investigated seemed to offer considerable possibilities and a different type of data was also needed to determine the commercial and analytical significance of the selective powers shown. Furthermore, there were other solvents known to possess, or which might possess, the qualifications necessary for wax removal. This paper deals with progress in the above fields.

SOLUBILITIES OF PENNSYLVANIA OILS AND PARAFFIN WAX IN NAPHTHA, TURPENTINE, ETHYLENE DICHLORIDE, METHYL ETHYL KETONE, *n*-BUTYL ALDEHYDE, ISOPROPYL ALCOHOL, AND *n*-AMYL ALCOHOL

With F. C. Fahnestock and E. L. Krall

Of the solvents investigated in the previous paper only seven were investigated quantitatively, although it was recognized that others in the group showed equal or nearly equal promise of high selectivity. The work covered in this section represents the completion of various solubility-temperature curves for this group.

It will be noted, however, that certain solvents are not represented in the accompanying graphs. The reasons for this are several. Ethyl alcohol, diacetone alcohol, acetic anhydride, glacial acetic acid, Cellosolve, and Methyl Cellosolve either possess very low solvent power for oil or seem to have little selective ability. Amyl acetate, xylene, mesityl

These data were collected to furnish fundamental information for commercial and analytical processes wherein it is necessary to separate paraffin wax from liquid hydrocarbons. The solubility-temperature data are shown graphically for *n*-amyl alcohol, a commercial mixture of amyl alcohols (Pentamol), isopropyl alcohol, *n*-butyl aldehyde, paraldehyde, ethyl chlorocarbonate, ethylene dichloride, butyl formate, methyl ethyl ketone, two solvent naphthas, and turpentine.

Furthermore, consideration has been given to the important factor of oil concentration on the solubility of wax in solvent-oil mixtures. Butyl acetate, paraldehyde, *n*-butyl alcohol, chlorobenzene, and Pentamol were investigated for this study.

Finally, in order to broaden the field of solvents available for dewaxing processes, twenty-six compounds on which data are practically non-existent have been investigated qualitatively.

when using fresh chemically pure solvent. In view of the considerable number of determinations necessary to obtain the desired data, it seems probable that ethylene dichloride, as such, is not undesirably reactive.

Experimental Procedure

The experimental procedure for the determinations reported in this paper was identical with that used in the previous work. For each temperature two determinations were made, and unless these checked within about 3 per cent of the total wax dissolved further determinations were run. In certain cases, usually with either very high or very low solubilities, it was necessary to make several determinations and average those which came close together. When a widely divergent solubility was observed, extra determinations were always made. Each point shown on the plot represents the average value for at least two independent determinations, which frequently were identical. The data are probably accurate to within 5 per cent of the total hydrocarbons dissolved.

Characteristics of Materials Used

The solvents used in this work were as follows: light naphtha—water white, A. P. I. gravity 59.9°, boiling range 88° to 138° C.; heavy naphtha—water white, A. P. I. gravity 49.5°, boiling range 157° to 231° C.; commercial turpentine; *n*-butyl aldehyde, technical grade; ethylene dichloride, chemically pure; *n*-amyl alcohol, chemically pure; methyl ethyl ketone, chemically pure; isopropyl alcohol, chemically pure.

¹ Received November 24, 1930.

Commercial paraffin wax, melting point 50° C.

Note—The wax used is identical with the "intermediate" wax mentioned in the first paper of this series. At that time three different waxes were examined. Actually the high and low waxes were derived from that melting at 50° C., by repeated recrystallizations from acetone, all material melting above the original wax in each case being placed in one fraction and all melting lower than this in the second fraction. In every instance it was found that the lower the melting point the greater was the solubility in any given solvent. Nevertheless, the curve for the original or intermediate wax was very close to a mean for the other two. Consequently, it was considered unnecessary in subsequent work to use more than the one wax.

Pennsylvania paraffin-base oil, specific gravity 0.877; viscosity at 100° F., 240 seconds Saybolt; pour test 20° to 25° F.; flash 400° F.; color about 5 N. P. A.

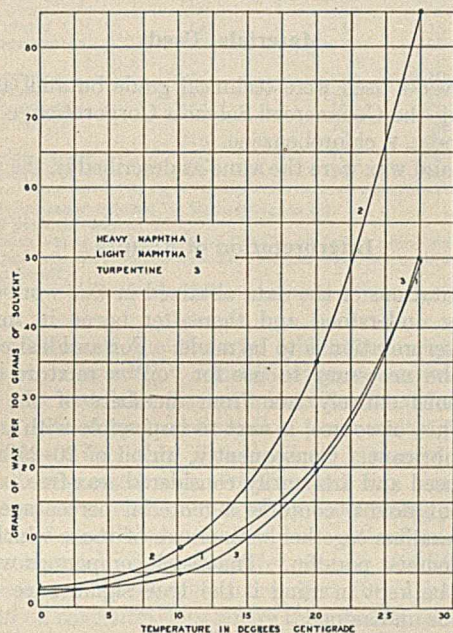


Figure 1—Temperature-Solubility Curves for Wax in Heavy Naphtha, Light Naphtha, and Turpentine

Interpretation of Results

The solvents with which this paper is concerned have been divided for convenience into two rough classifications. The first consists of those solvents which are completely miscible with oil and in which wax also becomes very soluble as the temperature is moderately increased. This type includes three solvents which are very similar chemically—solvent naphtha (gravity 59.9° A. P. I.), solvent naphtha (gravity 49.5° A. P. I.), and commercial turpentine (Figure 1). In view of the similar chemical nature of these compounds it is not surprising that their ability to dissolve the hydrocarbons in question should also be similar.

The second group of solvents (Figure 2) consists of ethylene dichloride, *n*-amyl alcohol, *n*-butyl aldehyde, methyl ethyl ketone, and isopropyl alcohol. Each of this group dissolves wax but sparingly over the range investigated and all but the last two appear completely miscible in oil. Since methyl ethyl ketone and isopropyl alcohol have only limited ability to dissolve oil, additional graphs drawn to a smaller scale (Figures 3 and 4) are included for these solvents. The corresponding curve for wax has also been included for purposes of comparison.

NAPHTHAS—Both light and heavy naphthas show selectivity in their solvent powers at low temperatures and seem completely miscible with oil in all proportions over the range in question. The wax solubility, however, increases rapidly with increase in temperature, and at no temperature investigated is it low enough to make these solvents attractive

commercially. The heavy naphtha has the lower wax solubility, but even here the value is greater than 20 grams per 100 grams of solvent at 20° C.

COMMERCIAL TURPENTINE—Like the naphthas, turpentine is completely miscible with the oil and shows marked selective properties at low temperatures, but above 10° C. the wax solubility increases rapidly, while at 20° C. it reaches a value of nearly 20 grams per 100 grams of solvent. The curve is, in fact, practically coincident with that of the heavy naphtha. In addition to possessing no decided advantages over the latter solvent, turpentine has the disadvantage of leaving in the oil a considerable residue, probably resulting from oxidation.

ETHYLENE DICHLORIDE—Among the solvents which possess very low wax solubilities at the temperatures investigated, ethylene dichloride is one which seems to show definite promise as a dewaxing agent. The value of the wax solubility for this solvent is less than 5 grams per 100 at the highest temperature investigated. Ethylene dichloride is miscible with oil in all proportions at the temperatures under consideration, and with such a high degree of selectivity it would seem well suited to serve as a dewaxing medium. No undesirable qualities were noted, while the low viscosity of the solvent rendered filtering comparatively easy.

AMYL ALCOHOL—Amyl alcohol possesses many of the same characteristics as ethylene dichloride. It is miscible with oil in all proportions and has a low wax solubility. In the latter respect it appears to be even better than ethylene dichloride.

On the other hand, this solvent is decidedly more viscous and filters with difficulty.

***n*-BUTYL ALDEHYDE**—In view of the solubility data above, *n*-butyl aldehyde would seem to have the same possibilities as a dewaxing agent as ethylene dichloride and amyl alcohol. On the contrary, it was found that, like turpentine, it leaves a residue on evaporation and thus becomes of doubtful value.

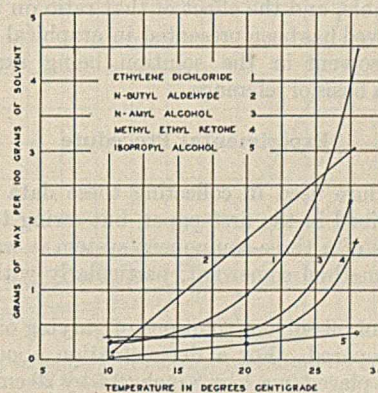


Figure 2—Temperature-Solubility Curves for Wax in Ethylene Dichloride, *n*-Butyl Aldehyde, *n*-Amyl Alcohol, Methyl Ethyl Ketone, and Isopropyl Alcohol

METHYL ETHYL KETONE AND ISOPROPYL ALCOHOL—Although methyl ethyl ketone and isopropyl alcohol both show marked selectivity for oil over wax, both possess limited power to dissolve oil. In the case of isopropyl alcohol this would appear to be a decided drawback, the solubility reaching no more than 14 per cent at 30° C. However, it does seem superior to acetone, inasmuch as it dissolves oil somewhat more readily and wax a little less readily than does that solvent. Possibly it might be used as an acetone substitute where a wax precipitant is desired in connection with a very powerful solvent. In one of the few cases where true solvent extraction is commercially used, the oil-wax mixture is dissolved in benzene, from which the wax is precipitated by acetone and a low-pour-test oil thereby produced.

EFFECT OF OIL ON SOLUBILITY OF WAX IN BUTANOL, BUTYL ACETATE, AND CHLOROBENZENE

With F. C. Fahnestock and E. L. Krall

The first paper of this series and the preceding section of the present paper have been concerned with two-component oil-solvent or wax-solvent systems. In the present section the effect of oil on the solubility of wax in each of three promising solvents is considered.

Although data on two-component systems are important in the development of the problem, it is evident that in all actual use of selective solvent power we will encounter systems of three components. In such systems, consisting of oil, wax, and solvent, it is logical to suppose that the variation of any one of the components will influence the relationship of the other two. Since without exception the miscibility of oil and solvent exceeds that of wax and solvent,

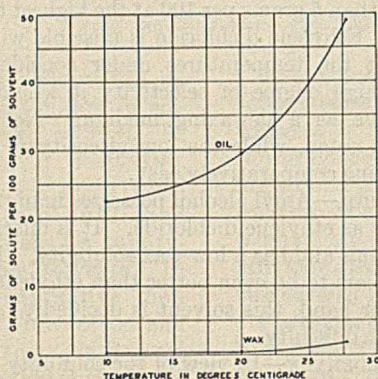


Figure 3—Temperature-Solubility Curves for Wax and Oil in Methyl Ethyl Ketone

the oil and solvent in some cases being miscible in all proportions, the oil-solvent ratio has been considered the independent variable, and the effect of that ratio on the amount of wax dissolved has been presented in graphical form. The quantity of solvent in the solution being examined has been used as a basis of reference.

Experimental Procedure

The procedure used in collecting these data was similar to that described in the first paper, but owing to the added complications of a three-component system it was necessary to alter the method somewhat, particularly with respect to calculations.

A number of oil-solvent solutions of varying oil concentration were prepared. For a determination about 50 cc. of solution were placed in a 1 by 8 inch (2.5 by 20 cm.) test tube, and sufficient melted wax was added to furnish an excess amounting to 1 or 2 drops. These tubes were then placed in a constant-temperature bath and allowed to remain overnight. The next morning a portion was forced by air pressure through a cotton filter into a tared weighing bottle. After weighing, the sample was evaporated to constant weight on a hot plate and under a mild air jet, the temperature being maintained at about 70° C. Blanks were run simultaneously on the original oil-solvent solution as a check on the oil-solvent ratio. From these data the quantities of wax, oil, and solvents were calculated. The solvent was considered equal to the loss by evaporation. The oil was found from the ratio of oil to solvent in the prepared mixture, the composition of which was simultaneously checked by the blank determinations. The wax was considered as being equal to the difference between the calculated oil and the residue remaining in the weighing bottle. In each case three determinations were made which, with a few explainable exceptions, deviated from

the mean by less than 2 grams of wax per 100 grams of solvent. With low solubilities the determinations were much closer than this, no values being considered which deviated 10 per cent from the mean value of wax dissolved. Except in isolated cases this deviation was less than 5 per cent. Occasionally high values were obtained, but such data were neglected on the ground of probable solvent evaporation. It will be seen from a consideration of the method that evaporation would cause the calculated oil to be less than the actual oil and raise the apparent wax-solvent ratio both by making the calculated quantity of wax too high and the calculated solvent too low. This matter of evaporation is probably the most serious deficiency of the method.

The data were then plotted in the manner shown.

Materials Used

The solvents used were technical grade butanol as manufactured by the Commercial Solvents Corporation, c. p. butyl acetate, and c. p. chlorobenzene.

The oil and wax were the same as described in the previous section.

Interpretation of Results

The limitations of the data obtained in this work must be completely understood and thereafter borne in mind if a correct interpretation is to be made. For an ideal condition it would be necessary to use for "oil" a mixture of liquid hydrocarbons entirely free from members of the paraffin series. This, of course, is next to impossible with any paraffin-base lubricant. Consequently, an oil of 20–25° F. pour test was used and arbitrarily considered wax-free. Such an oil, without doubt, contains a material percentage of low-melting paraffins together with traces of those which constitute commercial paraffin. That such compounds were present must be kept in mind if the true significance of these data is to be understood.

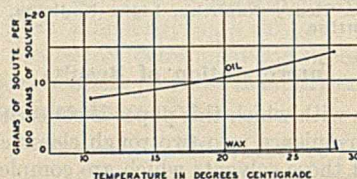


Figure 4—Temperature-Solubility Curves for Wax and Oil in Isopropyl Alcohol

Owing to this arbitrary placing of the wax origin on the plots, it has developed in certain cases—i. e., 0° and 10° C. curves for butanol—that the data show negative values for wax solubility. This means that the original oil, under the conditions of experimentation, has been further dewaxed by an amount corresponding to these negative solubilities. This feature can be understood best by referring to Figure 10, where grams of total solute per gram of butanol are plotted against percentage of wax in lubricating oil thus dewaxed.

Another limitation of these data is that they apply only to the particular types of oil and wax which have been used. For instance, it is not unreasonable to suppose that an oil of lower hydrogen-carbon ratio than the one here considered would have a greater tendency to increase the dissolved wax. It seems to be more or less generally true that the lower this ratio the greater is the capacity of the substance to enter solution with other organic compounds. Such a factor might appreciably change the character of analogous data.

Again it should be remembered that a commercial paraffin wax was used in collecting these data. Such a wax represents

Table I—Solubilities of Additional Organic Solvents. Qualitative Data

SOLVENT	B. P. ° C.	10° C.			21° C.			HIGHER TEMPERATURES		
		Penna.	Texas	Wax	Penna.	Texas	Wax	Penna.	Texas	Wax
Isoamyl alcohol ^a	130	0	100	0.5	-8	100	0.75	100 (33) ^f	100	12 (41)
sec-Amyl alcohol	118	100	100	0.5	100	100	0.5	100	100	12 (39)
Amyl chloride	106	100	100	6	100	100	22	100	100	100 (33)
Bromobenzene	157	100	100	3	100	100	19	100	100	100 (34)
Isobutyl alcohol ^a	106	0	100	0.5	-9	100	0.5	100 (42)	100	12 (41)
sec-Butyl alcohol ^a	99	0	0	0.7	0	0	0.7	-8 (40)	0	15 (43)
Butyl chloride	78	100	100	6	100	100	22	100	100	100 (31)
Butyl formate	107	100	100	0.75	100	100	2	100	100	25 (37)
Chloroform ^b	61	100	100	12	100	100	50	100	100	100 (30)
Crotonaldehyde ^c	104	0	25	0.8	0	100	0.8 (27)	100 (53)	100	12 (42)
Dichloroethylene	55	100	100	6	100	100	25	100	100	100 (29)
Diethyl carbinol	114	100	100	0.2	100	100	2.4 (24)	100	100	30 (38)
Ethyl bromide	39	100	100	5	100	100	25	100	100	100 (31)
Ethyl carbonate ^d	126	100	100	0.25	100	100	0.5	100	100	5 (40)
Ethyl chlorocarbonate ^e	94	100	100	...	100	100	2.5	100	100	45 (38)
Ethylene bromide	130	100	100	1.2	100	100	1.2	100	100	25 (34)
Ethyl formate ^f	54	-17	18	0.5	-17	18	0.5	-17	100	15 (43)
Ethyl propionate ^g	98	-12	100	0.6	-15	100	2.3	-25 (45)	100	12 (33)
Furfural	161	0	0	0	0	0	0	0	0	0 (65)
Methyl acetate ^h	57	6	-10	...	3	-15	...	-6	100	3 (50)
Paraldehyde ⁱ	124	-33	100	1.2	100	100	1.2	100	100	50 (40)
Pentachloroethane	161	100	100	6	100	100	20	100	100	100 (32)
Petroleum ether ⁱ		100	100	9.5	100	100	25	100	100	100 (28)
Pyridine ^e	115	-12	100	1	-25	100	1	100	100	25 (39)
Tetrachloroethylene	120	100	100	31	100	100	46	100	100	100 (29)
Trichloroethylene	87	100	100	20	100	100	40	100	100	100 (28)

^a Solvent layer colored by Pennsylvania oil.

^b 2.9 per cent wax at 1° C.

^c Pennsylvania oil insoluble at 43° C., solubility point sharp.

^d 20 per cent oil solution cloudy; 33 per cent oil solution clear with Pennsylvania oil.

^e Reacts with oil when heated to evaporate solvent.

^f Wax solution cloudy at high temperatures.

^g Solvent layer colored with both oils.

^h Pennsylvania oil completely miscible down to 14° C.

ⁱ 0.7 per cent wax at 4 degrees

^j Numbers in parentheses indicate temperatures in degrees Centigrade.

only a portion of the material which normally would be separated by dewaxing. Subsequent to its removal from the original wax distillate, the crude wax has been further separated and refined by the removal of lower melting waxes and by filtration. Probably if instead of commercial paraffin there had been used an unfractionated wax similar to the material which must be removed by a dewaxing process, the quantities of wax dissolved would have proved to be greater, possibly materially greater under certain conditions. One might expect a considerable increase at the higher temperatures and oil concentrations where the greatest solubilities are found. On the other hand, it is to be doubted that any appreciable difference would have been noted where negative solubilities were encountered. In such cases the oil itself has produced a wax of the type most easily dissolved by the solution, and the data can be considered as closely approximating those for conditions which actually would be met.

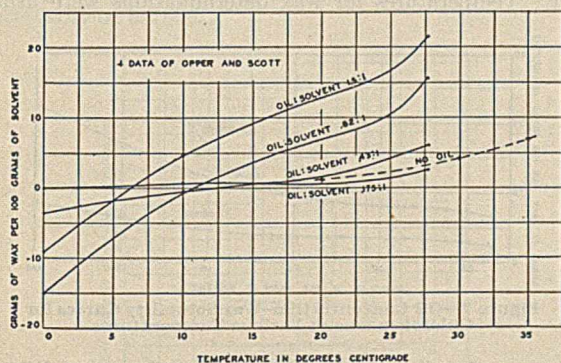


Figure 5—Temperature-Solubility Curves for Wax in Various Solutions of Oil and Butanol

Finally it is well to understand the limitations inherent in the procedure used to produce these data. Of such there seems to be one which, if proper care were not exercised, might be the source of serious inaccuracies. This is the matter of solvent evaporation. Although each test tube was tightly stoppered before being placed in the constant-temperature bath, it was not always possible to obtain good agreement of the three determinations. This trouble was

confined, without notable exceptions, to the higher temperatures and lower oil concentrations, from which it seems reasonable to deduce that the deviations were due to evaporation. In the accompanying plots, when an occasional high solubility determination was found, that particular value was neglected and the point on the plot located from two determinations only.

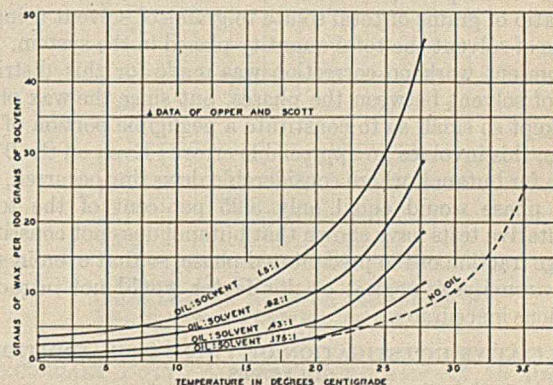


Figure 6—Temperature-Solubility Curves for Wax in Various Solutions of Oil and Butyl Acetate

In view of the nature of analysis to which the data were subjected and of the generally good coordination of values, it is believed that the data are reasonably accurate for the material used. The probable error is within 5 per cent of the wax dissolved, except at low solubilities, where a small absolute error develops a large error in percentage. In such cases the data probably are good to 0.20 gram of wax per 100 grams of solvent. This degree of precision should be sufficient for ordinary requirements and, considering certain of the limitations previously discussed, is probably better than application of these data would warrant.

As to the facts and tendencies shown by the plots themselves, little need be said. Figures 5 and 6 show how temperature affects the wax solubility, other factors being constant. Figures 7, 8, and 9 present the effect of oil on the solubility of wax, the 20–25° F. pour point oil being used as a reference point of zero concentration of wax. Figures

10, 11, and 12 are the most significant, indicating the extent of dewaxing which will occur as the quantity of dissolved material is varied.

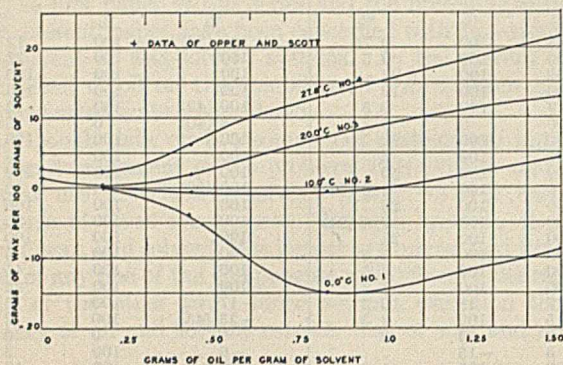


Figure 7—Oil Concentration-Wax Solubility Curves for Butanol at Various Temperatures

These plots clearly show that solution in a large quantity of solvent is by no means desirable, that the optimum composition for dewaxing may be one in which only a small proportion of solvent is used. It is also shown that this optimum point varies both with the nature of the solvent and the temperature of separation. In general, it seems that the higher the temperature the less should be the quantity of solvent used to obtain the best results, although the data by no means indicate that the higher temperatures are advantageous for wax separation.

In considering these curves it should be remembered that they are based, not on the solvent present in the whole system, but only on that present in what might be termed the "oil" phase. In many cases considerable solvent will also be held in the "wax" phase, so that it would be inexact to calculate the ratio of grams of total solute to grams of solvent using as grams of solvent the total quantity placed in the system. In the present work no correction was made for this distribution of solvent between the phases, but since the wax phase was kept so small as to constitute a negligible portion of the whole, this involves no appreciable error. Even on the 0° C. curve for butanol, where considerable dewaxing occurred, this solid phase would equal only 8.25 per cent of the total. Qualitative tests have shown that butanol does not constitute a large fraction of the precipitated phase, so that even in such an extreme case neglect of this factor would not introduce a serious inaccuracy.

QUALITATIVE INVESTIGATION OF TWENTY-SIX ADDITIONAL SOLVENTS

With W. C. Murray and R. M. Wilson

The results presented thus far have all been based on a group of twenty-eight solvents. Although there remained a considerable amount of data to be obtained on this group, it was deemed advisable to add certain new solvents to the list of those being studied, in some cases because of their having recently become available at prices consistent with their large-scale use, in some cases because of a desire to extend the range of chemical types of solvents being studied. The present section covers work on twenty-six solvents not included in former investigations.

Experimental Procedure

As with previous work, each solvent investigated was first subjected to approximate solubility determinations. Three solutes were considered—paraffin wax melting at 50° C., a light medium Pennsylvania oil, and a medium Coastal oil. The wax and Pennsylvania oil were the same as used in the previous sections. Chemically pure solvents were used.

The procedure in the case of the two oils was to place equal volumes of oil and solvent in a graduated cylinder, obtain the desired temperature, and then report as the "qualitative"

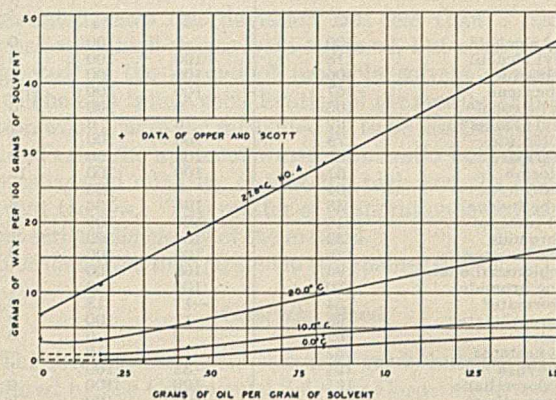


Figure 8—Oil Concentration-Wax Solubility Curves for Butyl Acetate at Various Temperatures

solubility of the oil the percentage decrease in the layer richer in oil. This method is exact only when there exists one type of solution, oil in solvent. Rarely, if ever, is such a circumstance encountered, although the solubility of oil in solvent usually seems greatly to exceed that of solvent in oil. Consequently, in this manner it is possible to indicate roughly the solution of oil in solvent.

It will be noted, by reference to Table I, that occasionally the oil layer increased (reported as negative solubilities). This means that the predominating solution is solvent in oil.

In the above manner determinations were made and recorded for both oils at three temperatures—about 10° C., about 21° C., and at some more elevated point. The last temperature was widely variant, being determined from a number of considerations: If the oils and solvents were not completely miscible at 21° C., the temperature of complete miscibility was usually chosen; if the oils were miscible at 21° C., the point was chosen somewhat above that at which the solubility of the wax began rapidly to increase; in case there was no point meeting one of the above requirements at moderate temperatures, determinations were made just below the boiling point, if that did not exceed 65° C.; they were made at 65° C. if the solvent boiled above that point. Temperatures for wax determinations were usually

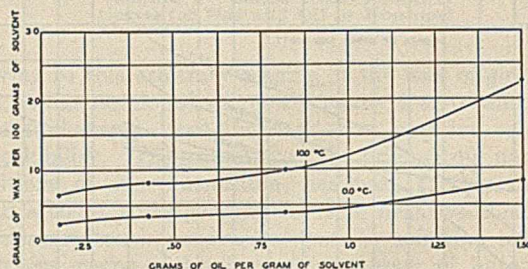


Figure 9—Oil Concentration-Wax Solubility Curves for Chlorobenzene at Various Temperatures

the same as for oils, but manipulation was somewhat different. A known quantity of warm solvent was placed in a test tube, and melted wax was added bit by bit from a 5-cc. graduate. The solution was then cooled to the desired temperature. If the solutions remained clear, wax was added until a slight cloud appeared. If the solution was cloudy after the first addition of wax, more solvent was added from a measuring buret and the quantity noted at the point where the cloud disappeared. The volume percentage of wax dissolved was then calculated from the data thus obtained.

The data from these determinations are shown in Table I.

Interpretation of Results

SECONDARY AMYL ALCOHOL, SECONDARY NORMAL AMYL ALCOHOL (DIETHYL CARBINOL), BUTYL FORMATE, ETHYL CARBONATE, ETHYL CHLOROCARBONATE, ETHYLENE BROMIDE, PARALDEHYDE—The qualitative data indicate that this group of solvents includes those most likely to be useful as dewaxing agents. Of these, a number possess certain properties which might restrict their usefulness. For instance, ethyl chlorocarbonate tends to react with the oil when the temperature is raised to remove the solvent. For commercial work this would probably constitute a serious drawback. On the other hand, its excellent selective qualities might make it very useful for certain types of analytical work.

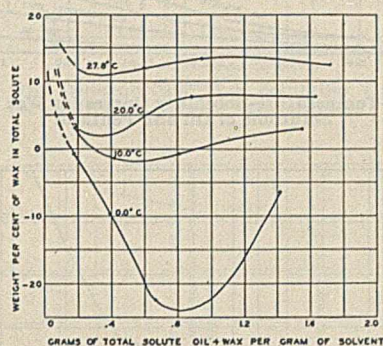


Figure 10—Effect of Hydrocarbon-Butanol Ratio on Percentage of Wax in Dewaxed Lubricating Oil

Certain others of this group might also prove to possess undesirably low volatilities. In fact, all except ethyl chlorocarbonate boil at a temperature above 105° C. Nevertheless, if these solvents do not tend to decompose up to the vaporization point of oil and wax, this problem could probably be solved. The greatest drawback would be the difficulty of removing the last traces from the separated wax or oil. Although the amount thus included might be insignificant from the viewpoint of solvent recovery, the presence of even traces in finished wax or lubricating oil would be dubiously permissible. Wax thus contaminated might prove most objectionable for domestic use. The oil might become less desirable from a number of angles. For example, resistance to emulsion and stability of color are two qualities which could conceivably be harmed.

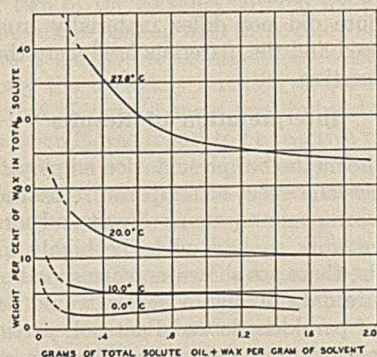


Figure 11—Effect of Hydrocarbon-Butyl Acetate Ratio on Percentage of Wax in Dewaxed Lubricating Oil

ISOAMYL ALCOHOL, ISOBUTYL ALCOHOL, CROTONALDEHYDE, ETHYL FORMATE, ETHYL PROPIONATE, METHYL ACETATE, PYRIDINE—These solvents constitute a group possessing solubility characteristics which would probably make its members of less general use than those already discussed. They are characterized by the low solubility of wax

and paraffin-base oil, but possess high miscibility with Coastal oil. Occasionally an oil coming roughly under the latter classification presents a dewaxing problem, although normally such a crude petroleum possessing the weaknesses of both paraffin-base and naphthene-base oils would not be used to produce lubricants. However, such cases do arise, a notable example being Mexican native lubricants, in which case manufacture from uneconomical sources is made possible by the protection afforded by a high import duty. Occasionally other factors, such as transportation difficulties, produce a similar result.

AMYL CHLORIDE, BROMOBENZENE, BUTYL CHLORIDE, CHLOROFORM, DICHLOROETHYLENE, ETHYL BROMIDE, PENTACHLOROETHANE, PETROLEUM ETHER, TETRACHLOROETHYLENE, TRICHLOROETHYLENE—This group also appears to have possibilities, but it is subject to temperature limitations. At the temperatures of experiment these solvents all dissolve undesirably large amounts of wax. If further investigations were made at lower temperatures, it would not be surprising to find that certain ones could effect excellent separations. However, low temperatures are not so convenient for operation as those of 20° C. or higher, and there seems to be no shortage of solvents which are selective at room temperature.

It will be noted that both oils are highly miscible with these solvents at the temperatures above 10° C. Wax solubilities at 10° C. vary from 3 to 31 grams per 100 grams of solvent. With the exceptions of chloroform and the two chlorinated ethylenes all dissolve wax to no greater extent than 6 parts per 100. While not so attractive as the first list, all with the three noted exceptions warrant further investigation.

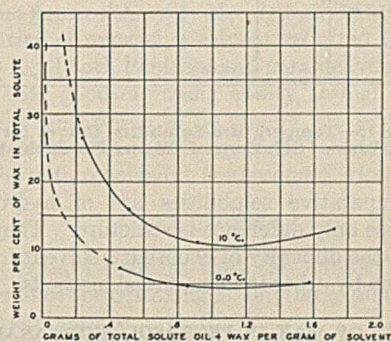


Figure 12—Effect of Hydrocarbon-Chlorobenzene Ratio on Percentage of Wax in Dewaxed Lubricating Oil

SECONDARY BUTYL ALCOHOL, FURFURAL—Of all the solvents covered in this work only the above two come into the category of no apparent value. Neither of these solvents appears to possess selective power to even a slight degree and further work with them would appear to be a waste of time.

An interesting fact, indicative of the need of testing each prospect separately, is shown by a study of these qualitative data. These data, with those published in the first paper, show how great an influence molecular structure has on the power of a solvent to form solutions with hydrocarbons. In four amyl alcohols and butyl alcohols at 10° C. the solubilities of various solutes were as follows:

SOLVENT	PENNA. OIL	TEXAS OIL	WAX	WATER ^a
<i>n</i> -Amyl alcohol	100	100	Slight	2.7 (220°)
Isoamyl alcohol	0	100	0.5	Slight (150°)
<i>sec</i> -Amyl alcohol	100	100	0.5	16.7 (150°)
Diethyl carbinol	100	100	0.2	
<i>n</i> -Butyl alcohol	30	100	Slight	8.3 (15°)
Isobutyl alcohol	0	100	0.5	9.5 (15°)
<i>sec</i> -Butyl alcohol	0	0	0.7	29 (20°)

^a Hodgman-Lange, Handbook of Chemistry and Physics, 14th ed., pp. 308 and 326.

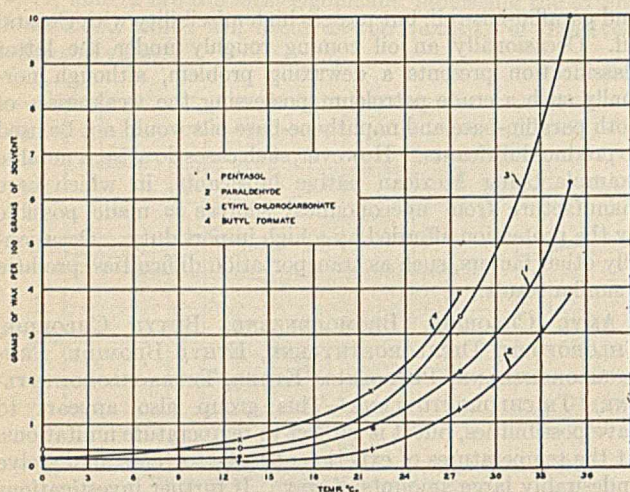


Figure 13—Temperature-Solubility Curves for Wax in Pentasol, Paraldehyde, Ethyl Chlorocarbonate, and Butyl Formate

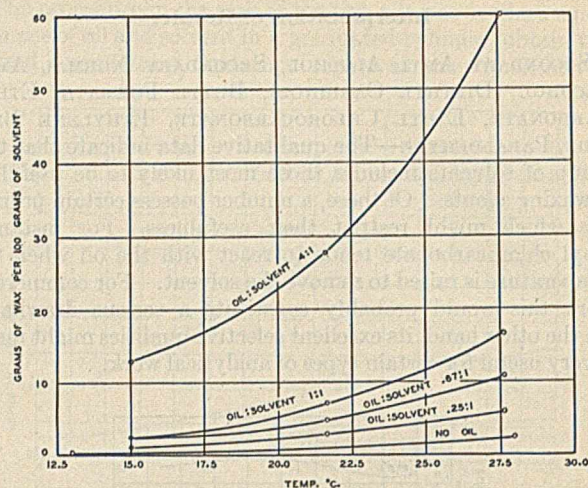


Figure 14—Temperature-Solubility Curves for Wax in Various Solutions of Oil and Pentasol

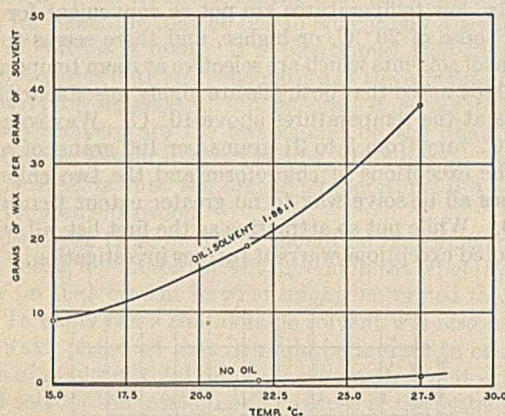


Figure 15—Temperature-Solubility Curves for Wax in Various Solutions of Oil and Paraldehyde

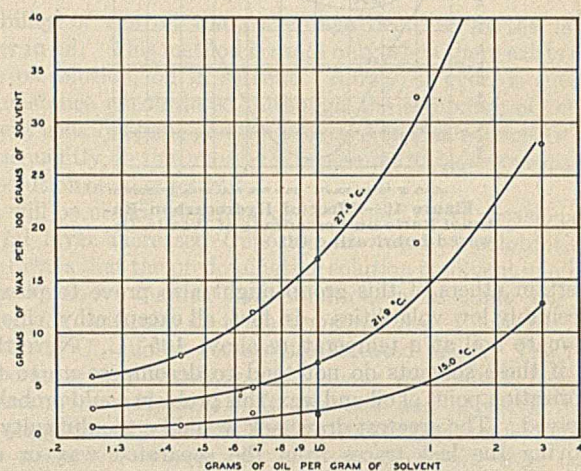


Figure 16—Oil Concentration-Wax Solubility Curves for Pentasol at Various Temperatures

These comparative solubilities are of hydrocarbons in solvents whose only difference is structure. They afford one indication of the difficulty of choosing a solvent for hydrocarbon separation by other than empirical methods.

SOLUBILITY OF WAX IN PENTASOL AND PARALDEHYDE

With W. C. Murray and R. M. Wilson

Four of the better prospects indicated by the preceding section were chosen for further study.

Of the solvents investigated qualitatively paraldehyde, ethyl chlorocarbonate, and butyl formate were selected, chemically pure material being used. The amyl alcohols as a group also seemed to merit study. It would have been desirable to study each of these five-carbon alcohols separately, but the time available was not sufficient to permit the continuation of the work on such a scale. It was therefore decided to consider a commercial mixture of five amyl alcohols which is marketed under the trade name of "Pentasol." This mixture, being easier to manufacture, is consequently cheaper and easier to obtain than any of its pure components. It should not be inferred, however, that its characteristics are representative of its various constituents. As was noted in the previous section, the isomeric five-carbon alcohols vary widely in their solvent powers, although a number do possess selective solvent power for oil over wax. Pentasol should be considered as a solvent possessing its own peculiar characteristics. Chemically it is a mixture of five compounds, and is described by the manufacturers as "a uniform mixture of pure amyl alcohols" as follows:

	%
$\text{CH}_3\text{CH}_2\text{CHOH}\text{CH}_2\text{CH}_3$	18
$\text{CH}_3\text{CHOH}\text{CH}_2\text{CH}_2\text{CH}_3$	8
$\text{CH}_2\text{OH}\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	32
$(\text{CH}_3)_2\text{CH}\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	16
$\text{CH}_2\text{OH}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	26

Experimental Procedure

The procedure did not differ materially from that previously discussed and the materials used were the same as in the preceding section.

Interpretation of Results

Following the method of presentation employed heretofore, Figure 13 shows the effect of temperature on the solubilities of wax in two component systems of wax and solvent. Since the qualitative work showed oil to be highly miscible with all the solvents, there are shown no corresponding curves for oil. To be sure data of such a nature would be interesting in the study of paraldehyde and Pentasol, particularly since at low oil concentrations the systems tend to separate into two phases. A knowledge of the composition of these phases would help one to finish those portions of the curves (in Figures 14 to 19) which fall in the region of low oil concentrations. In the case of paraldehyde and Pentasol the solvent-in-oil type seems to be that with which this investigation is interested. When oil concentrations became low the oil became saturated and the formation of another phase gave the mixture a cloudy appearance. This point is briefly discussed later.

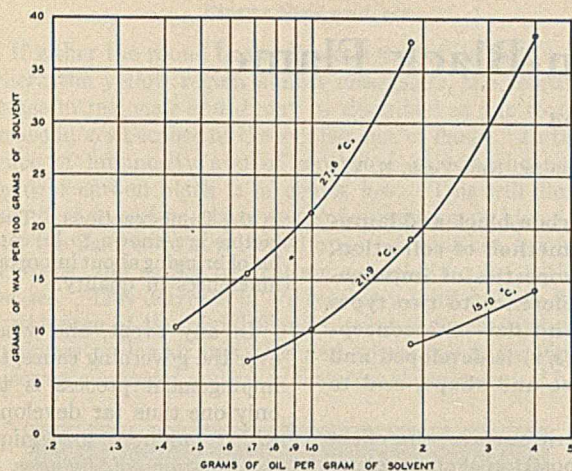


Figure 17—Oil Concentration-Wax Solubility Curves for Paraldehyde at Various Temperatures

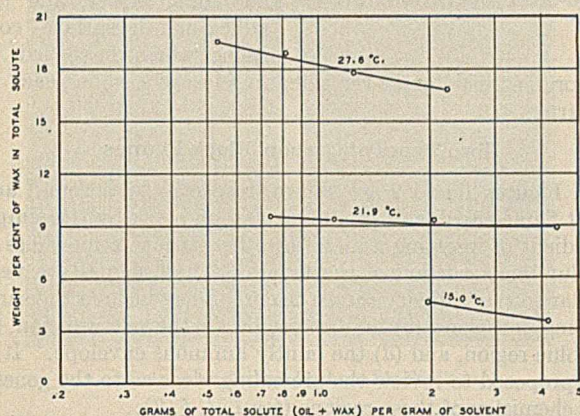


Figure 19—Effect of Hydrocarbon-Paraldehyde Ratio on Percentage of Wax in Dewaxed Lubricating Oil

As in previous work, three-component systems were next studied, determinations being made of wax solubilities in solutions of various oil-solvent ratios. These data are presented in Figures 14 to 19.

In general these curves are similar to the data discussed in the second section of this paper, although a few minor points should be noted.

First, only two of the solvents covered by Figure 13 are included in the curves dealing with three component systems. Butyl formate is absent for no other reason than failure to secure promptly the necessary quantity of solvent. On the other hand, ethyl chlorocarbonate was dropped from further consideration when it was found to be reactive with oil when heated to remove the solvent. However, this fact does not conclusively demonstrate that the solvent is useless for our purpose; it might possibly be separated under conditions which would not cause it to be reactive. That feature does, of course, make it less flexible of manipulation, and in view of the considerable number of good prospects it becomes correspondingly less worthy of attention.

With paraldehyde and Pentasol there is encountered the unusual type of miscibility previously mentioned. Apparently all hydrocarbons are but slightly soluble in these two solvents, but they both seem to be highly soluble in oils. Of the two, Pentasol is the more soluble. With temperatures as low as 15° C. and a Pentasol concentration as high as 4 parts per part of oil, no difficulty was encountered through two-phase formation. Data were collected, therefore, at 15°, 21.9°, and 27.6° C., using oil-solvent ratios varying from 0.25 to 4.0. At temperatures below 15° C. and oil-solvent

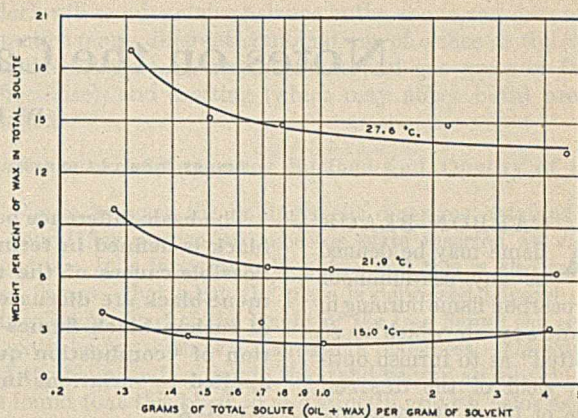


Figure 18—Effects of Hydrocarbon-Pentanol Ratio on Percentage of Wax in Dewaxed Lubricating Oil

ratios of less than 0.25 the formation of the other phase caused the solutions to become cloudy.

With paraldehyde the difficulties due to two-phase formation became more serious. Even at 27.6° C. no determinations could be made with oil-solvent ratios of less than 0.40. At 15° C. only two points could be determined. These facts do not eliminate paraldehyde as a dewaxing agent, however, since there is no trouble caused by the formation of two phases as long as the parts oil per part of solvent lie between values of 2 and 4.

As a matter of fact, since all the curves in Figure 19 slope downward to the right, it would seem desirable to work with low solvent concentrations. Furthermore, low solvent concentrations possess the very decided advantage of reducing the quantity of expensive solvent required to effect dewaxing. All in all both Pentasol and paraldehyde, possessing as they do fairly good dewaxing ability at high oil concentrations, might well prove to be among the best media for solvent separation. The accuracy of this work is about the same as for the data reported in the second section.

CONCLUSIONS

The reported data indicate that the number of solvents that might be used for dewaxing is very large and is made up of many divergent groups.

Analysis of the work thus far completed suggests that data of a different kind might profitably be secured. To the petroleum refiner the actual amount of wax left in an oil is of no interest or significance. The important point is the pour point of a finished oil. Consequently, it would be advisable to amplify the problem, using a hydrocarbon distillate containing its original wax. This distillate would be dissolved in the different solvents in varying oil-solvent ratios and the wax precipitated by cooling to the desired temperatures. Pour points of the oils thus dewaxed would be determined and curves drawn which would be analogous to those in Figures 18 and 19. Pour points would be used as ordinates in place of the present quantity or percentage values. To the average petroleum refiner such data would possess a definite practical significance.

Correction

In the "Chemical Kaleidoscope for 1930" published in the January, 1931, issue of *INDUSTRIAL AND ENGINEERING CHEMISTRY*, the credit for the isolation of the female sex hormone was given to A. Butenandt, of Göttingen. While Doctor Butenandt's work was in progress at the same time as that of E. A. Doisy, of the St. Louis University School of Medicine, it now appears that the latter was the first both to isolate the hormone and to report his findings.

Notes on the Carbon-Black Flame¹

W. B. Wiegand

BINNEY & SMITH COMPANY, 41 EAST 42ND ST., NEW YORK, N. Y.

A CARBON-BLACK flame may be defined as any self-luminous hydrocarbon flame burning in secondary air which is so "drafted" as to furnish optimum yield of the desired grade of black, it being understood that the black is caught by impingement upon a surface placed within the flame. From this same flame there may be produced the totally different pigment known as lampblack, provided only that the drafting be altered to induce the formation of free soot. This soot, collected (by whatever means) extraneously to the flame, constitutes lampblack, in one or other of its many forms.

With this distinction in mind it is readily understood why carbon black may be obtained from the flame of burning tar oils, even though not economically, and why lampblack may be and is made from the flame of burning natural gas. Hence also the synonyms "impingement black" and "channel black" for carbon black, the name "gas black" being less suitable because ambiguous.

The carbon-black flame is susceptible of almost infinite variations depending on the composition of the gas, the structure of the flame, the arrangement and motion of the collecting surface, size and shape of burning house, drafting, etc. Many of these factors, and by no means the least important ones, are exceedingly difficult to duplicate on a laboratory scale, a circumstance which has greatly impeded the systematic study of the various relationships. The present discussion will be restricted to some of the salient characteristics of the flame itself, as affecting the carbon black formed therefrom.

The question naturally arises, "Why does the collection, by impingement upon a surface within the flame, of the luminous carbon particles produce a black generically different from that which results when the flame is caused to smoke and the free soot collected?" No complete answer to this important question seems to have been offered. The following possible factors are put forward as merely suggestive:

Early Fixation. By quick removal of the carbon particles from the flame there tends to be less opportunity for growth or accretion, thus resulting in finer particle size.

Electrical Repulsion. The luminous carbon particles emit electrons, and as a result are positively charged (δ). This will tend to keep them apart up to the point of collection.

Gaseous Adsorption. The luminous particles of carbon are in an active condition due to the heat released by their own combustion, as also to that developed in the regions of gaseous combustion. They are bathed in carbon monoxide, carbon dioxide, hydrogen, nitrogen, as well as some oxygen (δ). As a result they carry with them, to the collecting plate or channel, an adsorbed layer of gases which is known profoundly to affect their properties. These conditions are totally different in the case of free soot.

Post-Impingement Conditions. Many layers of carbon are deposited on the channel in succession. They are thus exposed to continued high temperatures and to the various gases present

The basic difference between carbon black and lamp-black is defined in terms of the method of collection. Possible causes of the unique properties of impingement black are discussed. By reference to two types of carbon-black flames—round and flat—the conception of "combustion quotient" (s/v) is developed and applied to variations in flame size and shape, and to drafting.

The position of the impingement surface, the effect of flame, shape of gas flow, and of position of channel are briefly discussed in relation to the quality and quantity of black obtained.

Factors of importance in large-scale operations are mentioned.

in the flame reactions. These factors are known to be capable of bringing about important differences in quality.

In any event, and whatever the governing cause, the impingement process is the only one thus far developed which produces the unique combination of fineness of subdivision, brilliance and intensity of color, tinctorial and hiding power, and the "adhesion" or surface conditions which have led to

the present wide and ever extending use of carbon black in the arts.

Two Types of Carbon-Black Flames

In Figures 1 and 2 are shown, respectively, a round and a flat flame capable of producing carbon black by the simple expedient of inserting a metal or other surface somewhere in the luminous portion of the flames. These flames are very similar to the ordinary candle flame. They include the same four major regions, (a) the dark region, (b) the yellow region, (c) the blue region, and (d) the faintly luminous envelope. It is not proposed to review the prevailing ideas as to the genesis and chemistry of these regions (see 1, 4, 5, 7).

On examining more closely these two types of flame, it is seen that their essential difference is that in the latter case the flame is flattened out with consequent increase in surface area. This shape was developed in the days of gas illumination where the flat flame was found brighter, cleaner, and steadier, and thus proved a more satisfactory illuminant (β).

It will be useful to express the ratio of flame surface to flame volume by the quotient s/v . More broadly, s may be defined as the total combustion surface or approximately the sum of regions c and d ($v. s.$). By v will be understood the volume of gas contained within s . The expression s/v has been found convenient in the study of carbon-black flames, but having thus far not been worked out in mathematical detail it will at this time be employed solely in a qualitative sense.

The flat flame² clearly exhibits a greater s/v than the round flame. However, the flat flame is not uniformly flat. At both edges it swells, forming wings which approach a circle in cross section. This thickening has been ascribed to an overlapping effect (β). For this reason the s/v is not uniform at all points in the flat flame, being greater between than at the wings.³ This inequality may, however, largely disappear in the case of multiple flames in close proximity under the channel, as in the case of a carbon-black-burning house, and by control of drafting ($v. i.$)

In any case the round flame shows in general a lower and more uniform s/v .

² The type of flat flame here described is often called the "batwing." The "fishtail" variety of flat flame is really totally distinct in structure. The former issues from a narrow slot; the latter results from the impingement of two cylindrical jets.

³ In general the smaller the radius of curvature of similar bodies the greater s/v . In this case the central region of the flat flame is much thinner, so that s/v is greater despite the longer radius.

¹ Received September 20, 1930. Presented before the Division of Rubber Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Flame Size and s/v

If either the round or flat flame is turned down to a point where the yellow region almost disappears, the relative increase in regions c and d may be described as due to the increase in s/v because of the smaller size of flame. In the absence of luminosity and of separated carbon the possible yield of carbon black is of course low. This will illustrate the effect on carbon-black yields of an excessively high s/v .

If the flames are now turned up, s/v diminishes, luminosity develops, and so the free carbon available for deposition increases. This decrease in s/v reaches a limit in both flames. In the case of the round flame a point is reached where the thickness no longer increases and where the flame virtually becomes a cylinder and s/v is therefore independent of height.

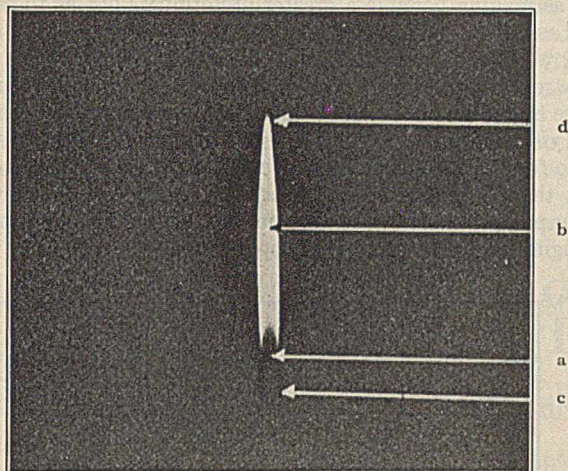


Figure 1—Round Carbon-Black Flame

In the case of the flat flame s/v also will reach a more or less constant value for the reason that increased flow of gas causes the flame to spread out laterally as well as vertically and without sensibly changing in thickness. We are thus virtually dealing with an increase in the size of a lamella of constant thickness—likewise a condition where the ratio of surface to volume remains constant.⁴

Thus with any given burner tip an increase in the size of flame can effect only a limited decrease in s/v . Further control of combustion is therefore dependent on the following:

Drafting

If a candle is allowed to burn itself out in a closed vessel, it will be seen that the flame increases in size before suffocation ensues. All flames tend to become larger the greater the volume of the gases required to complete combustion (4). Thus, one effect of drafting or limiting the supply of air may be to alter s/v through a change in the size of the flame. This applies to both the round and flat types.

It is also probable that the effect of "smothering" is to decrease the thickness of the combustion sheath or envelope so that the heating effect, and therefore the cracking effect, on the hydrocarbon gases within the flame is altered by the drafting. Since it is generally agreed that the presence of carbon particles in a luminous hydrocarbon flame is due to the thermal cracking of the gas, it is natural to expect that the quality and the yield of carbon black obtained from any given gas will depend upon the temperature and upon the combustion losses, and this in turn upon the size and shape of the flame and the drafting conditions.

The best flame for any given quality or grade of carbon

black will require a nice balance in the above variables and in practice many different combinations of orifice or tip (which regulates shape), channel distance and gas pressure (which affect size), and drafting (which may affect both) are employed.

Position of Impingement Surface and Quality of Black

Figure 3 shows the impingement diagrams obtained with a round flame upon an asbestos plate inserted at various heights. It is interesting to note—and this is also true for flat flames—that when the plate is depressed beyond about 50 to 60 per cent of the height of the free flame⁵ the central deposit begins to show a decrease in blackness. On scraping off the black and testing in the usual way in an oil vehicle, it is found that this black is of distinctly grayish color as compared with the deposit at the periphery. The decrease in color is also accompanied by decreased adsorptive activity. The explanation for these differences is not entirely clear. It seems, however, to be due to the lower temperature and decreased supply of oxygen.

Effect of Flame Shape on Quality of Black

The carbon black obtained from a round flame is different from that obtained from a flat flame, being in general characterized by a grayer color, lower oil absorption, increased "flow" characteristics, lower adsorptive activity, easier miscibility in rubber, but diminished reinforcing effects in rubber compounds. For example, when mixed to the extent of about 40 per cent on the rubber in a test mixing accelerated with diphenylguanidine the tensile strength at equivalent cure was 3800 pounds per square inch (266 kg. per sq. cm.) as compared with 4700 pounds per square inch (330 kg. per sq. cm.), and the elongation 580 per cent as compared with 630 per cent. The yield was also below the normal value for the flat flame.

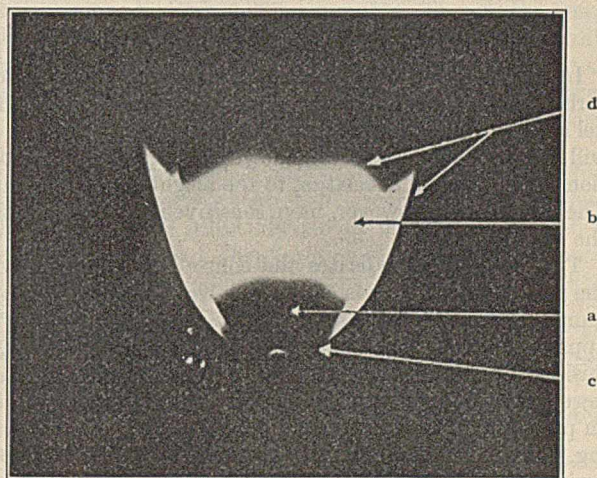


Figure 2—Flat Carbon-Black Flame

Factors Controlling Yield

The results summarized in Figures 4 and 5 were obtained in a laboratory set-up in which a short length of standard channel iron was mounted in a rebuilt fume cupboard. No attempt at smothering was made for these tests, it having been found practically impossible to obtain duplicate figures owing to variability in draft. The yield figures are therefore subject to a correction and so are not strictly comparable with field conditions. In the case of the round flames six

⁵ At about 30 per cent of height of free flame the deposit becomes very small in amount and for the most part gray.

⁴ These considerations do not apply when either the round or the flat flame is increased to the point of turbulence.

0.25-inch (6.3-mm.) round brass tips were employed with 2-inch (5-cm.) spacing. In the case of slotted tips three of 0.034-inch (0.86-mm.) opening were used spaced at 4 inches (10 cm.) In all cases the channel was scraped every 2 minutes. For convenience the gas used for these experiments was city gas of the following composition:

	%
Hydrogen.....	36.0
Carbon monoxide.....	26.4
Methane.....	16.4
Nitrogen.....	9.4
Illuminants.....	7.2
Carbon dioxide.....	3.8
Oxygen.....	0.8

The later substitution of methane made no essential change in the relationships.

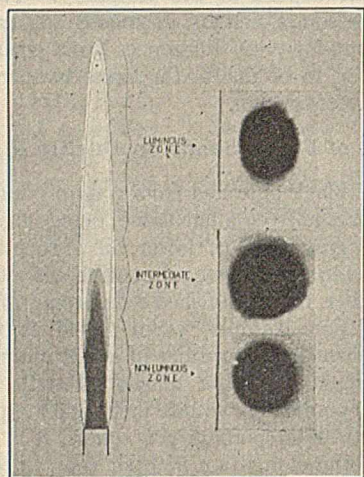


Figure 3—Impingement Diagrams Obtained with Round Flame

Yield vs. Channel Height

In Figure 4 are shown the comparative curves for yield of carbon black in the case of round and slotted tips as the channel height is varied but the rate of gas flow kept constant. It will be seen that in both cases the yield is sensitive to the position of the channel in relation to the height of the free flame. The flat flame is, however, more sensitive in this respect than the round.

The dotted line indicates the course of the curves when the flow of gas was adjusted, at each channel setting, to optimum yield. The marked upward extension of the curves, apparently indicating higher yields, must not, however, be misinterpreted. It might, from this, be supposed that a lower channel height would constitute a marked improvement. In practice this is not the case, because of the effect of drafting, which, as mentioned above, was not included in these experiments.⁶ It must be repeated that these curves do not represent conditions in actual large-scale operations; they are to be regarded only as a guide to certain general relationships.

Yield vs. Flow at Fixed Channel Height

In Figure 5 which shows the relation between flow of gas and yield of carbon black when channel height is fixed, there will be noted a striking difference between the behavior of the round flame and that of the flat flame. The former is

⁶ Drafting or smothering may be made to control the height of a flame issuing at given pressure from a given orifice. Thus an increase in smothering may induce the same increase in yield that would otherwise require a closer channel.

exceedingly sensitive to slight changes in flow, whereas the latter is relatively unaffected. This may be ascribed to the effect of gas pressure or flow on the heights of the free flames in the two cases. With the round burner tip increased flow results in increased height of free flame. In the case of the slotted burner tip, on the other hand, the flame expands laterally as much as, or even more than, it does vertically, so that in this case the position of the channel relative to the height of the free flame is influenced very little by alterations in pressure.

The practical significance of this difference between the two tips is obvious. In practice, on the large scale, it is difficult to keep the gas pressure absolutely uniform at all times and in all regions of a carbon-black-burning house. The slotted tip has therefore the advantage over the round tip as making possible a greater uniformity both as to yield and as to quality of product.

A word of explanation should be made with regard to the apparently higher maximum yield figures for the round flame. Here again the absence of smothering has adversely affected the yields from the slotted tip. It is probable that the s/v ratio for the round flame when undrafted is more nearly correct than that for the flat flame. The latter can, however, be improved as desired by careful control of smothering, thus bringing its s/v down to the proper value.

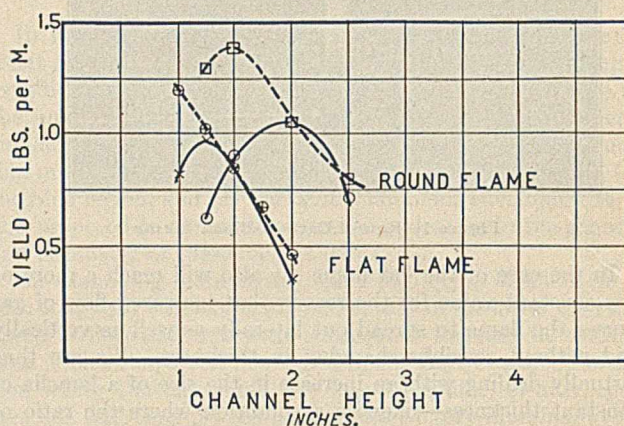


Figure 4—Yield vs. Channel Height at Constant Gas Flow

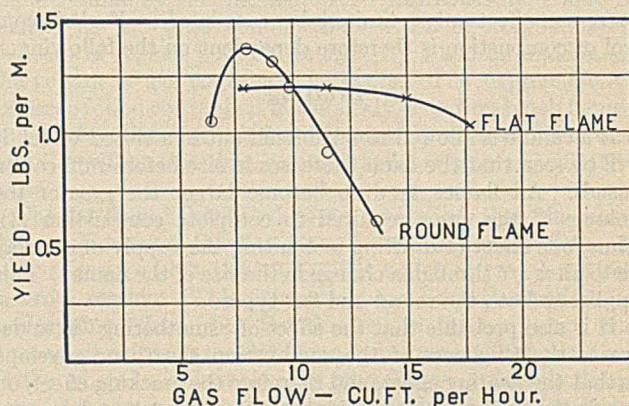


Figure 5—Yield vs. Gas Flow at Fixed Channel Height

Large-Scale Factors

In addition to the important matter of flame structure there are of course other elements affecting quality and yield of carbon black. The size and shape of the burning house; total combustion of gas in relation to the size of house and in relation to the area of channel exposed; the spacing, width, and speed of channels; spacing, angle, and accuracy of orifice of the tips are factors of importance requiring proper adjust-

ment in relation to the quality of carbon black being made. Most of these factors can be determined only through large-scale experimentation.

The prime importance of channel height and rate of gas flow may be deduced from the experimental data already given. Finally there is the question of proper draft control which, as well as being of prime importance, is also most delicate and elusive. Many attempts have been made to regulate the draft by means of continuous analysis of the flue gases which escape through the top of the house. This method is found more cumbersome, as well as less sensitive, than the method of drafting based upon what is called the "smoke blanket" of a burning house. This is a pall or cloud of smoke consisting, not of carbon black, but of sooty material which hangs at about the general level of the channels and which rises or falls in a remarkably sensitive manner as the influx of air is varied. In addition to the "smoke blanket" the degree of luminosity of the flames (described as the "lightness" or "darkness" of the house) serves as an additional optical guide to the state of drafting.

With any given set of conditions as to house construction, arrangement of flames, and channels, and with continuous

control of the quality of black produced, the operative in charge of the plant is able to determine by the hourly output of carbon black the exact drafting conditions that will yield the best results. Proper adjustments are necessary as between winter and summer and as between night and day.

Thus there rests a heavy load of responsibility on "Those Slaves of Fire who, morn and even," and in a climate already semi-tropical, tend the ten million flames which yield the carbon black of commerce.

Acknowledgment

It is desired gratefully to acknowledge the important assistance rendered by J. W. Snyder and H. A. Braendle.

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Action of Alkali Hydroxides on Elementary Sulfur and Mercaptans Dissolved in Naphtha¹

V. Vesselovsky² and V. Kalichevsky³

THIS investigation represents a qualitative and quantitative study of the effect of potassium and sodium hydroxides in various solvents on solutions of elementary sulfur and mercaptans in naphtha. The study of these reactions was undertaken with the purpose of determining the possibility of their utilization for sweetening and corrosion treatment of light petroleum distillates.

Previous investigators working along similar lines reported that anhydrous potassium hydroxide reacts with elementary sulfur and mercaptans in gasoline (8). Potassium carbonate in alcoholic solution likewise reacts with sulfur, while in water the same reaction proceeds at a much slower rate (3, 4). Partial removal of mercaptans by aqueous alkali hydroxides has been also investigated (2). These publications present interesting possibilities for studying similar reactions in a variety of solvents and stimulated the present research.

Materials

Sulfur purified by recrystallization from benzene.

Ethyl, *n*-butyl, and *n*-heptyl mercaptans (Eastman Kodak Company reagents).

Solvent naphtha of the following characteristics:

Color.....	20 Saybolt
Acidity.....	None
Sulfur.....	0.024 per cent by weight
Specific gravity.....	0.7887 at 60° F. (15.6° C.)
Engler distillation:	
Initial boiling point.....	311° F. (155° C.)
55 per cent off at.....	350° F. (176.7° C.)
End point.....	406° F. (207.8° C.)
Saybolt thermal viscosity.....	230
Copper strip test at 122° F. (50° C.).....	Negative
Doctor test.....	Negative

Anhydrous potassium and sodium hydroxides (C. P.).

Absolute ether, absolute ethyl and isopropyl alcohols.

¹ Received October 13, 1930.

² Senior student in Chemical Engineering, New York University, New York, N. Y.

³ 616 Livingston Road, Elizabeth, N. J.

Commercial 91 and 98 per cent isopropyl alcohols containing some butyl and amyl alcohols.

Analytical Methods

DETERMINATION OF SULFUR—Lamp method (check determinations agreed within 0.005 per cent). Though the lamp method for determining elementary sulfur in the oil usually gives low results, for purely comparative purposes observations made by this method should prove wholly satisfactory. For this reason the lamp method was used in favor of a more tedious analytical procedure.

QUALITATIVE TEST FOR ELEMENTARY SULFUR—Five cubic centimeters of the sample were shaken with 1 cc. of 1 per cent naphtha solution of ethyl mercaptan in the presence of 5 cc. of doctor solution. Discoloration indicated the presence of elementary sulfur. The method permits detection of less than 0.0025 mg. of sulfur per cubic centimeter of naphtha solution, while the standard copper-strip corrosion test at 122° F. (50° C.) fails to discover less than 0.005 mg. of sulfur per 1 cc.

QUALITATIVE TEST FOR MERCAPTANS—Standard doctor test.

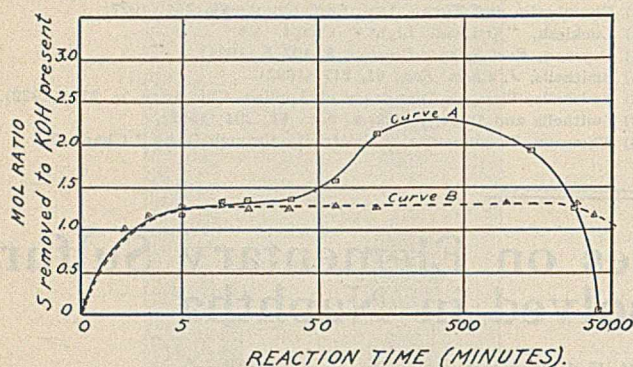
Reactions of Elementary Sulfur

On mixing at room temperature a 0.227–0.315 per cent solution of elementary sulfur in naphtha with varying quantities of potassium and sodium hydroxide solutions or suspensions in various solvents, the following observations were made:

On addition of the reagents to the naphtha solutions the oil develops an orange-yellow color and becomes turbid owing to separation of some minute particles of a white substance. A golden-yellow precipitate collects at the bottom of the reaction vessel, but the oil remains turbid. On further standing the precipitate acquires a dark yellow-brown coloration and the white substance which is responsible for the turbidity of the oil precipitates out. On washing with

water the naphtha regains its original color and the turbidity disappears while the water acquires a yellow coloration.

When potassium hydroxide solutions in absolute ethyl and isopropyl alcohols, absolute ether, and 91-98 per cent commercial isopropyl alcohol are used, the reaction proceeds almost instantaneously. The use of absolute alcohols as solvents for the potassium hydroxide results in the formation of solid, partially crystalline, red-brown precipitates, while the use of impure alcohols yields a heavy, dark-red liquid. The absolute-ether solution gives a very characteristic flocculent deep yellow precipitate. The saturated solution of potassium hydroxide in water also reacts with sulfur but at an extremely slow rate, and after several days of contact a considerable quantity of sulfur is still left in the naphtha. Solutions of sodium hydroxide in the same solvents react similarly but at a slower rate.

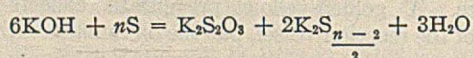


Small quantities of potassium hydroxide in the alcoholic or ether solutions are sufficient for the complete removal of sulfur, as shown by the following experiments: On adding 6 cc. of a 21.82 per cent solution of potassium hydroxide in ethyl alcohol to 200 cc. of a 0.227 per cent solution of elementary sulfur in naphtha, the sulfur was completely removed. This fact was ascertained by the negative copper-strip corrosion and ethyl mercaptan tests. However, on adding 4 cc. of the same potassium hydroxide solution to 200 cc. of the above sulfur solution, a very small quantity of sulfur remained in the oil, as indicated by the positive ethyl mercaptan test but negative copper-strip corrosion test.

The mechanism of the reaction was investigated with the solution of potassium hydroxide in absolute ethyl alcohol. The naphtha solution of elementary sulfur was treated with deficient quantities of alcoholic potassium hydroxide solution in order to effect only a partial removal of sulfur. Samples of treated oil were withdrawn from the main body of the reacting mixture at various intervals, thoroughly washed with water, filtered, and analyzed for their sulfur content. Two sets of experiments were made which differed only by the degree of agitating the oil with the reagent. The experimental data are presented in Table I, and shown graphically in the accompanying diagram.

The water washings were collected and evaporated to dryness. Potassium thiosulfate was identified in the residue by qualitative tests with hydrochloric acid, ferric chloride, and silver nitrate. The solid precipitate deposited in the reaction vessel showed the presence of polysulfides of potassium, as on acidifying its water solution hydrogen sulfide was evolved and free sulfur precipitated out.

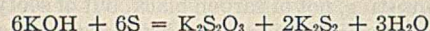
On the basis of these tests the reaction was assumed to proceed according to the following general equation:



This equation, however, does not express the intermediate stages of the reaction. The curves portrayed in the diagram

show that the removal of sulfur from the naphtha solution proceeds in steps. The reaction goes at a very rapid rate until the mol ratio of sulfur removed to potassium hydroxide present reaches approximately 1.3, which corresponds to the formation of potassium trisulfide. The presence of fairly large quantities of this substance at this stage of the reaction is further substantiated by the golden-yellow color of the precipitate formed.

Potassium trisulfide is, however, not the primary product of the reaction. The experimental data show that after the first 2 minutes the mol ratio of sulfur removed to potassium hydroxide present corresponds to the formation of potassium disulfide according to the equation:



Previous investigations on formation of polysulfides of alkali metals in the presence of an excess of free sulfur show that formation of polysulfides is always preceded by the formation of a monosulfide of the metal (7). For these reasons the primary products of the reaction under investigation must be potassium thiosulfate, potassium monosulfide, and water, the higher polysulfides being formed by the secondary reactions of straight addition of sulfur to the lower polysulfides.

Table I—Effect of Time in Treating a Solution of Elementary Sulfur in Naphtha with a Deficient Quantity of Potassium Hydroxide Dissolved in Absolute Ethyl Alcohol

KOH IN NAPHTHA Grams/liter	SULFUR IN NAPHTHA Grams/liter	TIME OF CONTACT Minutes	SULFUR IN SOLUTION %	MOL-RATIO OF SULFUR REMOVED TO KOH ADDED
One-minute agitation at beginning of treat followed by moderate occasional shaking of reacting mixture				
1.240	1.779	0	0.251	
		5	0.145	1.18
		10	0.133	1.32
		15	0.132	1.33
		30	0.130	1.35
		60	0.112	1.55
		120	0.062	2.11
		1440	0.080	1.91
		2880	0.138	1.26
One-minute agitation at beginning of treat only				
1.532	1.975	0	0.339	
		2	0.199	1.00
		3	0.176	1.17
		5	0.161	1.29
		10	0.161	1.29
		15	0.166	1.24
		30	0.167	1.23
		60	0.165	1.25
		129	0.166	1.24
		930	0.157	1.30
		2880	0.165	1.25
5900	0.179	1.14		

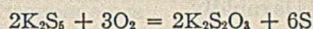
The experimental data further show that as soon as potassium trisulfide is formed the mol ratio of sulfur removed to potassium hydroxide present remains constant for a certain length of time and, if the mixture is not agitated, no higher polysulfides of potassium are obtained. These results are also in agreement with the chemical properties of potassium trisulfide, which is known to be a stable compound (5). On shaking, however, potassium trisulfide is kept in suspension in naphtha and absorbs additional quantities of sulfur to form still higher polysulfides, with the ultimate formation of potassium pentasulfide and possibly also of potassium hexasulfide. Formation of potassium pentasulfide is substantiated, not only by the increase in the ratio of sulfur removed to potassium hydroxide present, but also by the change in the color of the precipitate from golden-yellow to dark yellow-brown and by the hygroscopic properties of this precipitate, which easily deposits well-defined crystals of elementary sulfur on exposure to the air.

The experiments further show that after the removal of sulfur reaches its maximum the sulfur content of the naphtha begins to increase. This is distinctly demonstrated in both

sets of the experimental data, but is more pronounced when the reacting mixture is agitated. The solutions which showed such an increase were shaken with metallic mercury to remove all the elementary sulfur and then analyzed for their sulfur content. All the sulfur was found to be removed, thus indicating that sulfur is thrown back in the naphtha in its elementary form.

Experiments were made with the purpose of investigating this phenomenon in greater detail. Potassium hydroxide solutions in absolute ether, absolute isopropyl, and 91 per cent isopropyl alcohol were added to the solution of elementary sulfur in naphtha. The amount of potassium hydroxide used was sufficient to effect a complete removal of sulfur, and the ratio of potassium hydroxide added to the sulfur present was the same in all samples. These samples were examined at regular intervals by the ethyl mercaptan test to detect when the elementary sulfur reappeared in naphtha. It was found that the sulfur first reappeared in the sample treated with the solution of potassium hydroxide in absolute ether and then in the sample treated with the solution of potassium hydroxide in absolute isopropyl alcohol. The sample treated with the potassium hydroxide solution in 91 per cent isopropyl alcohol remained free of elementary sulfur for a very considerable length of time. As absolute ether is a good oxygen carrier and as the experiments were made in the presence of air, it was assumed that the observed phenomenon was due to the oxidation of the reaction products.

Potassium polysulfides are known to liberate sulfur according to the typical equation (6):



Potassium thiosulfate is also liberating sulfur on oxidation:



If these reactions actually take place in treating solutions of elementary sulfur in naphtha with potassium hydroxide dissolved in various solvents, the observed phenomenon should not occur in the absence of air. Experiments were therefore made in a neutral atmosphere by displacing the air within the reaction vessel by nitrogen. It was found that under these conditions sulfur was not liberated. These observations showed conclusively that oxidation of the reaction products with the oxygen of the air is responsible for the reappearance of the elementary sulfur in naphtha and that the presence of an oxygen carrier such as alcohol or especially ether greatly promotes the oxidation process.

Reaction of Mercaptans

On adding potassium or sodium hydroxide solutions in absolute alcohols² to naphtha solutions of ethyl, *n*-butyl, and *n*-heptyl mercaptans, a heavy, dark brown liquid separated at the bottom of the reaction vessel. After this treatment the naphtha solution of the mercaptans was sweet to the doctor test. The time required for the reaction to go to completion varied with the nature of the reagent used. Sodium hydroxide solutions sweetened the oil almost instantaneously, whereas potassium hydroxide solutions required a certain length of time before the same results are accomplished. Similar tests showed that anhydrous sodium hydroxide also removes the mercaptans quantitatively, while anhydrous potassium hydroxide is considerably less active.

² The presence of 1 to 2 per cent of water in alcohols is permissible as this small quantity of water is insufficient to hydrolyze the mercaptides to mercaptans to the extent which can be detected by the doctor or ethyl mercaptan tests.

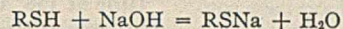
The mechanism of the reaction was investigated by adding to the naphtha solution of *n*-butyl mercaptan deficient quantities of alcoholic sodium hydroxide in order to effect only a partial removal of mercaptan. The experimental data are presented in Table II.

Table II—Removal of *n*-Butyl Mercaptan from Its Solution in Naphtha by Sodium Hydroxide Dissolved in Absolute Ethyl Alcohol

NaOH ADDED TO 50 CC. OF MERCAPTAN SOLN. ^a	SULFUR IN SOLN. %	MOL RATIO OF MERCAPTAN REMOVED TO NaOH ADDED
0	1.580	
3	0.906	0.98
6	0.218	0.99

^a 0.1128 gram NaOH per 1 cc. of solution.

These results show that the mol ratio of mercaptan removed to sodium hydroxide added is, within the limits of the experimental error, very close to unity. It was therefore assumed that the product of the reaction is sodium mercaptide, which is formed according to the general equation:



This assumption was tested for its validity by acidifying the sludge formed in the reaction with dilute hydrochloric acid. The separated oil was sour, thus indicating the reappearance of the mercaptan and the correctness of the assumed mechanism of the reaction.

In the course of the investigation it was observed that on leaving the treated solution in contact with the sludge the sulfur content of the naphtha shows a gradual increase and the sweetened oil again becomes positive to the doctor test. A sample of the solution of *n*-butyl mercaptan in naphtha with an initial sulfur content of 0.435 per cent was treated with a deficient amount of alcoholic sodium hydroxide and showed 0.255 per cent sulfur after 5 days' standing. On the eleventh day, however, the sulfur content of the same oil increased to 0.308 per cent. Another sample of the mercaptan solution was completely sweetened with the alcoholic sodium hydroxide, but after 4 days' standing it was positive to the doctor test. On adding water to the sweetened oil in the presence of the sludge, a similar effect was observed, but only in a much shorter time. These tests show that the increase in the sulfur content of the oil is undoubtedly due to at least a partial hydrolysis of the sodium mercaptide originally formed.

Conclusions

1—Potassium and sodium hydroxides in the anhydrous state or in solutions or suspensions in various organic solvents remove quantitatively sulfur and mercaptans from petroleum oil. Sodium hydroxide is particularly well adapted for the removal of mercaptans, and potassium hydroxide for the removal of elementary sulfur.

2—The products of the reaction between potassium hydroxide in alcoholic solution and elementary sulfur dissolved in naphtha are potassium thiosulfate, potassium mono- or polysulfides, and water. Higher polysulfides are formed by direct addition of sulfur to the lower sulfides. Potassium trisulfide is the highest polysulfide formed if the reacting mixture is not agitated. If, however, the reagent is kept in intimate contact with the sulfur solution potassium, penta- and possibly hexasulfides are found among the final products of the reaction. On keeping the precipitated substances in contact with naphtha for a considerable length of time, some of the sulfur is returned to the oil in its elementary form. This is shown to be due to the effect of the dissolved air.

which oxidizes the polysulfides and the thiosulfate with the liberation of free sulfur.

3—The products of the reaction between sodium hydroxide in alcoholic solution and mercaptans dissolved in naphtha are sodium mercaptide and water. On keeping the precipitate in contact with naphtha some of the mercaptans are returned to the oil owing to partial hydrolysis of the sodium mercaptide.

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Effect of Mild Heat Treatments on the Chemical Composition of Wood¹

L. F. Hawley and Jan Wiertelak²

FOREST PRODUCTS LABORATORY, MADISON, WIS.

THE many studies of the decomposition of wood by heat have been concerned almost entirely with the exothermic reaction occurring at about 275° C. during which the main chemical constituents of the wood are completely decomposed. It has been noted that much lower temperatures affect the color and strength of wood and that these physical changes were probably accompanied by chemical changes, but at the time the analyses reported here were undertaken there were no quantitative data on the subject.³

Experimental Procedure

Samples of white ash and Sitka spruce that had been subjected to different temperatures for various periods of time were available together with well-matched specimens of unheated wood for comparison. For the present work those samples were selected that had been heated to 138° C. for 2, 4, and 8 days. The details of the heat treatments can be found in the articles describing the effect of the treatment on various physical properties of the wood (4, 5). The wood was heated in sealed iron tubes contained in a small steam retort, the temperature being regulated by the steam pressure. The wood was previously dried to about 10 per cent moisture content so that it was not in contact with a large amount of water during the heating period.

The samples were analyzed according to the methods in use at the Forest Products Laboratory. These methods as described by Bray (1) were modified only in that alcohol-benzene was used instead of ether for the extractions previous to the lignin determination. Additional determinations were made of the methoxyl content of the isolated lignin and of the hydrolysis number (3) of the isolated cellulose.

The complete analytical results are shown in Table I,

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² Research Fellow from Poland.

³ Campbell and Booth have recently published an article bearing upon this subject (2).

Analyses are recorded of white ash and Sitka spruce wood before and after heat treatments in a closed iron tube at 138° C. for 2, 4, and 8 days. In both woods the losses are largely in the carbohydrate constituents and there are also gains in the lignin and the alcohol-benzene soluble. In both woods the methoxyl content remains practically constant.

In the ash wood the carbohydrates lost are entirely pentosans, but in the spruce wood they are largely hexosans and even the stable (not readily hydrolyzed) cellulose is decomposed.

In the ash wood the acetic acid by hydrolysis is rapidly decreased to a minimum at the fourth day.

The changes in composition are discussed in the light of the empirical analytical methods used in determining the changes in composition.

The indications of a change from carbohydrates to a lignin-like substance are so important that a special investigation of the change has been started.

together with the losses in weight observed during the heat treatments.

General Changes Common to Hardwood and Softwood

The solubility of the wood in cold water, alcohol-benzene, and 1 per cent caustic soda after different periods of heating varied in the same manner. The solubilities were increased at first and later decreased, in some instances becoming a little less than those of the original wood.

In both the hardwood and the softwood the general effects of the heating are

a decrease in the carbohydrate components and an increase in lignin. The increase in lignin may be only apparent, since the Forest Products Laboratory method for determining lignin is based on its insolubility in 72 per cent H₂SO₄ and in other characteristics the "lignin" formed by heating may be different from the lignin present in the unheated wood. The isolated lignins from the heated and unheated samples were analyzed for methoxyl content as shown in Table I. There was always a lower percentage of methoxyl in the isolated lignin from the heated samples than from the corresponding unheated samples, indicating that, in this characteristic at least, there is a difference. In another (qualitative) characteristic, however, the isolated lignins were similar. It was found that they could all be put into solution by the treatment used in the analytical method for isolating cellulose—namely, chlorination followed by treatment with sulfites.

Although it is not maintained that by this heat treatment carbohydrates have been transformed into lignin, yet certain carbohydrates have lost some of their carbohydrate characteristics and have been transformed into a material that possesses some of the characteristics of lignin. These indications of the transformation of carbohydrate to lignin by long-continued low-temperature heating are, however, so important in the field of the relationships between the carbohydrates and lignin in wood that further experiments are now under way in the similar heat treatments of pure wood carbohydrates.

The variations in the figures for methoxyl in Table I are

within the limit of error of the determination or at least within the limit of variation of matched samples, so that it can be safely concluded that the methoxyl remained constant throughout the heating periods.

Table I—Chemical Composition of Wood Heated at 135° C. for 2, 4, and 8 Days
(All figures in percentages of dry unheated wood unless otherwise noted)

CONSTITUENT	WHITE ASH				SITKA SPRUCE			
	Not heated	Days heated			Not heated	Days heated		
		2	4	8		2	4	8
Loss in weight on heating (3)		5.0	5.8	7.7		1.6	1.3	5.6
Ash	0.48	0.64	1.31	0.93	0.29	0.14	0.47	0.25
Cold-water soluble	3.6	6.9	5.7	4.6	3.1	6.9	5.4	2.9
Hot-water soluble ^a	1.2	1.4	1.1	0.9	3.1	1.0	1.0	1.4
Soluble ^b in 1 per cent NaOH	14.3	19.4	20.1	18.2	10.2	11.2	11.8	11.0
Ether soluble	0.9	0.6	0.4	0.9	0.9	0.5	0.7	1.7
Alcohol-benzene soluble	3.9	10.9	10.1	8.5	3.7	7.4	6.3	3.8
Acetic acid by hydrolysis	3.6	2.2	0.5	0.5	0.6	0.4	0.5	0.8
Lignin	27.0	27.0	31.0	32.6	28.5	33.6	37.3	38.4
Cross and Bevan cellulose	55.9	51.1	48.0	48.0	56.8	51.0	50.4	48.1
Total pentosans	22.6	10.8	5.4	4.5	7.0	4.7	4.2	3.6
Pentosans in cellulose	11.0	6.2	3.1	3.1	2.4	2.3	2.0	1.5
Pentosans not in cellulose	11.6	4.7	2.2	1.5	4.7	2.5	2.1	2.0
Total methoxyl	0.9	0.9	7.1	7.0	5.3	5.3	5.1	5.4
Methoxyl in lignin	5.2	4.1	4.5	4.1	4.0	4.2	4.5	4.3
Methoxyl in lignin (on basis lignin)	19.4	15.2	14.6	12.5	14.0	12.7	12.2	11.2
Readily hydrolyzed cellulose ^c	12.8	7.9	4.0	4.6	9.6	7.0	7.2	6.4
Stable cellulose ^c	43.1	43.2	43.1	43.4	47.2	44.0	43.2	41.7

^a After subtracting cold-water soluble.

^b After subtracting hot- and cold-water soluble.

^c Calculated from hydrolysis number determination made on the Cross and Bevan cellulose.

Changes in Certain Constituents

For a more detailed study of the changes in certain components and for a ready comparison of the hardwood and softwood, Table II has been prepared. In this table certain data from Table I have been calculated in terms of decreases or increases at the different stages of heating.

With the hardwood the decreases in Cross and Bevan cellulose correspond almost exactly with the decreases in pentosan in cellulose and with the decreases in unstable cellulose, which indicates that the unstable cellulose is composed entirely of pentosans in cellulose. The stable cellulose, as calculated from the hydrolysis number determination, remains practically constant. In the softwood the amount of decomposition of Cross and Bevan cellulose is about the same, but the decomposed cellulose material is made up of different constituents. There is not only much less pentosan in cellulose in the softwood than in the hardwood (2.4 and 11 per cent, respectively) but even the small amount present is relatively more resistant to the effects of heat. After 8 days' heating the 2.4 per cent in the softwood has been reduced only to 1.5 per cent, a 37 per cent decrease, while the 11.0 per cent in the hardwood has been reduced to 3.1 per cent, a 72 per cent decrease. The decomposition of the softwood Cross and Bevan cellulose is seen to occur almost entirely in the hexosan constituents, and even more in the stable cellulose than in the unstable cellulose.

The pentosans not in cellulose decrease rapidly and continuously in both woods, but the proportion of them removed is greater at all stages in the hardwood. At the end of 8 days' heating 88 per cent of the pentosans not in cellulose in ash had been decomposed, but only 42 per cent of those in spruce.

Since there are two main constituents of the ash wood that are decomposed (the pentosans in cellulose and the pentosans not in cellulose) and two main constituents that are increased in amount (the lignin and the alcohol-benzene

soluble) together with some volatile decomposition products corresponding to the loss in weight, it is impossible to tell which products are formed from each of the constituents decomposed. Since, however, the constituents decomposed are all pentosans, although of two different types, it can be stated that the pentosans decompose to form volatile products, alcohol-benzene soluble-products, and a substance that has some of the characteristics of lignin. The alcohol-benzene soluble material is apparently an intermediate product between the pentosans and one or both of the final products because it increases rapidly during the first period of heating and then decreases.

Although there is no apparent increase in lignin during the first 2 days' heating a closer examination of Table I shows that there must have been some formation of a lignin-like product because there had been a decrease in a lignin constituent and yet the total lignin was the same. In the figures showing the percentage of methoxyl (on the basis of the original wood) in the isolated lignin (Table I) it is seen that 5.2 per cent methoxyl was in the lignin isolated from the original wood, but only 4.1 per cent in the lignin from the wood heated for 2 days. Therefore the lignin determination should have shown 1.1 per cent less lignin on the 2-day sample. Since the lignin remained constant there must have been 1.1 per cent of lignin-like material formed to take the place of the 1.1 per cent less methoxyl in the lignin. The figures in Table II showing the increases in lignin as calculated from the lignin determination should therefore be corrected for the differences in methoxyl content from those of the original woods. This has been done in line 3.

Table II—Changes in Certain Constituents on Heating Wood for 2, 4, and 8 Days
(All figures in percentage of dry unheated wood: + increase, - decrease)

CONSTITUENT	WHITE ASH			SITKA SPRUCE		
	Days heated			Days heated		
	2	4	8	2	4	8
Lignin	+0	+4.0	+5.6	+5.1	+8.6	+9.9
Lignin (cor.)	+1.1	+4.7	+6.7	+4.9	+8.3	+9.6
Alcohol-benzene soluble	+7.0	+6.2	+4.6	+3.7	+2.6	+0.1
Cross and Bevan cellulose	-4.8	-7.9	-7.9	-5.8	-6.4	-8.7
Pentosans not in cellulose	-6.9	-9.4	-10.1	-2.2	-2.6	-2.7
Pentosans in cellulose	-4.8	-7.9	-7.9	-0.1	-0.4	-0.9
Readily hydrolyzed cellulose	-4.9	-7.9	-8.2	-2.6	-2.4	-3.2
Stable cellulose	+0.1	0	+0.3	-3.2	-4.0	-5.5
Loss in weight:						
Calcd. ^a	3.6	6.4	6.7	0.6	1.9	1.7
Obsd.	5.0	5.8	7.7	1.6	1.3	5.6
Obsd. minus calcd.	+1.4	-0.6	+1.0	+2.2	+3.2	+3.9

^a From sum of losses in cellulose and pentosans not in cellulose and sum of gains in alcohol-benzene soluble and lignin (corrected).

While the decomposed products in ash wood are entirely pentosans, in spruce wood they consist largely of hexosans, so that differences in the products of decomposition may be reasonably attributed to the presence of hexosan decomposition products. The main differences between the decomposition products of spruce and ash are the greater increases in lignin and the lesser increases in alcohol-benzene soluble in the case of spruce. There is also considerably less loss of weight (formation of volatile products) with spruce. It might be concluded, therefore, that the hexosans, in comparison with the pentosans under the same conditions of heat treatment, are transformed less into volatile products and more into lignin-like substances and that alcohol-benzene-soluble substances are not so important intermediates in these transformations.

If the sum of the gains in the various exclusive constituents is subtracted from the sum of the losses, the calculated losses may be obtained for comparison with the observed losses.

This has been done with the figures in Table II adding the losses in the Cross and Bevan cellulose and in the pentosans not in cellulose and adding the gains in lignin (corrected for methoxyl) and in alcohol-benzene soluble. With the ash wood the differences between the observed and calculated losses are not consistently of the same sign, but they are perhaps within the limit of error of the sums of determinations involved. With the spruce wood, however, the observed loss is always greater than the calculated and this difference is consistently greater with longer time of heating. It is probable, therefore, that certain substances in the heat-treated spruce were isolated and weighed in more than one determination. For instance, it is readily conceivable that a partly degraded cellulose might resist the action of the chemicals used in isolating both the lignin and the cellulose.

The changes in "acetic acid by hydrolysis" in the ash wood are of interest in connection with the obscure origin of this product. If the "acetic acid by hydrolysis" comes from acetyl groups that are not isolated with the cellulose or lignin, then the losses in this constituent due to heating should be included in the calculated losses of Table II. When such losses are included, the calculated losses become 5.0, 9.5, and 9.8 per cent instead of 3.6, 6.4, and 6.7 per cent, and are further from the observed losses of 5.0, 5.8, and 7.7 per cent, respectively, for the three periods of heating. Furthermore, the differences between the observed and calculated losses are of opposite sign from those of the softwood. (The changes in "acetic acid by hydrolysis" in the softwood are negligible.) It seems likely, therefore, that the acetic acid by hydrolysis is formed from some other constituent determined by the analytical methods used and decreases along with that constituent. Since in the ash wood the pentosans are the only constituents that decrease, the indications are

that acetic acid by hydrolysis has its origin in the pentosans. There is shown in Table I a certain amount of parallelism between the figures for pentosans in cellulose and those for acetic acid by hydrolysis. In the ash wood they both decrease during the first two periods and then remain constant during the third period. In the spruce the changes in both of these constituents are very slight.

The experiments recently reported by Campbell and Booth (2) on the analysis of green, air-dried, kiln-dried, and oven-dried oak were primarily for the purpose of showing the differences between the green and the dried wood, but there were also differences between the air-dried and the artificially dried samples that might be ascribed to the higher temperatures accompanying the latter treatments. The heat effects on lignin and pentosans were naturally much less than those reported here on account of the lower temperatures used by them, but in these constituents there are no inconsistencies between the higher and lower temperature treatments. In the case of the methoxyl, however, the results are apparently inconsistent. Even at the low temperatures used they obtained a marked reduction of methoxyl, whereas in the present higher temperature treatments the methoxyl remained practically constant. This can perhaps be explained by the different conditions under which the heating took place. Campbell and Booth heated their wood in the open air, whereas the wood used in the present analyses was heated in a sealed tube.

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Study of Wax from Low-Temperature Tar¹

Joseph D. Davis² and Kenneth M. Ireys³

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

DURING the years 1924 and 1925, a primary or low-temperature tar was produced in quantity by continuous carbonization of Mesa Verda (Utah) coal at 700° C. in superheated steam. The composition of this tar (1, 2, 3) and of the gas (6) and light oil as well have been subjects for previous investigation. This tar consisted of an oily portion, liquid at ordinary temperatures, and two solid portions, one lighter and one heavier than water. These have been termed tars I, II, and III, respectively, by the previous investigators.

The tar consisted of 28.85 per cent tar I, 40.35 per cent

It has been shown that the wax from Utah coal is a paraffin hydrocarbon wax containing a small percentage of unsaturates. This wax is of a superior grade as compared with commercial petroleum wax, as it has a higher melting point, and is a relatively dry wax.

The bituminous coals are found to yield a tar of low wax content as compared with that of the Utah coal and the sub-bituminous coals. Carbonization with superheated steam tends to increase the yield of wax in a tar, but it is not required to obtain an appreciable amount of wax from a coal high in wax-producing constituents.

tar II, and 30.80 per cent tar III. Table I gives the distribution of chemical groups in tars I, II, and III, and Table II shows the distribution of oils, waxes, and resins in the neutral oils from these tars. It was noted that the wax content of all these tar portions was higher than that reported in the literature; it is seen, for example, in Table II that the amount

of wax in the combined portions exceeds 10 per cent of the total tar. On considering this and the fact that the wax was of high melting point (54° C.), further investigation seemed worth while for possible industrial utilization of this constituent of low-temperature tar. Accordingly, the work described was undertaken.

Enough wax was recovered from tar II for purification, determination of physical constants, and approximate constitution of the purified wax. It was found to consist mainly of pentacosane (melting point 54° C.) and heptacosane (melting point 60° C.). Waxes were then recovered from tars of several bituminous and sub-bituminous coals, listed in Table V, which were carbonized at low temperatures in

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² Fuels chemist, U. S. Bureau of Mines.

³ Research Fellow, Carnegie Institute of Technology.

laboratory apparatus, and melting points of the waxes were determined. In no case was enough wax available for complete investigation, but the melting points were within the range of those obtained from the Utah coal tar. The inference is that they were similar in composition. Tars from bituminous coals did not yield more than 2 per cent wax; those from the sub-bituminous coals yielded 4.5 to 8.6 per cent. Three low-temperature tars made on a large experimental (semi-commercial) scale from bituminous coals were examined for wax content and found to contain only a fraction of 1 per cent of wax.

Table I—Distribution of Classes of Compounds in Utah Coal Tar

CLASSES OF COMPOUNDS	TAR I	TAR II	TAR III	CLASSES IN TOTAL
				TAR INCLUDING AQUEOUS CONDENSATE
	%	%	%	%
Insoluble (in sulfuric ether)	1.0	0.85	9.5	3.46
Carboxylic acids	0.3	2.25	2.5	2.14
Alkali-soluble (phenols)	23.4	15.0	40.0	26.85
Tar bases	1.7	1.55	3.0	2.07
Neutral portion	66.0	80.0	45.0	63.21
Working loss	7.6	0.35	0.0	2.27

Table II—Oil, Wax, and Resin in Total Tar

	TAR I ^a		TAR II ^a		TAR III ^a		TOTAL		
	%	Kg.	%	Kg.	%	Kg.	Kg.	% ^b	% ^c
Oil	85	7.12	57.2	8.12	68.9	4.20	19.44	67.78	42.8
Wax	10	0.84	24.1	3.42	10.4	0.63	4.89	17.05	10.8
Resin	5	0.42	18.6	2.64	19.8	1.21	4.27	14.89	9.4
Resin present in insoluble matter									2.3
Neutral portion as per cent of fraction	66	8.38	80.0	14.2	45.0	6.10	28.60	99.72	65.3
Total									

^a Neutral portion.

^b As per cent of total neutral portion from first three tar portions

^c As per cent of total tar, including that from aqueous condensate.

Method of Recovery and Analysis of Wax

The neutral oil was separated from the tar in sulfuric ether solution. The tar acids were extracted with caustic soda and the bases were removed by washing with 10 per cent hydrochloric acid. The ether was then distilled from the neutral oil, leaving a semi-solid material when cooled to room temperature. The neutral oil was steam-distilled with an oil bath kept at 250° C. under the flask containing the neutral oil. This process carried over most of the light oils. The residue was then refluxed with 5 volumes of acetone and filtered at 5° C. The residue was allowed to dry in the air and was then recrystallized from 12 volumes of acetone. Wyant and Marsh (10) used 10 volumes of acetone to recrystallize the paraffin wax they investigated, but this proved insufficient to take the wax completely from the Utah tar into solution with refluxing. The recrystallized wax was filtered at 0° C. and washed with 2 volumes of cold acetone. It was then heated on a steam bath to remove any solvent remaining. This wax had a creamy color before it was melted, but when it was fused it turned a dark brown. Repeated crystallization with acetone would not remove this color. Hereafter, this wax will be spoken of as crude wax. The melting point, as determined by the A. S. T. M. (5) method (using a Centigrade instead of a Fahrenheit thermometer), was 55° C. The cooling curve (Figure 1) has five distinct rest points or fusion points. This would indicate five different compounds.

The iodine value was determined by the Wijs (7) method. This involves the action of iodine trichloride and iodine dissolved in acetic acid solution. The wax had an iodine value of 23, which means that 23 grams of iodine are absorbed by each 100 grams of wax. This value is approximately 8

grams too high, as a certain amount of substitution takes place, probably occurring in the end carbon atom, as explained by Johansen (8).

The acid and ester value, as determined according to Holde (7), was 1.1 for acid and 5.6 for ester value, the total, 6.7, being the number of milligrams of potassium hydroxide required to saponify 1 gram of wax. The physical constants of the crude wax were as follows:

d_{15}^{20}	0.9211
Melting point, ° C.....	55
Iodine value plus substitution value.....	23
Acid value.....	1.1
Ester value.....	5.6

As there was considerable resin in the original neutral oil (see Table II), it was thought possible that the crude wax might contain some resin. As this is but very slightly soluble in petroleum ether (boiling point 40° to 60° C.) and the wax is completely soluble, some of the wax was dissolved in petroleum ether and filtered. There was no measurable amount of resin left on the filter paper, although this was colored slightly. The petroleum ether solution was then treated with 80 per cent sulfuric acid to remove unsaturates. This

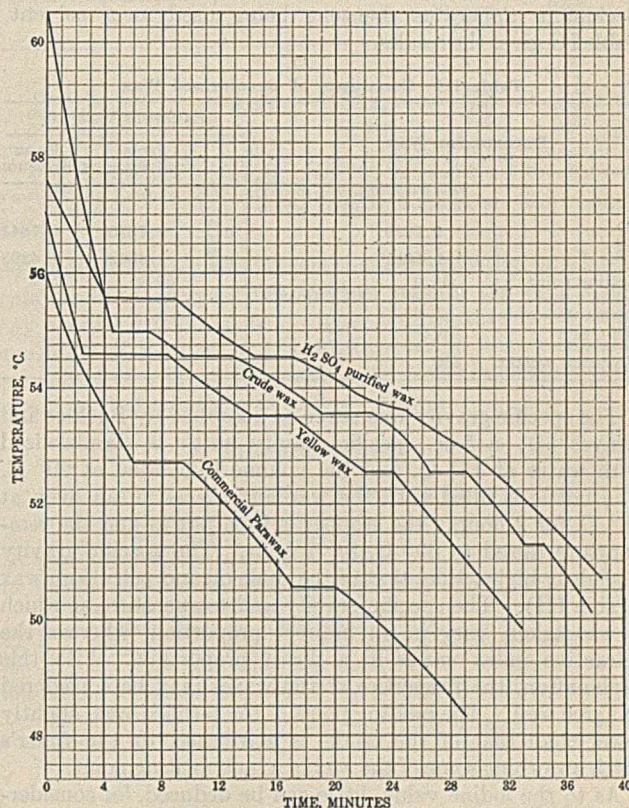


Figure 1—Cooling Curves for Wax

sulfuric acid solution was colored, but did not indicate the removal of more than 1 or 2 per cent of substance. The solution was then treated with 95 per cent sulfuric acid, which should remove the aromatics. This formed a rather thick sludge and indicated the removal of a considerable portion of substance. It is possible that the 80 per cent sulfuric acid failed to remove the unsaturates and the larger portion of the latter sulfuric acid sludge was unsaturates. The petroleum ether solution was then washed with water and a weak solution of sodium hydroxide to remove all traces of the acid, after which it was distilled to 100° C. to remove the ether. As it was difficult to eliminate all the petroleum ether in this manner the wax was crystallized from 12 volumes of acetone. An 85 per cent yield of paraffin wax resulted, and its melting point

was 55.6° C. (Figure 1). This wax has only three fusion points, which would indicate that two compounds had been removed from the original crude wax by the purification described. These three definite fusion points may indicate three different paraffin hydrocarbons present in relatively large quantities. The lower fusion point is of very short range and indicates a very slight amount of soft wax. The purified wax was a white crystalline compound before melting, but when fused it took on a brown color, but noticeably lighter than the melted crude wax.

As the crude wax was so dark and of such an undesirable character, a method for decolorizing it was worked out. It was found that filtering through fuller's earth in a hot water funnel gave the best results. A white wax could be obtained by repeated filtration, changing the fuller's earth several times. As the supply of wax was limited and the fuller's earth absorbed some of it, it was not completely decolorized, but a wax slightly tinted was obtained for further examination.

This was examined in a similar fashion to the crude wax. The determination of the refractive index was made with an Abbé refractometer at a temperature of 60° C. The molecular weight was determined by the ebullioscopic method in a Beckmann apparatus, benzene being used as a solvent. Table III gives the results.

Table III—Constants of Decolorized Wax

DECOLORIZED WAX		PARAFFIN WAX (9)	
		From oil shale	From petroleum
d_{16}^{60}	0.7929	d_{25}^{73}	0.7875
n_D^{60}	1.4425	n_D^{73}	1.4382
Melting point, ° C.	54.6		56.0
Iodine value	9.91		55.4
Substitution value	5.83		
Acid value	0.62		
Ester value	1.10		
Molecular weight	350		
	%		
	13.7 (max.)		

The specific gravity was taken as described by Buchler and Graves (4); a 5-cc. specific gravity bottle is standardized with water at 15° C. and the volume calculated at 60° C. The bottle is filled with the wax and placed in an oven at 58° C. for 2 hours; the stopper is then put in and the temperature raised to 60° C. for 1 hour. The specific gravity is slightly higher than that of the shale oil and petroleum wax (Table III). The specific gravity and temperature at which it was taken vary in an indirect proportion, whereas the refractive index varies in a direct proportion. With this explanation, the properties of the waxes may be considered to agree well. The melting point of the purified wax, slightly lower than that of the crude, is attributed to the fuller's earth absorbing some of the wax of a high melting point.

As to the iodine value, little can be deduced, for considerable unsaturation may be present in a given unsaturated molecule; or there may be only one double bond present. If we suppose it to be one double bond in a molecule with a molecular weight of 350, unsaturates would amount to 13.7 per cent of the wax. This would be the maximum amount of unsaturates in the wax. The percentage of acids and esters was calculated by taking a theoretical molecular weight, and from this the percentage of oxygen may be calculated. By taking the molecular weight of camic acid ($C_{14}H_{27}COOH$, melting point 55° C.) which is 242.0, the percentage of acid was calculated to be

$$\frac{0.00062}{56} \times 242 \times 100 = 0.268 \text{ per cent}$$

A molecular weight of 350 was taken for the determination of the per cent of esters:

$$\frac{0.0011}{56} \times 350 \times 100 = 0.7$$

From the above data the calculated percentage of oxygen is 0.0668. The ultimate analysis of the decolorized wax gave 85.24 per cent carbon, 14.74 per cent hydrogen, 0.05 per cent nitrogen, and no sulfur.

As the method of analysis is not accurate to better than 0.1 per cent, the calculated value of oxygen is in agreement with the results. If the wax were a pure pentacosane ($C_{25}H_{52}$); the theoretical percentage of carbon and hydrogen would be 85.24 and 14.76, respectively.

In conclusion, from the ultimate analysis and study of the composition of the wax with its physical properties, it may be safely classified as a paraffin wax of the hydrocarbon series.

By fractional crystallization of the decolorized wax with ethylene dichloride (CH_2ClCH_2Cl) it separated largely into two major portions, as shown in Table IV.

Table IV—Fractional Crystallization of Decolorized Wax

MELTING POINT	AMOUNT CRYSTALLIZED
° C.	%
47.8	12.2
50.1	6.85
54.3	33.0
57.6	8.05
59.6	32.7
63.6	6.8

The wax is clearly composed of a series of hydrocarbons, and these data indicate a predominance of pentacosane ($C_{25}H_{52}$, melting point 54° C.) and heptacosane ($C_{27}H_{56}$, melting point 60° C.) with a small amount of soft wax. On repeated crystallization of the decolorized wax the melting point was constant, which proves it to be a wax free from oil. This indicates a superior grade of dry wax with a melting point higher than the marketable petroleum waxes.

Utilization of Wax

Several crayons were molded from the decolorized wax, using suitable pigments to obtain the desired color. When these crayons were warmed in the palm of the hand and pressure was applied, they remained firm, whereas commercial crayons or those made from parawax were pliable when subjected to the same treatment. This would indicate a good raw material for candles or a good grade of wax paper and other waterproof materials. Upon analysis, the commercial crayons proved to be approximately a 1 to 1 mixture of paraffin and fatty acid. Crayons made by adding 10 per cent stearic acid to the wax from Utah tar seemed to have no more desirable characteristics than the crayon made from pure wax.

Wax Content of Other Coals

As there is considerable industrial interest in the wax content of tars, it was thought advisable to determine the wax content of tars from several typical coals. Enough coal was carbonized in a manner similar to that of the Utah coal (superheated steam) to determine the wax content of the resultant tar.

One-hundred-gram samples of coal were carbonized by heating to 630° C., at which temperature it was held for 1 hour. The tar was extracted with ether from the water distillate. The ether was evaporated and the tar weighed to find the percentage yield. The wax content was then determined by dissolving the tar in 5 volumes of acetone and cooling to -10° C., at which temperature it was filtered. It was then dried in the oven at 105° C. and weighed. Where the higher percentage of wax was found, it was dissolved in petroleum ether (boiling point 40° to 60° C.), filtered, and the

Table V—Assay Results and Wax Content of Typical Coals

COAL	SOURCE			COKE				COKE, TAR, PURE IN AND COAL PURE WATER				ULTIMATE ANALYSIS OF COAL					ASH CALORIFIC VALUE	WAX IN TARS	APPROX. MELTING POINT OF WAX ° C.	
	Mine	Bed	County	Town	%	TAR	WATER GAS ^a	%	%	%	%	C	H	O	N	S				%
1 Alabama (Bituminous)	Sayreton	Mary Lee	Jefferson	North Birmingham	80.3	10.3	1.0	8.4	91.6	88.8	11.6	76.3	5.1	6.0	1.6	0.8	10.2	13,640	1.06	52
2 Illinois (Bituminous)	Orient	No. 6	Franklyn	West Frankford	68.0	13.0	7.4	11.6	88.4	88.1	14.65	71.5	5.8	15.2	1.6	1.4	4.5	12,760	1.83	54
3 Thyssen (Bituminous)		No. 7		Thyssen District Ruhr, Germany ^d	80.0	7.9	1.0	11.1	88.9	94.1	8.4	83.0	4.9	4.9	1.6	0.7	4.9	14,380	0.61	54
4 Banning (Bituminous)		Pittsburgh	Fayette	Van Meter	80.3	15.2	1.4	3.1	96.9	92.5	16.4	78.8	5.4	6.8	1.7	1.2	6.1	14,160	1.37	55
5 Utah ^b (Sub-bituminous)	Hiawatha M. & M.	Mesa Verda	Carbon	Hiawatha Thermopolis, Wyo.	66.5	13.1	3.4	17.0	83.0	89.1	14.7	72.4	5.4	12.4	1.5	0.8	7.5	13,240	10.39	54
6 Thermopolis ^c (Sub-bituminous)				Hot Springs	62.7	9.8	10.4	17.1	82.9	77.4	12.7	60.4	5.5	19.4	1.2	1.3	12.2	10,540	5.3	56
7 Manderson ^e (Sub-bituminous)	Flagstaff		Big Horn	Manderson, Wyo.	60.0	10.7	16.5	12.8	87.2	73.2	14.6	54.9	6.0	24.7	1.1	2.1	11.2	9,740	8.61	54
8 Wilton ^e (Lignite) CARBONIZED WITHOUT STEAM	Wilton		Burleigh	Wilton, N. D.	42.8	3.4	39.7	14.1	85.9	54.3	6.26	38.6	7.1	46.7	0.6	1.0	6.0	6,570	4.55	57
4					78.7	13.3	1.4	6.6	93.4	92.5	14.4	78.8	5.4	6.8	1.7	1.2	6.1	14,160	0.49	..
5					65.1	12.8	3.4	18.9	81.1	89.1	14.2	72.4	5.4	12.4	1.5	0.8	7.5	13,240	9.06	..

^a By difference.
^b Mesa Verda coal from which original wax was obtained, but freshly carbonized on laboratory scale.
^c Davis and Galloy, *IND. ENG. CHEM.*, **20**, 612 (1928).
^d See Fischer, *Brennstoff-Chem.*, **6**, 33 (1925); also Davis and Reynolds, *IND. ENG. CHEM.*, **21**, 1295 (1929).

petroleum ether evaporated on the steam bath. This removed any resin present. Two of these coals were carbonized without using superheated steam to compare the relative merits of carbonization with and without steam for the production of wax in the tars. Table V gives the results.

From Table V it is evident that none of the bituminous coals, except the Utah coal, yield an appreciable amount of wax. It is difficult to classify this coal; it cannot be considered a true bituminous coal. The sub-bituminous coals and the one lignite yield a tar containing considerable quantities of wax. It seems probable that these waxes are paraffin hydrocarbons similar to the wax from the Utah tar. This conclusion is based on the melting points of the waxes, as they range from 52° to 57° C., but insufficient quantities were available to prove this conclusively.

In the carbonization without superheated steam the wax content of the tar is lower, but not alarmingly so in the case of the Utah coal. From this one can conclude that carbonization with superheated steam favors a higher yield of wax in the tar. To compare these results with commercially carbonized tars, three tars which the writers investigated were analyzed for their wax content as given in Table VI.

Table VI—Wax in Commercial Tars

COAL	PROCESS	TEMPERATURE ° C.	WAX IN TAR %
Illinois ^a	Parr	800	0.12
Pittsburgh and Sunday Creek ^b	Wisner	500	0.62
Pittsburgh ^c	Hayes	750	0.37

^a Harrisburg premium coal, No. 5 bed, Harrisburg, Saline County, Ill.
^b No. 5 block bed, Campbells Creek, W. Va., and No. 6 bed, Sunday Creek, Athens County, Ohio, mixed in equal proportions.
^c Pittsburgh, No. 8 bed, Panama mine, Moundsville, Marshall County, W. Va.

From these data it would seem that carbonization on a large scale tends to decrease the yield of wax in the tar. This may also be attributed to a higher temperature in the carbonization of the Parr and Hayes tars. The Wisner tar was carbonized at a lower temperature than the laboratory prepared tars, but still the wax content is low.

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Analysis of Color Characteristics of Paints

Committee D-1 on Preservative Coatings for Structural Materials of the American Society for Testing Materials, 1315 Spruce St., Philadelphia, Pa., has adopted as standard a method of analysis for the color characteristics of paints in terms of fundamental physical units. More satisfactory analyses of colors could be obtained by means of instruments capable of measuring in terms of fundamental physical units, since these do not necessitate constant checking. The use of an apparatus of the primary type enables determination of the spectral distribution curve of the colors selectively reflected by any given sample within the limits of the visible spectrum.

The proposed method consists of the characteristic spectral reflectance in terms of fundamental physical units, determined in accordance with certain stipulations, the specific description of the standard reflecting surface used, and the complete description of the character of illumination employed.

Effect of Cod-Liver Oil on Calcium Metabolism of Young Chicks¹

Arthur D. Holmes and Madeleine G. Pigott

RESEARCH LABORATORIES, THE E. L. PATCH COMPANY, BOSTON, MASS.

The poultry industry contributes materially to the agricultural income of this country and constitutes a valuable home market for a large amount of wheat, corn, other grains, and by-products of the packing-house, dairy, and fishing industries. The increased per capita consumption of poultry and eggs, coupled with the perfection of artificial incubation and brooding equipment, has revolutionized the poultry industry, placing poultry raising on a mass-production basis. Formerly chickens were raised during the summer months, when an abundance of green plants and sunshine provided adequate vitamin supplements for almost any kind of a ration. The demand for winter broilers and the shift of high prices for eggs from winter to the fall season necessitates hatching and starting chicks during the winter months, when green plants are not available and when the quantity and quality of sunshine are limited. Coupled with this has come a demand for more rapid growth and earlier maturing birds. As a consequence present-day poultry nutrition has become a very complicated and difficult problem.

A good grade of tested cod-liver oil will supply the

vitamins formerly obtained from green plants and sunshine, but this does not solve all problems of poultry nutrition. To secure satisfactory growth and bone development, attention must be given to the quantity and quality of proteins, supplementary sources of calcium and phosphorus, the ratio of these two minerals, and the influence of vitamins on the metabolism of the various constituents of the ration.

This laboratory has been engaged in a study of these factors for over three years, and the results have served as a guide for modifying the usual type of "growing mash." By making a distinct change in the proteins, lowering the calcium content, changing the calcium-phosphorus ratio, and insuring an adequate supply of vitamins, it has been possible to secure more rapid growth and better feathering at a materially lower cost for feed. In the experiments reported here attention was centered upon the effect of cod-liver oil on calcium metabolism of growing chicks when the calcium was obtained from different sources, was fed at different levels, and was available in different ratios to phosphorus.

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CHICKENS formerly were raised under conditions closely approximating those for wild birds. The hen incubated twelve to fifteen eggs and brooded the resulting chicks. Ordinarily she was allowed free range, which provided a wide variety of bugs, worms, green plants, and many hours daily in the sunshine. Under these conditions the owner had no occasion to consider balanced rations, vitamins, or sanitation.

With the advent of extensive artificial incubation, colony brooding, and more recently, the battery brooder system, the problem of poultry nutrition has become extremely complicated. The modern poultryman must operate on an intensive scale and employ expensive equipment, high-priced labor, and high-priced feeds. He must, therefore, resort to mass production under conditions which little resemble those provided by nature. For instance, chicks are hatched by the thousands during the winter months, when the temperature may be at or below zero (the hatchery from which this laboratory regularly obtains baby chicks for experimental purposes hatched nearly a third of a million chicks during October, 1929, to March, 1930, inclusive). At that season of the year green plants and sunshine as sources of vitamins for commercial poultry raising are non-existent and reliance must be placed upon supplementary vitamin feeding.

In growing chicks the poultryman is confronted with two major problems. First, he must convert his cockerels and surplus pullets from baby chicks into broilers in the least possible time and at the least possible expense. The battery brooder system is especially adapted to this purpose; chicks may be grown by the hundreds or thousands upon wire platforms tiered one above another. This system minimizes costs for buildings, heat, feed, and labor. It also minimizes the occurrence of coccidiosis and some other poultry diseases,

but the chickens receive little if any sunlight and poultry nutrition under this system is beset by many difficulties.

Secondly, the poultryman must produce large, well-developed, disease-free pullets which possess the stamina to produce continuously a profitable yield of eggs for a 12- or 14-month period. Formerly the peak price for eggs came early in January. Then the pullets could be hatched during the spring and raised during the summer months, when a maximum of green feed and sunshine are available. During recent years the time of the peak price for eggs has steadily advanced, until it is now at or just before Thanksgiving. Obviously, the poultryman is desirous of producing as many eggs as possible during the period of high prices—September, October, and November. Thirty days or more are required for the pullet, just coming into production, to lay her small or "pullet" eggs. Thus the poultryman must plan the hatching of his pullets so that they will come into production about the last of July. The length of the growing period varies with the breed of birds and rate of growth. In some instances 4½ months may suffice. However, since an allowance of 2 or 3 weeks is made for the young pullets to recover from the effects of vaccination, the poultryman ordinarily plans to hatch his chicks nearly 6 months before the production period. Thus the modern poultryman, operating on an intensive scale, must obtain a one-third or more of the growth of his chicks before green plants and sunshine are available in sufficient quantity and quality to afford adequate vitamin protection. As a consequence the need for adding a supplementary source of vitamins to the poultry ration has become imperative.

The obvious solution of this problem seemed to be to incorporate cod-liver oil in poultry feeds. Experience has shown, however, that the mere addition of cod-liver oil to a "growing" or "laying" mash does not, by any means, solve all the problems of poultry nutrition. The rate of growth of chicks may be, to quite an extent, controlled by varying the

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protein content of the ration. However, varying the protein level, and thereby the rate of growth, also necessitates a consideration of the calcium and phosphorus content of the ration and the amount of vitamins required adequately to supplement rations of different protein and mineral levels. The calcium level of a growing mash may be conveniently raised by the addition of ground limestone or similar material—a profitable procedure for the quarry owner and feed manufacturer—but, as shown by the experiments reported here, rations containing too much calcium and too high a ratio of calcium to phosphorus produce unsatisfactory growth accompanied by excessive feed costs.



Figure 1—All-Metal Battery Brooders

The investigation of which the experiments reported here form a part was undertaken to collect data concerning the interrelationship of vitamin levels, protein levels, calcium and phosphorus levels, and ratios of calcium to phosphorus. This report deals with the effect of cod-liver oil on calcium metabolism of growing chicks when the calcium was obtained from different sources, was fed at different levels, and was available in different ratios to phosphorus.

Nature of Rations

A ration quite similar to those widely used in this locality was selected as the basal ration. The components were ground and mixed by a commercial feed manufacturer. The composition of the basal ration is given in Table I.

Table I—Experimental Ration

	Lbs.
Coarse yellow corn meal	200
Wheat bran	100
Wheat flour middlings	100
Ground oat groats	100
Meat scraps (50 per cent protein)	25
Fish meal (50 per cent protein)	25
Dried skim milk	50
Alfalfa leaf meal (less than 20 per cent crude fiber)	40
Common salt	5

Nature of Cod-Liver Oil

The cod-liver oil used in this investigation was of American origin. It was separated from fresh livers by the direct steam process and filtered to remove all trace of liver tissue. The oil was fed in its natural state; that is, the cod-liver stearin was not separated as is the case in the manufacture of medicinal oil. The biological test showed this oil to have a vitamin potency of more than 500 units of vitamin A per gram and more than 75 units of vitamin D per gram.

The oil and calcium supplements were added to the ration at frequent intervals by means of a laboratory size batch mixer.

Brooders

The chicks were housed in all-metal battery brooders (Figure 1), which provided 18 square feet of floor space for each group of chicks. The brooders were equipped with

screen floors and with automatically controlled electrically heated hovers which occupied one-half of the floor space. The brooders were located in a room maintained at a constant temperature of 72° F. The temperature of the hovers was 100° F. for the first week and was decreased 5° F. per week until the fifth week, when the hovers were removed from the batteries. The light entering the room came through two sets of windows.

Chicks

The experimental birds were Rhode Island Red chicks obtained as day-old chicks from an accredited flock which had been maintained under satisfactory feed and management conditions. Inasmuch as only about 9 hours elapsed from the time of removal of the chicks from the incubator until the first feeding, the chicks were not subjected to a starvation period such as ordinarily occurs in the commercial poultry industry.

Sources of Supplementary Calcium

In order to provide supplementary calcium from a variety of sources similar to those used in the poultry industry, a supply of commercial grade of edible bone meal, powdered calcium carbonate, powdered tricalcium phosphate, powdered oyster shells, and limestone flour were procured on the open market. Table II gives the chemical analyses of the calcium and phosphorus content of these materials.

Table II—Calcium and Phosphorus Content of Calcium Supplements

	CALCIUM	PHOSPHORUS
	%	%
Edible bone meal	43.00	32.00
Calcium carbonate	38.93	...
Tricalcium phosphate	31.75	23.84
Oyster shells	38.93	...
Limestone	31.29	...

Experimental Procedure

On arrival at the laboratory the chicks were divided into lots of thirty-six which were as nearly identical as possible. Feed and water were constantly before the chicks. The chicks were weighed at weekly intervals. Five birds, judged to be typical of the pen, were removed from each pen at the end of the third, sixth, and ninth week. The basal ration was supplemented with varying amounts of calcium, phosphorus, and cod-liver oil as shown in Table III.

Table III—Supplements Added to the Basal Ration

PEN	ADDED MATERIAL
1	Bone meal
2	Bone meal and 1 per cent cod-liver oil
6	1 per cent cod-liver oil
7	No cod-liver oil
8	Calcium carbonate and 1 per cent cod-liver oil
9	Calcium carbonate, no cod-liver oil
10	Tricalcium phosphate and 1 per cent cod-liver oil
11	Tricalcium phosphate, no cod-liver oil
12	Oyster shells (flour) and 1 per cent cod-liver oil
13	Oyster shells (flour), no cod-liver oil
14	Limestone (flour) and 1 per cent cod-liver oil
15	Limestone (flour), no cod-liver oil

Table IV—Ash, Calcium, and Phosphorus Content of Experimental Rations

PEN	ASH %	CALCIUM	PHOSPHORUS	RATIO Ca to P
		%	%	
1	9.89	2.29	1.41	1.62
2	9.80	2.18	1.44	1.51
6	6.64	0.99	0.88	1.12
7	6.66	0.95	0.86	1.10
8	11.08	3.86	0.76	5.08
9	11.03	3.87	0.75	5.16
10	11.06	3.80	2.82	1.35
11	11.05	3.80	2.83	1.34
12	11.01	3.86	0.83	4.65
13	11.10	3.97	0.79	5.02
14	13.47	4.15	0.82	5.06
15	13.40	4.10	0.84	4.88

As a result the different rations contained calcium from different sources, at different levels, and at different ratios to

phosphorus. The chemical analyses of the rations gave the mineral compositions shown in Table IV.

The effectiveness of the various rations as a source of bone-building materials was judged by the rate of growth and bone development as indicated by the size, weight, ash, calcium, and phosphorus content of the tibiae removed from typical chicks at the end of the third, sixth, and ninth week of the experiment.

calcium to phosphorus being 1.35 to 1. The next best growth was obtained in pen 2, which received a ration containing 1.4 per cent phosphorus and 2.2 per cent calcium with a ratio of calcium to phosphorus of 1.15 to 1. As pointed out above, the ratio of calcium to phosphorus for the remaining pens was practically 5 to 1. Considered merely on the basis of rate of growth, it appears that cod-liver oil was quite effective in producing growth in birds that received the ra-

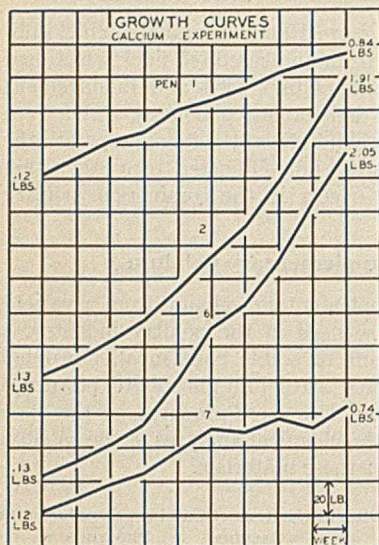


Figure 2

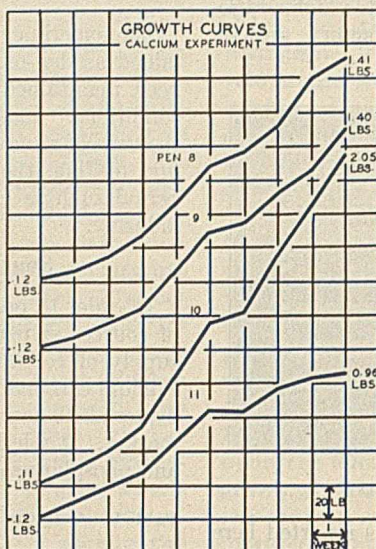


Figure 3

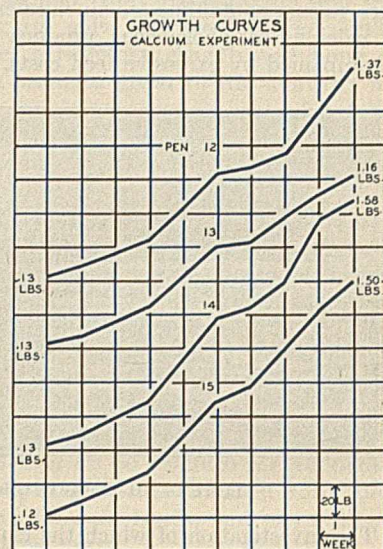


Figure 4

Growth of Chicks

Each pen of chicks was weighed as a group at weekly intervals and the weights were reduced to a per-chick basis. The results thus obtained are reported in Figures 2, 3, and 4.

It will be noted that the birds in pen 2, which received 1 per cent cod-liver oil, grew at approximately twice the rate of the birds in pen 1, which received no cod-liver oil. Similarly, the birds in pen 6, which received cod-liver oil as a supplement to the basal ration, grew at approximately three times the rate of the birds in pen 7, receiving the same ration without oil. The rate of growth for pen 8, which received 1 per cent cod-liver oil, was practically the same as for pen 9, the control pen. The ration consumed by pens 8 and 9 contained nearly 4 per cent of calcium and the ratio of calcium to phosphorus was slightly over 5 to 1. The rate of growth for pen 10, which received 1 per cent of cod-liver oil, was approximately twice that for pen 11, which received no oil. The calcium supplement for these pens was tricalcium phosphate. The ration contained nearly 4 per cent of calcium, but the ratio of calcium to phosphorus was only 1.35 to 1. Pen 12, which received 1 per cent cod-liver oil, made only slightly better gain than pen 13, without oil. The calcium supplement for these pens was finely pulverized oyster shells. The rate of growth for pen 14, which received 1 per cent cod-liver oil, and 15, which received no cod-liver oil, were practically the same. These pens received finely ground limestone as a source of calcium. The rations fed to pens 12, 13, 14, and 15 contained about 4 per cent of calcium and the ratio of calcium to phosphorus was approximately 5 to 1.

The best growth was obtained in pens 6 and 10—the birds averaging over 2 pounds at 9 weeks of age. The ration of pen 6 contained less than 1 per cent of calcium and phosphorus and the ratio of calcium to phosphorus was 1.12 to 1.

The ration of pen 10 contained nearly 2 per cent of phosphorus and nearly 4 per cent of calcium, the ratio of

tions in which the ratio of calcium to phosphorus was relatively low. When the ratio of calcium to phosphorus was approximately 5 to 1, the addition of cod-liver oil to the ration did not produce increased rate of growth. Furthermore, neither the cod-liver oil nor the control birds grew so satisfactorily as when this ratio was lower.

In considering growth it should be noted that there was no cannibalism or feather pulling in any of the pens during the period of the experiment. The birds in those pens that received rations containing a low ratio of calcium to phosphorus and supplemented with cod-liver oil were particularly well feathered at the conclusion of the experiment. The birds in all the pens receiving no cod-liver oil and those in nearly all the pens receiving rations having a calcium to phosphorus ratio of 5 to 1, even though supplemented with cod-liver oil, were poorly feathered. The larger portion of those birds developed the scrawny feather growth typical of chick rickets.

Bone Development

At the end of the third, sixth, and ninth weeks five chicks were removed from each of the experimental pens. The left tibiae were dissected, freed of tissue and dried at 95° C., measured, weighed, and analyzed for total ash, calcium, and phosphorus. The right tibiae were dissected, freed of tissue, and examined by the modified McCollum "line" test to determine the extent of calcification.

The development of tibiae taken from the test chicks at different stages of the experiment can be seen in Figure 5. When the chicks were 3 weeks old it was possible to detect differences in the bone development of birds from the different pens. At 6 and 9 weeks of age these differences became progressively more pronounced. During the last portion of the experiment the lack of calcification was so pronounced in some pens, notably pens 12 and 13, that the ends of the tibiae were very soft and apparently nothing but cartilage.

The left tibiae of each test chick at 3, 6, and 9 weeks was measured and weighed separately, but for the sake of con-

venience the results are reported below for each pen on an average per chick basis. Table V contains data on the left tibiae of chicks at 3, 6, and 9 weeks.

Table V—Data Concerning Dried Tibiae of Chicks

PEN	LENGTH Mm.	DIAMETER Mm.	AV. WT. Grams	ASH ^a %	CALCIUM %	PHOSPHORUS %	RATIO Ca to P
AT 3 WEEKS OF AGE							
1	47.6	3.7	0.64	34.19	11.69	6.27	1.87
2	52.5	3.7	0.78	40.15	14.41	7.39	1.95
6	51.6	3.7	0.80	40.99	14.47	7.20	2.01
7	45.8	2.6	0.49	34.11	12.04	5.98	2.01
8	49.3	3.2	0.67	40.65	15.16	6.91	2.09
9	42.3	2.7	0.39	38.69	14.01	6.59	2.12
10	50.9	3.7	0.76	43.78	15.96	7.86	2.04
11	49.7	3.7	0.70	36.56	12.84	6.46	1.99
12	49.1	3.2	0.60	38.90	14.57	6.28	2.32
13	47.0	3.2	0.50	36.02	13.12	5.90	2.21
14	49.6	3.3	0.63	43.85	16.22	7.75	2.09
15	46.6	3.0	0.52	40.08	14.57	6.86	2.13
AT 6 WEEKS OF AGE							
1	52.1	4.4	1.04	35.25	12.63	6.11	2.07
2	66.4	6.2	2.42	46.31	16.76	8.30	2.02
6	70.9	5.4	2.22	44.81	16.33	8.07	2.02
7	63.3	4.1	1.31	41.20	14.70	6.91	2.13
8	67.8	4.8	1.86	41.26	15.31	7.06	2.17
9	65.8	4.3	1.53	34.64	12.46	5.69	2.09
10	74.9	3.2	2.49	44.48	15.92	7.96	2.00
11	56.2	4.9	1.29	37.94	13.10	6.73	1.95
12	52.5	4.3	1.12	34.76	11.59	6.25	1.86
13	63.2	5.4	1.70	31.97	11.24	5.31	2.12
14	69.1	4.8	1.72	44.65	16.40	7.75	2.09
15	68.9	4.9	1.82	39.86	14.35	6.86	2.09
AT 9 WEEKS OF AGE							
1	69.6	5.2	2.05	37.28	12.52	6.66	1.88
2	102.4	7.4	5.94	46.21	16.74	8.20	2.05
6	98.8	7.3	5.12	48.45	17.55	8.73	2.01
7	58.8	5.1	1.39	36.35	12.44	6.56	1.90
8	93.8	6.4	4.42	47.14	17.42	8.47	2.06
9	89.4	5.7	3.52	37.75	13.62	6.37	2.14
10	102.3	7.3	5.39	48.67	17.76	8.71	2.04
11	69.4	6.4	2.46	38.47	13.39	6.77	1.98
12	74.8	5.3	2.33	35.80	13.08	6.19	2.11
13	74.9	5.1	2.79	34.99	12.35	5.78	2.14
14	95.7	7.1	4.89	48.82	18.16	8.50	2.18
15	89.5	5.9	3.59	40.68	14.80	7.04	2.05

^a Ash percentage calculated upon dry extracted tibiae.

From this table it will be noted that through the entire experimental period the ash, calcium, and phosphorus content

of the tibiae of pens 2, 6, and 10, which received 1 per cent cod-liver oil, was decidedly greater than those from pens 1, 7, and 11, respectively, which were control pens that received no cod-liver oil. In the case of pens 8 and 9, which received calcium carbonate, 12 and 13, which received powdered oyster shell, and 14 and 15, which received powdered limestone, the differences between those receiving cod-liver oil and those receiving no oil were not so significant. The ratio of calcium to phosphorus in the ration fed to these pens was approximately 5 to 1.

It is particularly interesting to note the ratio of calcium to phosphorus in the tibiae of chicks killed at 3, 6, and 9 weeks of age. Although the amount of ash present in the tibiae of birds from different pens varied over wide limits, the ratio of calcium to phosphorus remained quite constant. In fact, regardless of the rate of growth of the chicks and regardless of whether or not the bone development was normal or rachitic, the ratio of calcium to phosphorus was approximately 2 to 1. On the basis of this evidence it would seem that, if the calcium and phosphorus were present in the ration in equally utilizable form, the ration should supply these elements in a ratio of about 2 to 1.

Histological Report

The right tibiae of the chicks removed from the experimental pens at the end of the third, sixth, and ninth weeks were freed of tissue, split longitudinally, and stained. They were examined and a record was made of the extent of calcification of each bone, but for the purpose of this discussion the results obtained for the individual bones of the different groups have been averaged. A section of the bone judged to be typical of the group was selected and photographed (Figure 6).

From these photographs and the histological report (Table VI) it is apparent that differences in calcium utilization by the

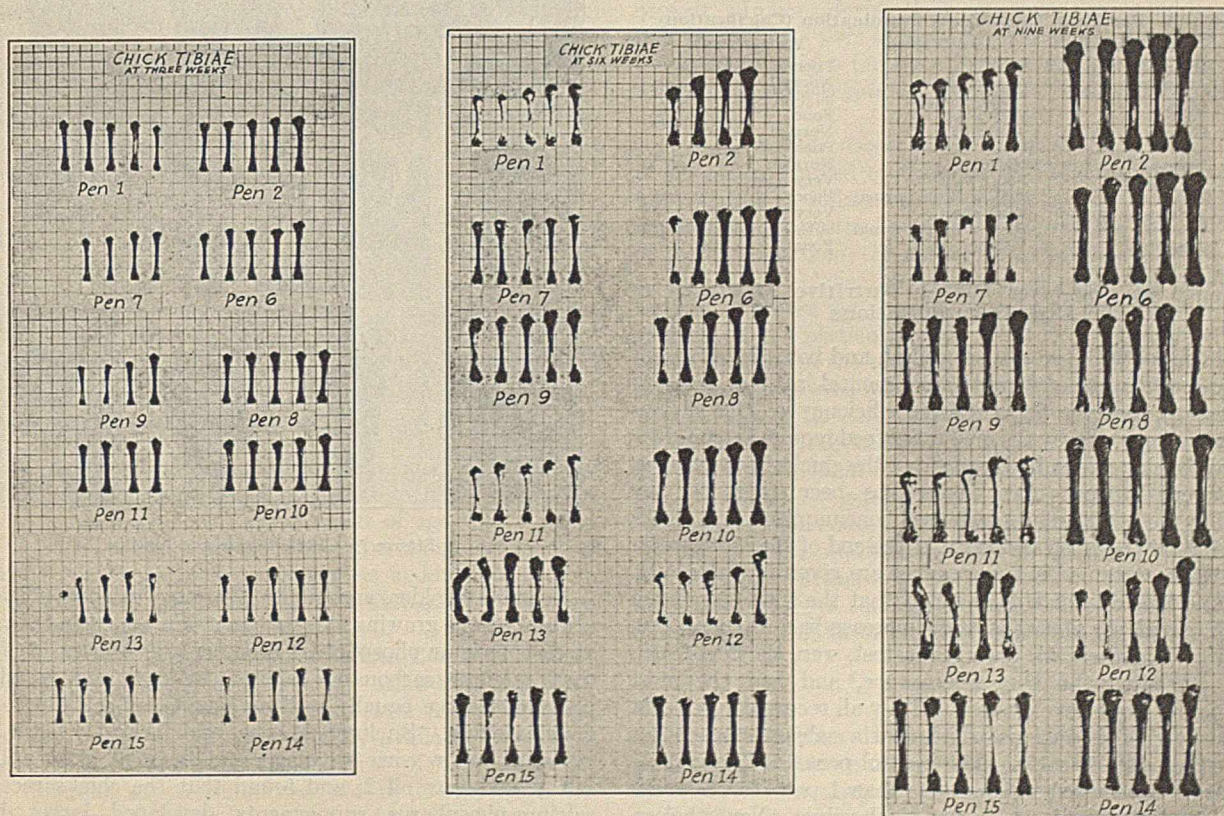


Figure 5

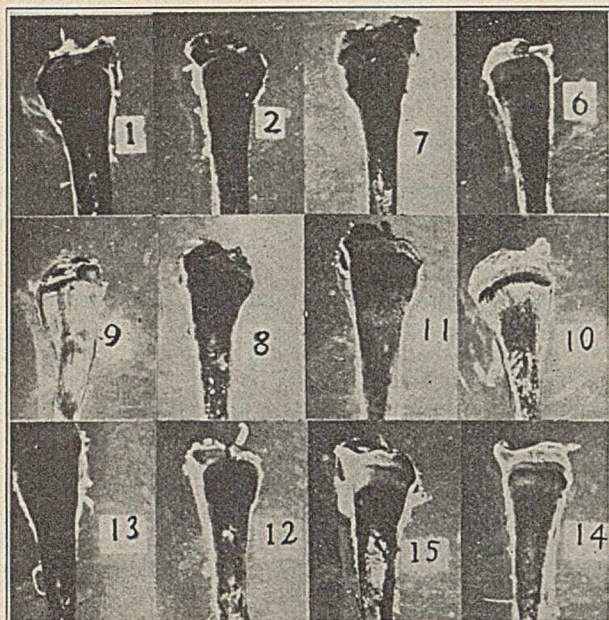


Figure 6—Chick Tibiae at 3 Weeks

various pens were discernible by the end of the third week. As the experiment progressed the differences in calcium metabolism became more pronounced. At the termination of the experiment it was quite evident that the calcification in birds from the pens receiving cod-liver oil was greater than in the corresponding control pens. In those pens receiving rations which contained approximately five times as much calcium as phosphorus, regardless of whether oil was added or not, the birds did not grow, feather so well, or show so satisfactory calcification of tibiae as when the ratio of calcium to phosphorus was lower.

Table VI—Results of Histological Examination (Calcification)

PEN	At 3 WEEKS	At 6 WEEKS	At 9 WEEKS
1	Irregular	Poor	Poor
2	Abnormal	Abnormal	Normal
6	Poor	Nearly normal	80% of birds normal
7	Poor	Very poor	Poor
8	Normal	Abnormal	Normal
9	Poor	Poor	Poor
10	Normal	Normal	Normal
11	Very poor	Poor	Very poor
12	Poor	80% of birds normal	Poor
13	Extremely rachitic	Very poor	Very poor
14	Normal	60% of birds normal	80% of birds normal
15	Abnormal	Poor	Poor

Influence of Cod-Liver Oil on Nutritive Efficiency of Experimental Rations

Coincident with the rate of growth and bone development obtained with the different experimental rations, it is of interest to consider the nutritive efficiency of the various rations as indicated by the amount of feed required to produce equivalent increase in body weight of the chicks in the various experimental pens. This factor has been computed by dividing the average per-chick food consumption for 9 weeks by the average per-chick weight at the end of the ninth week. The results obtained in this manner are given in Table VII.

From these data it will be noted that the least amount of feed required per pound of body increase was for pens 2, 6, and 10. These chicks grew the fastest, were the best feathered, presented the best appearance, and had the most satisfactory bone development. They all received 1 per cent of cod-liver oil in rations which had a calcium-phosphorus ratio of about 1.5 to 1.0. The control pens—1, 7, and 11—contained chicks that weighed less than 1 pound at 9 weeks of age and thus were of no practical value. Nevertheless, the control birds required about 1½ pounds more feed per

pound of body increment than was necessary for the experimental birds. The chicks in pens 8, 12, and 14, which received cod-liver oil, required practically the same amount of feed as the control birds in pens 9, 13, and 15 to produce a pound of increase in body weight. The rations fed to these six pens contained approximately 4 per cent of calcium and the ratio of calcium to phosphorus was approximately 5 to 1. From this it appears that when calcium is fed under these conditions, whether it be as calcium carbonate, oyster shells, or limestone, cod-liver oil does not increase the nutritive efficiency of the ration to the same extent as when the calcium content of the ration is lower and when the calcium-phosphorus ratio is approximately 1.5 to 1.0.

Table VII—Efficiency of Rations for Increasing Body Weight

PEN	AV.	AV.	FEED REQUIRED
	FEED CONSUMED	BODY WEIGHT	TO PRODUCE 1 LB.
	FIRST 9 WEEKS	AT 9 WEEKS	OF CHICK
	Lbs.	Lbs.	Lbs.
1	4.11	0.84	4.90
2	6.48	1.91	3.40
6	6.18	2.05	3.00
7	3.43	0.74	4.64
8	5.73	1.41	4.06
9	5.58	1.40	3.98
10	6.84	2.05	3.33
11	4.17	0.96	4.34
12	5.25	1.37	3.88
13	4.99	1.16	4.30
14	6.44	1.58	4.06
15	6.22	1.50	4.14

These results are more or less in accord with those obtained in other studies of factors influencing the metabolism of calcium by young chicks. However, it is not possible to make close comparisons of the results of various investigations, since the rations and experimental conditions were not uniform.

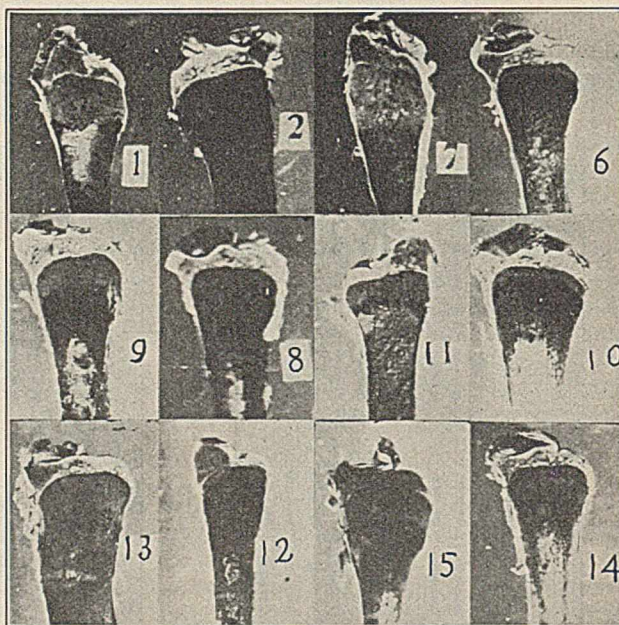


Figure 7—Chick Tibiae at 6 Weeks

Kennard, Holder, and White (7) found calcium efficiently utilized by the growing chick when it was added to the ration as carbonate or phosphate. Buckner and Martin (3) found that calcium carbonate, calcium sulfate, and tricalcium phosphate serve equally well as sources of calcium for the growing chick. Buckner, Martin, and Insko (4) fed a basal ration of yellow corn 80, wheat middlings 20, skim milk 20, salt 1, cod-liver oil 2, and found that the chicks receiving calcium-phosphorus supplements developed larger bones than those birds which received calcium supplements that

did not supply phosphorus. In a later paper these authors (5), using a similar basal ration supplemented with varying amounts of limestone, raw bone meal, or both, concluded that raw bone meal is equally good, if not better, than raw bone meal and limestone as a source of calcium for supplementing the basal ration used.

The Ohio Agricultural Experiment Station (9) has reported a study in which white Leghorn chicks were fed a basal ration of yellow corn meal 62, middlings 25, casein 10, salt 1, cod-liver oil 2, supplemented by calcium from calcium carbonate, calcium sulfate, calcium lactate, tricalcium phosphate, dicalcium phosphate, raw rock phosphate, raw bone meal, spent bone black, ground limestone, bone ash, and precipitate bone flour. The best growth was obtained from either tri- or dicalcium phosphate, raw bone meal, spent bone black, or bone ash—that is, supplements containing phosphorus.

These observations of Buckner and his associates and the Ohio station—that better growth and bone development were obtained from calcium supplements containing phosphorus than with the calcium supplements that did not contain phosphorus—are in agreement with the results obtained in the present experiments. When calcium, supplied by calcium carbonate, tricalcium phosphate, powdered oyster shells, or powdered limestone, was fed at an approximately 4 per cent level supplemented by cod-liver oil, decidedly better growth and bone development were obtained with the tricalcium phosphate than with the other supplements which did not supply phosphorus.

Massengale and Platt (8), using a ration containing a wide variety of constituents, found that *c. p.* calcium carbonate was not so efficient a source of calcium supplements as calcium carbonate in the form of oyster shells or limestone. This conclusion is not in agreement with the results of the present writers. From the data obtained for pens 8 and 9 (calcium carbonate), pens 12 and 13 (powdered oyster shells), and pens 14 and 15 (powdered limestone) it will be noted that all pens received calcium at approximately 4 per cent level but that the birds that received calcium carbonate were definitely superior to those receiving powdered oyster shells and slightly inferior to those receiving powdered limestone.

Bethke, Kennard, Kick, and Zinzalian (2) fed white Leghorn chicks yellow corn 70 parts, wheat middlings 17, meat meal 12, and salt 1. They concluded that:

Within certain limits of concentration the ratio of calcium to phosphorus is of greater significance in calcification and growth than the amounts of these elements in the ration. The addition of vitamin D, or its equivalent, to the ration or environment of a chick makes possible a greater variation in the Ca:P ratio and concentration without seriously interfering with growth and normal bone formation. The optimum, or near optimum, ratio of calcium to phosphorus for the growing chick lies between 3:1 and 4:1. The requirements for the antirachitic factor are at a minimum at this relationship.

In connection with these conclusions it may be noted that in all instances the chicks showed somewhat subnormal growth, since when they were 8 weeks of age they weighed only about $\frac{3}{4}$ pound, whereas in the experiment here reported the chicks in those pens considered as making satisfactory growth averaged approximately two and one-fourth times this weight or about 1.7 pounds.

In a later study using a similar ration, Bethke, Kennard, and Kick (1) determined the relative utilization of calcium from the carbonate, sulfate, lactate, and phosphate salts. They found that calcium was equally available from these sources. However, the average weight of the chicks fed these different supplements was not optimum, since the chicks averaged less than $\frac{3}{4}$ pound at 8 weeks of age.

In an investigation conducted simultaneously with those

of Bethke and associates, Hart, Scott, Kline, and Halpin (6) fed white Leghorn chicks a basal ration of yellow corn 74 parts, skim milk 25, and salt 1. They found that the optimum calcium-phosphorus ratio for growing chicks with respect to both growth and calcification lies between 2.0 to 1.0 and 4.0 to 1.0, and that with a minimum supply of vitamin D the optimum calcium-phosphorus ratio is more limited than with an adequate supply. However, they did not find a ratio and level of calcium-phosphorus in their experiment whereby both growth and calcification in the absence of supplementary vitamin D were equal to those obtained when it was

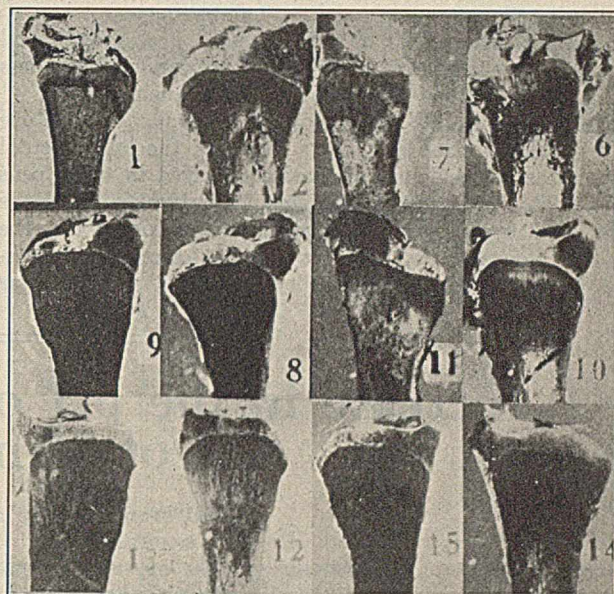


Figure 8—Chick Tibiae at 9 Weeks

present. In considering their conclusions it should be noted that their chicks were apparently of subnormal growth, since the average weight for the chicks of the various pens was, with one or two exceptions, less than $\frac{1}{2}$ pound at 6 weeks of age.

It is not easy to ascertain the cause of the greater growth of the chicks studied by the writers. The rate of growth of baby chicks is influenced by many factors—the inherited capacity to grow, the breed, the temperature and humidity of the brooder room, the nature of the ration (all-mash type, no freedom of choice, or the freedom of choice type), the number of chicks per pen, the amount of floor space allowed each chick, and particularly the quantity and biological value of the proteins in the ration. In selecting the ration for the experiments reported here, an attempt was made to duplicate to some extent the “starting” and “growing” rations used in actual feeding practice, and reference to the composition of the ration reveals that it contained a wider variety of proteins from animal and vegetable sources than that of the rations in the investigations noted. Hence the results obtained in the various calcium studies cited are not susceptible of close comparison. Furthermore, this situation will continue to exist until at least the larger portion of the factors which influence the results of chick experiments are standardized.

Summary

The investigation discussed above was undertaken to determine the influence of cod-liver oil on calcium metabolism in young chicks when supplementary calcium was obtained from different sources, fed at different levels and was available in different ratios to phosphorus.

Four hundred and thirty vigorous, day-old Rhode Island Red chicks were divided into twelve comparable pens and fed a typical all-mash poultry ration which had been prepared under commercial conditions. Data were collected concerning rate of growth and bone development as indicated by length, diameter, weight, ash, calcium and phosphorus content of tibiae removed from typical birds when 3, 6, and 9 weeks old.

The best growth, 2 pounds at 9 weeks, was obtained in pens receiving cod-liver oil as a supplement to rations containing from 1 to 4 per cent calcium and having a maximum calcium to phosphorus ratio of 1.5 to 1.0. Other rations containing 4 per cent of calcium, but having a calcium to phosphorus ratio of 5.0 to 1.0, produced poor growth and unsatisfactory feathering and physical appearance regardless of whether or not cod-liver oil was added to the ration.

Judged by chemical and histological examination of tibiae of test chicks, killed at various stages of the experimental period, the best calcium utilization occurred in those pens receiving cod-liver oil as a supplement to rations in which the ratio of calcium to phosphorus was relatively low; where the ratio of calcium to phosphorus was 5.0 to 1.0 calcium utilization was decidedly unsatisfactory. Even when there was

little difference in the growth of experimental birds and corresponding controls, chemical and histological examination of the tibiae showed that with a calcium to phosphorus ratio of 5.0 to 1.0 calcium was better utilized by birds receiving cod-liver oil than by corresponding control birds.

On the basis of the data obtained in this investigation, it is apparent that cod-liver oil is very effective in promoting calcium utilization when calcium comprises 1 to 4 per cent of a typical all-mash poultry ration and when the ratio of calcium to phosphorus in the ration is low. It was found to be less effective in promoting calcium metabolism when the ratio of calcium to phosphorus was 5.0 to 1.0, even though the calcium content of the ration did not exceed 4 per cent and the calcium was obtained from a variety of sources.

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Increase in the pH of the White and Yolk of Hens' Eggs¹

Paul Francis Sharp and Charles Kelly Powell

DEPARTMENTS OF DAIRY INDUSTRY AND POULTRY HUSBANDRY, CORNELL UNIVERSITY, ITHACA, N. Y.

THE importance of the hydrogen-ion concentration in determining the rate of denaturation and hydrolysis of proteins is beginning to be realized more clearly by investigators. As the H-ion concentration departs from the isoelectric region the rate of alteration of the protein increases. The pH is an important factor in controlling the rate of deterioration of eggs. The pH of the white was found to vary from pH 7.6 to 9.7, which is a rather marked departure from the isoelectric point of egg albumin, pH 4.7. The white becomes watery much faster at the high pH values and the yolk weakens much faster. Some of the relationships between keeping quality of eggs and pH have been discussed by Sharp (17).

Under normal conditions this marked change in pH is brought about by the escape of carbon dioxide from the egg. It is important to know the rate of escape of carbon dioxide and the corresponding change in pH, so that eggs may be handled in the light of this information to maintain the highest quality. While the carbon dioxide escapes fairly rapidly from unprocessed eggs, yet it escapes more slowly at the lower temperatures. If eggs are kept cool during the first few days, an added preserving effect is obtained, owing to the lower pH of the egg contents, and more carbon dioxide is retained to exert a preserving effect later. A pH of about 9.25 will be reached in 2 days at 37° C., in 5 days at 16° C., and in 10 days at 2° C. under well-ventilated conditions. If low temperatures are not available on the poultry farm, the eggs should be marketed and placed in refrigerated rooms with the loss of as little carbon dioxide as possible. If it is necessary to ship eggs at a relatively high temperature, they should be shipped on the day they are laid if possible, because a considerable preserving effect will be obtained before the escape of most of the carbon dioxide. After most

of the carbon dioxide has escaped, reliance must be placed mainly upon low temperatures.

Oil-dipping or processing is practicable for extensive commercial use and largely prevents the escape of moisture and carbon dioxide. If eggs are oil-dipped as soon as they are laid, the maximum preserving effect, on the yolk, of the natural carbon dioxide of the eggs is obtained. A better general condition of the white of oil-dipped eggs is obtained, however, if a little carbon dioxide is allowed to escape before oil-dipping. The thick white does not become so turbid, and it will be slightly greater in amount. If most of the carbon dioxide escapes before the eggs are oil-dipped, little preserving effect, aside from the prevention of the escape of moisture, is obtained.

Previous Work

Scholl (14) found that if the red color produced on the addition of phenolphthalein to egg white was discharged by the addition of acetic acid, it reappeared again on standing. This process could be repeated many times with the same result. He showed that fresh egg white contained considerable carbon dioxide, and concluded that the greater part was present as the bicarbonate. He bubbled carbon dioxide free-air through egg white and obtained 0.07688 per cent of carbon dioxide. After adding acetic acid to the egg white 0.1577 per cent was obtained.

Aggazzotti (2) concluded that before the egg is laid the liquid of the egg has a partial pressure of carbon dioxide corresponding to that in the tissues of the hen. When the egg is laid the air cell is formed and a part of the carbon dioxide passes into it.

Aggazzotti (1) reports observations on the pH of egg white and yolk during 32 days of storage at room temperature and during incubation. His data are of little value as indicating

¹ Received August, 22, 1930.

the true pH changes of the egg. Gueylord and Portier (10) determined the pH of the white and yolk during incubation. Their observations are more nearly in agreement with those of the writers but their experimental error is apparently very great. Healy and Peter (11) determined the pH of the white and yolk colorimetrically. They observed that the pH of the white rose from pH 8.2 to 9.6

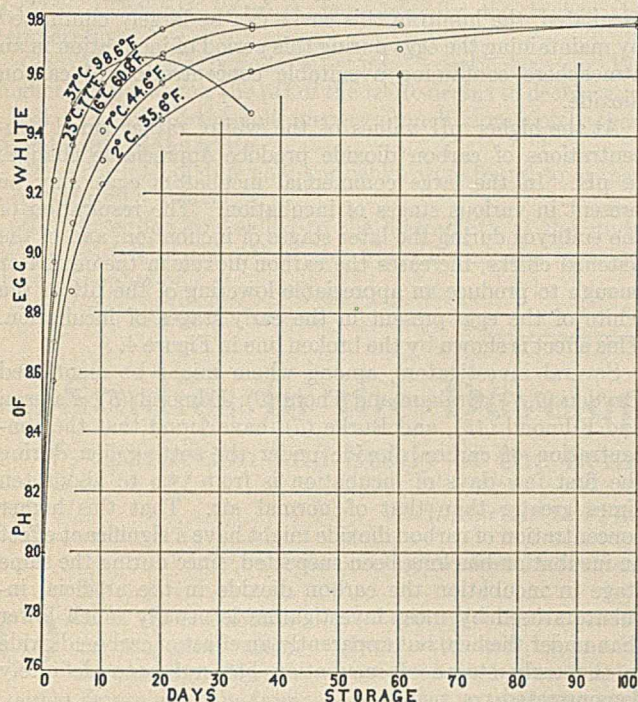


Figure 1—Change in pH of White of Hens' Eggs When Stored at Various Temperatures

soon after the egg was laid and that during incubation it decreased again. They reported that the yolk showed little change except a slight increase during incubation. Romanoff and Romanoff (13) confirmed the results of these earlier studies on the pH of incubated eggs. Healy and Peter explain the changes in the pH of the white as due to the bicarbonate buffer system and show that in the presence of carbon dioxide the pH of the white is decreased.

Wladimiroff (19) determined the pH of the white during incubation after it had been freed from carbon dioxide.

Schweizer (15, 16) and Baird and Prentice (4) studied the possibility of using the pH as a means of recognizing fresh eggs.

Increase in pH of Egg White When Held at Various Temperatures

Eggs were stored at different temperatures and examined at increasing intervals of time. They were placed in desiccator jars in which the humidity was regulated to a little below 80 per cent by means of a saturated solution of sodium chloride. A dish containing a few small pieces of soda lime was also placed in the jar to maintain a low level of carbon dioxide. The eggs were placed in the jars within 2 to 4 hours after they were laid. Three eggs from each jar were examined at the various time intervals. As soon as the egg was broken into a dish the white was pipetted into a test tube and immediately covered with mineral oil. The hydrogen-ion determinations were made at 25° C., using a Leeds and Northrup type K potentiometer and a modified Bailey (3) electrode. The pH determinations were made within at least 3 hours after opening the eggs and usually within a much shorter time. It is impossible by following

this procedure to prevent the loss of some carbon dioxide, so the value taken for the white of fresh eggs, pH 7.6, is probably too high.

The data obtained are plotted in Figure 1. This figure shows the very rapid increase in pH of the egg white with time, especially at the warmer temperatures. It is noted that at 37° C. the pH starts down again after several days; this is probably due to some actual breaking down of the constituents of the egg white and a change in the buffer system. This effect has been observed repeatedly and is in line with observations made by Tice (18) that the alkalinity as determined by titration decreases after long periods of storage. That a somewhat similar change is taking place in the white during incubation is indicated by the data of Wladimiroff (19), who freed the white from carbon dioxide before determining the pH. His data show that the pH of the white falls after the first 3 days of incubation even when the carbon dioxide is removed.

Table I—Change in pH of Egg White in Ordinary Air of Room at Different Storage Temperatures

(Each value is the average of four eggs.)

AGE OF EGGS	35° C.	25° C.	15° C.	10° C.	3° C.
Days	pH	pH	pH	pH	pH
0	7.60	7.60	7.60	7.60	7.60
1	9.00	8.89
2	9.18	9.05
3	9.32	9.18	9.04	8.95	8.98
5	9.44	9.33	9.34	9.26	9.18
7	9.50	9.39	9.28	9.26	9.16
10	9.47	9.37	9.44	9.27	9.25
14	9.49	9.46	9.52	9.47	9.41
17	9.46
21	9.37	9.38	9.48	9.46	9.42
28	..	9.36	9.47	9.43	9.42
56	..	9.25	9.43	9.37	9.48
94	..	8.95	9.26	9.41	9.49

This experiment has also been carried out by placing the eggs in the ordinary air of the rooms having various temperatures. The results obtained are presented in Table I, and are essentially the same as those in Figure 1, except that the change in pH was slightly less rapid and the highest pH values reached were near 9.5.

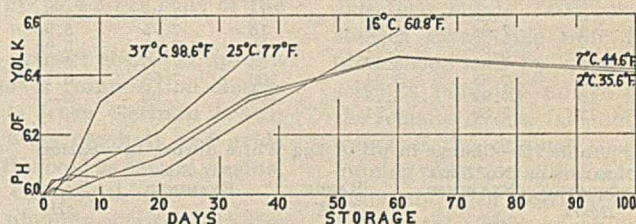


Figure 2—Change in pH of Yolk of Hens' Eggs When Stored at Various Temperatures

Increase in pH of Egg Yolk When Held at Various Temperatures

The fresh egg yolk is quite viscous and consequently is difficult to saturate with hydrogen. A dilution of the yolk with water would overcome this difficulty. In order to determine the effect of dilution, the yolks of several fresh eggs were mixed and increasing amounts of water were added to 10-cc. portions and the pH was determined. At the same time the effect of dilution on the pH of the white was determined. The results are given in Table II. Apparently dilution has very little effect on white of this pH. The higher dilutions caused a slight increase in the pH of the yolk. The data indicate that no appreciable error would be involved if the pH determinations were made on a 1 to 1 dilution of the yolk with distilled water, and the result assumed to be the pH of the undiluted yolk.

The average pH of the yolks of fresh eggs is 6.00 or slightly below. Figure 2 represents the increase in the pH of the yolks of the same eggs examined for the data in Figure 1. The pH of the yolks increased more rapidly at the higher

temperatures, but the change in pH was not so great nor so rapid as in the case of the white. The pH values obtained with yolks of eggs subjected to different treatments show proportionately greater variation than do the whites. The pH of the yolk is a better index of the unfavorable treatment of the egg than is the pH of the white.

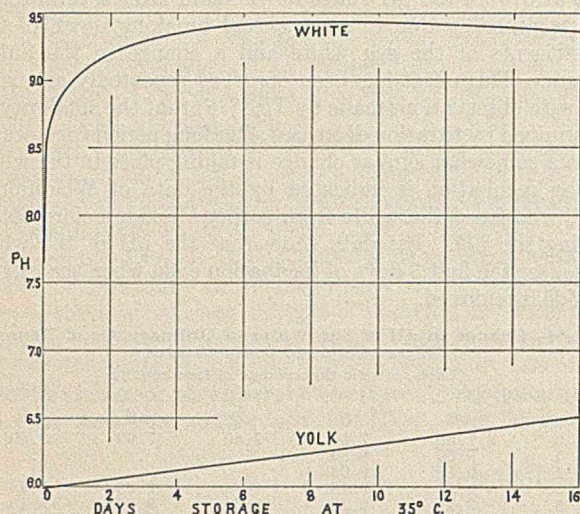


Figure 3—Difference in pH and Rate of Change in pH of White and Yolk

In Figure 3 are plotted the results obtained in another experiment in which eggs were stored in ordinary air at 35° C. This figure gives a good graphical representation of the great difference in pH of the white and yolk and their comparative rates of change.

Table II—Effect of Dilution on pH of Egg White and Egg Yolk (Each value is the average of four experiments.)

WATER ADDED TO 10 cc.			WATER ADDED TO 10 cc.		
Egg Cc.	WHITE pH	YOLK pH	Egg Cc.	WHITE pH	YOLK pH
0	7.82	5.93	14	7.92	5.96
2	7.88	5.89	16	7.95	5.95
4	7.86	5.91	20	7.89	5.96
6	7.95	5.92	50	7.95	6.07
8	7.88	5.94	100	7.93	6.12
10	7.92	5.95	200	7.93	6.23
12	7.89	5.94			

Table III—Change in pH of Egg White during Incubation

DURATION OF INCUBATION Hours	No. EGGS EXAMINED	RANGE pH	No. EGGS EXAMINED	RANGE pH
0	..	7.60
6	4	8.50-8.60
18	12	8.83-9.02
30	11	9.00-9.20
43	6	9.20-9.30
53	5	9.28-9.35
72	7	9.10-9.25
FERTILE EGGS				
77	4	9.00-9.15	1	9.48
96	12	8.5-9.18	2	9.3-9.35
117	6	8.15-8.75	7	9.3-9.5
168	6	7.75-8.20	1	9.43
INFERTILE EGGS				

Changes in pH of White during First Few Days of Incubation

Results typical of those obtained in a small commercial incubator are given in Table III. The incubator used was electrically heated and of about 100-egg capacity. It will be observed that up to the third day the values obtained for the eggs examined all fall within a very narrow pH range, but from that point on a distinct difference appears between the fertile and infertile eggs. The pH of the infertile eggs remains high while that of the fertile eggs decreases. At the fourth day there is a considerable spread in pH among the fertile eggs. This is probably due to a variation in the extent of development of the embryos in the different eggs.

The difference between the fertile and infertile eggs is

shown more clearly in Figure 4. It was found in other experiments that the pH of the white exerted a marked influence on the permeability of the yolk membrane and it would be of scientific interest at least to see how a decrease in the pH of the white during this early stage of incubation would affect the developing embryo. Since the pH of the white during this period of incubation is controlled by the carbon dioxide concentration of the atmosphere in which the egg is incubated, the hump in this curve can be largely eliminated by maintaining the eggs during this period of incubation in an atmosphere containing a suitable concentration of carbon dioxide.

At the higher pH values of the white, rather small concentrations of carbon dioxide produce appreciable changes in pH. In the large commercial incubators eggs may be present in various stages of incubation. The respiration of the embryos during the later stages of incubation, and of the hatched chicks, increases the carbon dioxide in the incubator enough to produce an appreciable lowering of the pH of the white of the eggs present in the early stages of incubation. This effect is shown by the broken line in Figure 4.

Several investigators, among whom might be mentioned Dryden (6, 7), Graham and Thom (9), Edmond (8), Lamson and Edmond (12), and Burke (5), have found that the concentration of carbon dioxide under the setting hen during the first few days of incubation is from two to about ten times greater than that of normal air. That this higher concentration of carbon dioxide might have a significant effect on incubation has long been suspected, since during the same stage in incubation the carbon dioxide in the artificial incubators used by most investigators is usually much lower than under the hen, but apparently an effect of carbon dioxide in the early stages of incubation has not been definitely demonstrated.

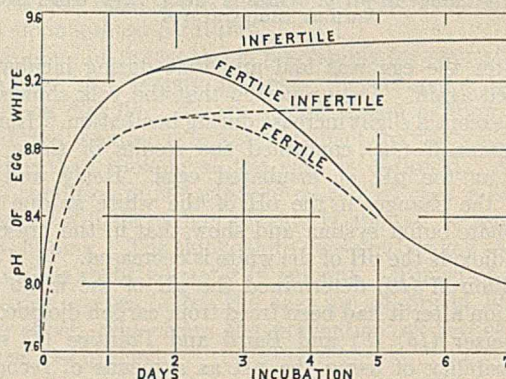


Figure 4—Change in pH of White of Fertile and Infertile Eggs during First Few Days of Incubation

Solid lines represent results obtained with a small incubator in which eggs were added at one time. Broken line represents results obtained in a large commercial incubator in which eggs were present in all stages of incubation.

It was found that embryos were able to develop, for 6 days at least, in a concentration of carbon dioxide sufficiently high (about 5 per cent) to prevent the white from going above pH 8.0.

Equipment was not available adequately to control the other factors involved in incubation, so a conclusion as to the effect of the control of the pH on the first few days of incubation was not justified.

It is possible that the majority of eggs which are candled out of an incubator as infertile are not actually infertile but are eggs in which the embryo died before its growth could be detected before the candle. It is possible that decreasing or eliminating the hump in the curve in Figure 4 may exert a favorable influence on the number of embryos which survive the first few days of incubation.

The holding of eggs for incubation in a sealed glass jar has been recommended and may be of advantage because the pH of the white may be kept down to about 8.0-8.2.

Summary and Conclusions

(1) The pH of the white of untreated eggs rises very rapidly after the eggs are laid, owing to the escape of carbon dioxide. The pH increases more rapidly the higher the temperature.

(2) After long periods of storage, particularly at the higher temperatures, the pH of the white begins to decrease.

(3) The pH of the yolk increases much more slowly than does the pH of the white.

(4) The pH of the yolk and white were found to change very little on dilution.

(5) Attention was called to the desirability of the study of the control of the pH of the white during the first few days of incubation.

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Studies in the Development of Dakota Lignite V—Extraction and Study of the Benzene-Soluble Portion of Dakota Lignite^{1,2}

E. E. Harris,³ C. F. Belcher, and A. W. Gauger⁴

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH DAKOTA, GRAND FORKS, N. DAK.

ONE of the characteristic properties which distinguishes North Dakota lignite not only from other ranks of coal, but from other lignites or "brown coal" as well, is the low tar yield given upon destructive distillation. In connection with an investigation of the possibility of making a coherent coke from this lignite it became advisable to study the tarry substances present in the original material.

Previous Work on Coal Extraction

According to Francis and Wheeler (16) coals can differ from each other in respect to both the proportions and the properties of the constituents, but there is some evidence

that the chemical compositions of the free hydrocarbons, resinous compounds, and organized plant entities (spore exines and cuticular tissues) do not vary greatly whether those constituents form part of a lignite, a bituminous coal, or a semi-anthracite. The composition of the ulmin compounds (resulting from the decay of vegetable tissues) does vary

Lignite from the Velva deposit in North Dakota has been extracted by the method of Bone and a study made of the benzene-soluble portion. For comparison purposes extractions by the Fischer method are also reported.

Benzene used under pressure, as in the apparatus described, has a considerable solvent action on Velva lignite, and extracts at least up to 4.3 per cent of the dry, ashless coal substance.

At least that portion of the extract obtained up to a pressure of 17 atmospheres has a composition closely analogous to the montan wax from German brown coal. It was resolvable into waxy alcohols and acids (some of which are present in the coal as esters), resins, and compounds of unknown composition.

It seems probable that any phenols occurring in the portion of the extract obtained at pressures higher than 17 atmospheres are the result of some breakdown or thermal decomposition of the Estevan. Assuming that Bone (5) did not have decomposition of his lignite during the extraction, then Velva lignite differs from the Estevan in that the acidic portion of the benzene extract consists of aliphatic acids instead of phenols.

widely, according to the coals from which they are obtained.

Extraction with solvents has found extensive application as a means of determining the composition of coals and their origin. The substances extractable from a bituminous coal by organic solvents normally contain the remains of oils, fats, and waxes of the original coal-forming plants, in addition to resins and their degradation products. This extract is often erroneously classed as the resinous portion.

Bedson (2) first suggested pyridine as a solvent for resolving the coal conglomerate. Clark and Wheeler (9) resolved bituminous coal into alpha, beta, and gamma com-

pounds: alpha insoluble in pyridine, beta soluble in pyridine but insoluble in chloroform or benzene, and gamma soluble in chloroform and pyridine. Pearson (21) also supports pyridine as a mechanical solvent for the colloidal mass of coal.

Cockram and Wheeler (10) used a similar procedure. They also resolved the gamma constituents further into gamma^I, II, III, IV fractions by means of light petroleum ether and acetone, respectively. Gamma^I consists mainly of saturated and unsaturated hydrocarbons; gamma^{II} mainly of resins and resin degradation products; gamma^{III} and gamma^{IV} of resin-like substances, soluble and insoluble in acetone but similar in character.

Bone (4) used a pyridine-amyl alcohol mixture for extracting and isolating the resins in bituminous coal.

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² This material was presented by C. F. Belcher in partial fulfillment of the requirements for the degree of master of science, University of North Dakota.

³ Associate professor of organic chemistry, University of North Dakota.

⁴ Director, Division of Mines and Mining Experiments, University of North Dakota.

Pyridine extracts a larger percentage of the coal substance than other solvents, but it is quite probable that it has other effects than mere solvent action. Fischer and Gluud were the first to apply benzene pressure extraction to coal as a means of increasing the yield of extract. In work on brown coal (from Fabrik Webau der Riebeck'schen Montan Werke A.-G.) Fischer obtained a 11 per cent yield with a Soxhlet extractor at atmospheric pressure, whereas another sample of the same coal when extracted successively four times with benzene under pressure yielded 25 per cent of extract. The first extract represented essentially the montan wax of commerce.

Montan wax, according to Schneider and Tropsch (24), consists of a mixture of carboceric and montanic acids both free and esterified with tetracosanol and ceryl and myricyl alcohols. When heated to about 200° C. the wax begins to decompose, yielding solid and liquid hydrocarbons. Schneider and Tropsch also found that benzene-pressure extraction gave an importantly higher yield of montan wax.

The extractions made by Fischer and Gluud (15) were carried out in a steel bomb capable of withstanding a pressure of 200 atmospheres. Each charge of coal (1 to 2 kg.) was broken to the size of hazel nuts and extracted with 3 to 3.5 liters of benzene, heat being applied to the bomb externally by means of a powerful triple burner surrounded by a sheet of iron. The temperature was gradually raised to 275° C. corresponding to a pressure of about 55 atmospheres, and maintained at such degree for an hour, after which the heat was cut

off and the bomb allowed to cool slowly. Each sample of coal was repeatedly extracted in this manner, usually four to five times. The resulting benzene solution, which had a strong greenish fluorescence in reflected light and a dark port-wine color when viewed in thin layers by transmitted light, was distilled on the water bath and the residual extract weighed.

Fischer (13) extracted bituminous coal with benzene under pressure at 250° C. and obtained an extract which he divided into two main components by means of petroleum ether—one soluble, termed "oily bitumen," and the other a solid brown, insoluble substance, termed "solid bitumen." Fischer ascribes the coking quality of a coal to the oily bitumen, which consists apparently only of hydrocarbons. (In mineralogy the term "bitumen" includes all natural substances which contain notable proportions of hydrocarbons.) Fischer, Broche, and Strauch (14) have suggested that with increasing geological age of the coals the ratio of free hydrocarbons to resins increases while the decomposition temperature of the resins is raised.

Bone, Pearson, and Quarendon (6) have improved upon the Fischer apparatus by constructing a bomb which operates on the Soxhlet principle. A comparison of yields by the two methods by Bone on a strongly coking Durham coal gave a total extract of 12.4 per cent with the Fischer type of bomb and 15.6 per cent with the Soxhlet type bomb.

The benzene extract from bituminous coals was resolved

into four fractions by means of light petroleum and ethyl alcohol: fraction I a yellow-brown, non-nitrogenous portion soluble in light petroleum; fraction II, a nitrogenous, red-brown solid of low softening point, soluble in a mixture of 4 parts of light petroleum and 1 part benzene; fraction III, a non-nitrogenous resinous portion soluble in ethyl alcohol; and fraction IV, a group of nitrogenous bodies of humic type, insoluble in ethyl alcohol.

Morwell brown coal (Australia) when extracted by this method yielded about 15 per cent of extract. Owing to the different nature of this extract, another method of resolution was employed which separated it into acidic, saponifiable, and neutral portions. By treating the benzene solution with 5 per cent aqueous solution of potassium hydroxide in the cold, the solution was divided into acidic and non-acidic portions. The non-acidic benzene-soluble portion was also refluxed with alcoholic potash and a small amount of esters saponified. Bone (6) classes these portions from Morwell brown coal as (a) non-acidic and unsaponifiable resene-like portion, (b) resene ester portion, and (c) aliphatic or alicyclic portion. Later Bone, Horton, and Tei (5) in the resolution of Morwell brown coal and Estevan lignite (Saskatchewan, Canada) extracts, obtained by the Soxhlet type benzene pressure apparatus, state that between 50 and 60 per cent of the extract was phenolic in character (and resolvable into phenol, para-cresol, and catechol) and about 40 per cent was neutral oils. This work of resolution, in so far as it refers to Morwell brown coal, seems to contradict Bone's previous analysis, for in the earlier paper the content of polyhydroxy phenols from the Morwell coal was reported as almost negligible (6, p. 624).

Preparation of Lignite Samples

In the work at North Dakota lignite was used from the Velva deposit (near Minot, N. Dak.), which the authors believe should be comparable to the Estevan lignite since it is apparently of the same geological age.

The lignite samples were ground and screened and the 20–40 mesh portion was air-dried for 24 hours and then oven-dried for 1 hour at 105° C. They were then sealed in mason jars until ready for use. Moisture and ash determinations were made upon opening for use.

Extraction

APPARATUS—The apparatus (Figure 1), which is essentially the same as that used by Bone (5), consists of a chrome-vanadium steel container, *A*, 60.96 cm. inside depth and 7.62 cm. inside diameter, of about 3 liters capacity, the lower half containing the solvent, and is heated electrically by a coil of nichrome wire wound on an alundum cylinder, *B*, of 7 inches (17.8 cm.) diameter. The cup, *C*, is equipped with a Soxhlet siphon tube and has a screened false bottom about an inch above the actual bottom. This cuplike bottom is screwed on and can be detached to remove accumulations of powdered coal which may tend to clog the siphon tube. This cup is attached to a head, *H*, which is held in place by a threaded collar, *E*, the joint being made tight by a lead gasket. To the head *H* in turn are attached the pressure gage, *F*, and one end of the closed steel condenser, *D*; the other end of the condenser attaches to an opening in the side of the cylinder. The vapor of the hot solvent ascends the condenser tube from this opening, is condensed in passing downward through the coil, and the resultant liquid falls upon the coal in the siphoning cup, *C*. The heating unit can be adjusted to give varying pressures up to 750 pounds per square inch (about 50 atmospheres).

PROCEDURE—The siphoning cup was charged with 200–250 grams of the dried and sized lignite, about 1 liter of pure,

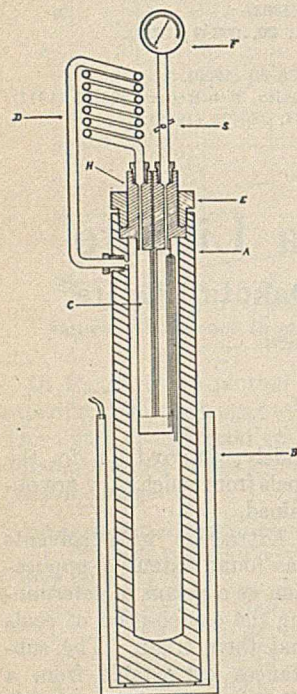


Figure 1—Pressure Extractor

dry benzene was added and the apparatus evacuated (attachment being made at the valve *S*) and then filled with nitrogen at atmospheric pressure. The extraction was allowed to proceed in successive stages over periods of 5 to 8 days at pressures of 10 to 44 atmospheres (corresponding to temperatures of about 180° to 280° C.). At the end of each stage the solution therein was removed and replaced by fresh solvent. Most of the extract was obtained during the first stage. The extractions were continued until the amounts of the resulting extracts were negligible.

By closing the opening on the side of the container and replacing the Soxhlet type head with a head to which was attached a copper gauze container having a capacity of about 1200 grams of coal, the apparatus was readily transformed into the type of extractor employed by Fischer and Gluud (15). Extractions were made by the Fischer method at an average pressure of 10 atmospheres and were continued until 100 grams of the solvent-free extract had been accumulated for resolution.

DATA—The results of the extraction by the two methods are given in Tables I and II.

Table I—Extraction of Dakota Lignite by Fischer Method

SAMPLE	WT. OF DRY, ASHLESS COAL		NO. OF EXTRACTIONS	WT. OF SOLVENT-FREE EXTRACT		PRESSURE Atm.
	Grams			Grams		
A	791.5		1 ^{a,b}	6.53		
			2	5.91		10
			3	2.19		10
			4	1.36		10
				15.99 (2.0%)		
	682.8		1 ^a	13.26		
			2	3.53		
			3	1.54		
			4	0.97		
				19.30 (2.8%)		Av. 10
	778.5		1	14.81		
			2	5.21		
3			1.75			
4			0.95			
			22.72 (2.9%)		Av. 10 ^c	
B	681.6		1	9.92		
			2	1.44		
			3	0.65		
				12.01 (1.8%)		Av. 10 ^c

^a A small amount of water came off with the first extract probably due to insufficient drying.

^b Low pressure due to a slight leak in the head.

^c No water or excess gas pressure was noted.

Table II—Extraction of Dakota Lignite by Bone Method

SAMPLE	NO. OF EXTRACTIONS	TIME Days	PRESSURE		WT. OF DRY ASHLESS COAL Grams	WT. OF SOLVENT-FREE EXTRACT Grams
			Lbs.	Atm.		
A	1 ^a	6	125-150	8.3-10.0	189.2	4.40
	2 ^a	7	125-150	8.3-10.0		0.44
						4.84 (2.55%)
A	1 ^b	7	125-150	8.3-10.0	190.9	Siphon plugged
	2 ^b	6	100-125	6.7-8.3		3.08
	3 ^b	7	150-175	10.0-11.7		0.70
						3.78 (1.98%)
A	1	8	250-275	16.7-18.3	194.3	6.53
	2	6	250-275	16.7-18.3		0.21
						6.74 (3.47%)
B	1 ^b	7	150-175	10.0-11.7	217.8	4.05
	2 ^b	7	150	10.0		0.16
	3 ^c	5	550	36.7		1.02
	4 ^b	6	650	43.7		2.95
	5 ^b	6	650	43.7		1.28
						9.46 (4.3%)

^a Small amount of gas but no water observed.

^b No gas or water noted.

^c Considerable gas and small amount of water.

Though the fourth and fifth extractions of sample B by the Bone method showed no excess gas pressure or water, the third, fourth, and fifth extractions had a characteristic odor of phenols and responded to the qualitative tests of Liebermann and Hoffman (1). The fifth extract was golden brown and from the trend of yields it seems probable that the yield of extract would have been greater if the extraction had been carried further.

Treatment of Benzene Extract

The benzene extract, which had a greenish fluorescence when viewed by reflected light and a golden brown color by transmitted light, was freed from the solvent by distillation over a water bath under diminished pressure toward the last. The residual extract was dried in the atmosphere for several hours and then weighed.

The extract was then redissolved in benzene and treated with an aqueous solution of potassium hydroxide (5 per cent) according to the method of Bone (6) on Morwell brown coal and Estevan lignite. A light brown precipitate was formed immediately, some of which settled in the aqueous layer but much of which remained suspended and finally formed a layer between the aqueous portion and the benzene. The benzene containing the soluble substances was drawn off from the top, but owing to the formation of an emulsion even after several weeks only a little more than half of the benzene solution had been recovered. By treatment of the mixture with additional benzene more of the benzene-soluble substances were recovered. Undoubtedly, however, some benzene-soluble substances still remained, but in order to remove the solvent remaining in emulsion the mixture was steam-distilled. After this removal of the benzene the deep brown to black alkaline solution remained.

The benzene-soluble portion was refluxed for 8 to 10 hours three times with alcoholic potassium hydroxide (2 per cent) to saponify any esters present; after each period of refluxing it was washed with water to remove the alkali-soluble portion. A small amount of brownish substance was thus removed and added to the aqueous alkali-soluble portion. The benzene-soluble portion was then placed on the water bath and the solvent removed, whereupon the residue when cool set to a deep reddish brown solid of resinous odor. The extract was thus roughly divided into 50 to 55 per cent alkali-soluble and 45 to 50 per cent benzene-soluble portions.

Treatment of Alkali-Soluble Portion

In the belief that the alkali-soluble portion must consist of phenols, as had been reported by Bone (5) in the extract from Estevan lignite, qualitative tests were applied but were negative.

When the alkaline solution was acidified with hydrochloric acid a light brown, gelatinous precipitate appeared, which when washed and dried in the atmosphere gave a light brown powder. This powder was found to melt from 80° to 85° C. and on cooling solidified to a hard, brittle cake. Since it was found to be acidic, it was suspected that it might be the so-called montanic acid or wax which Lewkowitsch (19) states melts at 80-86° C., his sample having been obtained from Thuringian (German) lignite. Fischer (15) and Schneider and Tropsch (24) have obtained montan wax from Rhenish brown coal by benzene extraction under pressure, and from this they isolated carboceric and montanic acids, along with tetracosanol, ceryl, and myricyl alcohols.

Fractionation of Acidic Mixture with Ether and Acetone

The brown cake was removed from the liquid and dried, first on the steam bath and then in air. It was then placed in a Soxhlet and exhaustively extracted successively with ether and acetone, according to the method of Pschorr and Pfaff (22).

	YIELD FROM 19.3 GRAMS SUBSTANCE		YIELD FROM 11.0 GRAMS SUBSTANCE	
	Grams	%	Grams	%
Ether extract	10.36	53.7	6.96	63.2
Acetone extract	4.12	21.3	1.51	13.7
Residue	4.82	25.0	2.53	23.1

The ether extract was a viscous, chocolate-brown mass when warm and a hard, brittle cake when cool. The solvent was re-

moved by drying strongly on the water bath. The acetone extract was of similar color, viscous when warm, but setting to a crumbly cake when cool. The residue was light brown to gray and readily crumbled to a powder when touched.

Saponification of Fractions

The fractions were next separately saponified by refluxing for a period of 5 to 6 hours on the water bath with a mixture of three-fourths alcohol and one-fourth benzene and one-fifth their weight of solid potassium hydroxide. Calcium chloride, double the weight of the potassium hydroxide, was then added and the mixture refluxed 2 hours longer. This converts the potassium salts of the acids to the calcium salts which are insoluble in acetone.

Part of the solvent was then evaporated on the water bath and the thick, flowing mass poured into hot water. That which adhered to the flask upon cooling was scraped loose and added to that in the hot water. The dark brown mass finally collected as a cake on the surface of the water when cool. It was removed and dried strongly on the steam bath, after which it was placed in a Soxhlet and exhaustively extracted with acetone to remove the alcohols and unsaponifiable material. From 17.32 grams of the ether fraction 2.64 grams of alcohols and unsaponifiable compounds were extracted; 5.63 grams of the acetone fraction yielded only 0.68 gram of alcohols and unsaponifiable compounds; 7.36 grams of the residue yielded 1.14 grams of alcohols and unsaponifiable compounds. It appears that the ether and acetone extractions merely concentrated the unsaponifiable portion.

Treatment of Alcohols and Unsaponifiable Compounds

The crude mixture of alcohols and unsaponifiable compounds was acetylated by warming on the water bath under a reflux condenser with four times its weight of acetic anhydride for 2 hours. The mixture was then poured into water and warmed a half-hour on the water bath with stirring to remove the excess of acetic acid. After cooling, the cake was separated from the water and without drying was put into a large amount of alcohol. This dissolved the acetate but left most of the resinous substances undissolved. The alcoholic solution was decanted off and boiled with animal charcoal to decolorize, and then filtered through a hot filter. As the alcoholic solution cooled the acetate separated out in tiny needle-like crystals of silky luster.

The acetate mixture from the residue after this treatment gave after two recrystallizations almost snow-white crystals, but the acetate mixture from the ether and acetone fractions required numerous recrystallizations from alcohol before a pure product was obtained. The mother liquor was difficult to remove and had to be evaporated off on the water bath. The acetate melted to a nearly colorless oil and hardened to a white wax. From the ether fraction and the residue fraction were obtained acetate mixtures melting at 62–63° C. The acetate from the acetone fraction melted at 61–62° C.

Fractionation of Acetate Mixture

The acetate mixture was dissolved in about ten times its volume of alcohol-ether (1:1) mixture and evaporated on the water bath in stages. Each time, before further evaporation, it was allowed to cool and the crystallized portion separated by use of a suction filter. Two fractions melting at 58–60° C. and 64–65° C. were obtained as well as a mixture melting at 62–63° C. Upon further recrystallization the two fractions gave melting points of 59° and 65° C. These correspond to the acetates of tetracosanol ($C_{24}H_{50}O$, m. p. 59° C.) and ceryl alcohol ($C_{26}H_{54}O$, m. p. 65° C.). Upon saponification of the acetates with alcoholic potassium hydroxide and reacylation of the resulting alcohol, the acetate

which formerly melted at 65° C. gave a melting point of 66° C. This was saponified and gave an alcohol melting at 80–81° C. Upon saponification the acetate melting at 65° C. gave an alcohol melting at 80–81° C. Reacylation of this gave an acetate melting at 66° C. The acetate with melting point of 59° C. gave an alcohol which must have been a mixture, as the melting point was not sharp, ranging from 80° to 83° C. Recrystallizations did not change the melting point.

Determination of Saponification Number and Molecular Weight of Acetate

The determination was made according to the method of Benedikt and Ulzer (3) and gave the following results:

ACETATE OF MELTING POINT 66° C.	
Weight of acetate.....	0.1132 gram
0.09723 N KOH used.....	2.69 cc.
Saponification number.....	129
Calculated saponification number of ceryl acetate.....	132.3
If acetate had one acetyl group its molecular weight would be.....	433
Ceryl acetate (mol. wt. calcd.).....	424
Molecular weight of acetate in camphor, about.....	400

The amount of the acetate of melting point 59° C. was too small to permit a satisfactory determination of the saponification number and molecular weight.

Preparation of Montanic Acids after Removal of Alcohols and Unsaponifiable Compounds

The substance remaining in the extraction thimble after the removal of the unsaponifiable portion and alcohols, which consists of the calcium salts of the acids and unknown substances insoluble in ether and alcohol, was decomposed by refluxing 4 to 5 hours with strong aqueous hydrochloric acid. Above the aqueous layer was added a layer of benzene which took up the organic acids as they were freed, thus leaving the hydrochloric acid free to work upon the undecomposed calcium salts.

After refluxing, the benzene layer was separated and evaporated on the water bath. The residue was added to water; the organic acids formed a hard, dark brown cake. The cake was separated from the aqueous portion and dried on the water bath.

The organic acids were next esterified by refluxing 4 to 5 hours with absolute alcohol and anhydrous hydrochloric acid. On cooling a dark brown layer was formed at the bottom. This was removed, leaving the alcohol solution of the ester a light brown. When the hot alcoholic ester mixture was poured into water, the ester was precipitated in light brown flocs, whereas the darker brown portion previously noticed in the bottom of the flask hardened into a stringy, pitchlike mass. The mixture was then filtered off from the water and the ester taken up in hot alcohol, which left most of the pitchlike substance undissolved. The ester solution was treated with animal charcoal and passed through a hot filter. After several crystallizations the acid ester crystallized from either alcohol or acetic acid as microscopically fine needles which aggregated in bushlike clusters and were nearly snow-white. The melting points of the crude ester mixture from the three fractions were from 68° to 70° C.

The acid ester was saponified by heating about an hour on the water bath with alcoholic potassium hydroxide and then decomposing the potassium salt of the acid with hydrochloric acid, which gave the free acid. This was separated by suction and washed with cold water. The free acid was taken up in hot alcohol, from which it again crystallized in fine needles. The crystals melted to a nearly colorless oil, which upon cooling set to a very pale yellow wax. A thin layer of the wax viewed by transmitted light appeared white. The acid melted from 80–82° C.

Determination of Molecular Weight of Acid

The molecular weight of the acid was determined by saponification of the acid ester in a manner similar to that applied to the acetate. From the potassium hydroxide used the molecular weight of the acid was calculated.

ACID-ESTER, M. P. 68° TO 70° C.

Weight of acid-ester used.....	0.1664 gram
0.09634 N KOH used.....	3.83 cc.
Molecular weight of ester calcd. for one COOH group....	451
Molecular weight of acid.....	423
Weight of acid-ester used.....	0.2504 gram
0.09634 N KOH used.....	5.50 cc.
Molecular weight of acid calcd. for one COOH group....	444

The molecular weights of montanic acid according to the formulas are $C_{29}H_{58}O_2 = 438$ and $C_{28}H_{56}O_2 = 424$.

The approximate resolution of the alkali-soluble portion based on the total weight of the benzene extract indicates:

	%
Alcohols.....	8
Acids.....	32
Residues, unknown compounds.....	15
	55

Further Treatment of Benzene-Soluble Portion

As it was suspected that the benzene-soluble portion might contain some of the waxy alcohols found in the unsaponifiable part of the KOH-soluble portion, it was acetylated by refluxing for 2 hours with excess acetic anhydride. Upon pouring the warm mixture into water to remove the acetic acid, a reddish brown cake was formed. By treating this with hot alcohol the acetate was taken up leaving the neutral or so-called resinous portion nearly undissolved. The acetate obtained represented approximately half of the benzene-soluble portion. The alcoholic solution of the acetate was decanted from the resinous residue, boiled with animal charcoal to decolorize, and filtered through a hot filter. The acetate crystallized from the alcohol in pale yellow microscopic needles and melted between 62° and 64° C. Further recrystallization gave a nearly white product.

The mixture was then fractionally crystallized from an alcohol-ether (1:1) mixture and gave fractions melting at 58–59° C. and 65–67° C. as well as a mixture melting over the whole range. The fraction melting at 58–59° C. was small. Saponification of the two acetate fractions with alcoholic potassium hydroxide gave the alcohols melting at 80–83° C. and 80–81° C., respectively. These acetate fractions are apparently the same as those recovered from the acidic portion of the extract. Here again the acetate melting at 58–59° C. fails to give an alcohol of sharp melting point. Obviously, other methods than fractional crystallization must be employed to effect a sharp separation of the acetates and subsequently the alcohols.

Approximate Resolution of Benzene Extract

The resolution of the benzene extract from Velva lignite has shown the following apparent composition:

	%
Alcohols.....	30
Acids.....	32
Neutral, resinous compounds.....	23
Residues, unknown compounds.....	15
	100

Pschorr and Pfaff (22) gave the following resolution of the montan wax obtained from German brown coal:

	%
Free montanic acid, at least.....	17
Montanic esters.....	53
Compounds of unknown composition.....	30
	100

Comparison of the grouped alcohols and acids of the Velva lignite extract with the grouped montanic acid and the mon-

tanic esters indicate that the lignite extract has a composition similar to montan wax.

Discussion of Results

Inasmuch as the Velva lignite examined is very probably of the same age as the Estevan lignite examined by W. A. Bone and co-workers, one would expect that the resolution of the benzene extract from the two lignites would be similar. Bone (5), however, found the acidic portion of the Estevan lignite extract to consist almost entirely of phenols, whereas the authors obtained positive qualitative tests for phenols only in the portion of the Velva lignite extract obtained at pressures above 17 atmospheres. Since some gas and water were found after extraction at higher pressures, it is apparent that some breakdown of the lignite must have occurred. One must conclude that the phenols found in the extract from Estevan lignite are the result of thermal decomposition or that the extract obtained from Velva lignite is of almost entirely different character. This work indicates that the Velva lignite extract is similar to the montan wax from German brown coal.

Various investigators have resolved the so-called montan wax into waxy alcohols and acids. Pschorr and Pfaff (22) were able to isolate three waxy alcohols, tetracosanol, $C_{24}H_{50}O$ of m. p. 83° C., as well as montanic acid, to which they ascribe the formula $C_{28}H_{56}O_2$ and a melting point of 83.5° C. They separated the alcohols from the acid by first converting the acid to the calcium salt and then extracting the alcohols with ether and acetone. They then acetylated the alcohols and separated the acetates by fractional crystallization from an alcohol-ether (1:1) mixture. The alcohols were obtained by saponification with alcoholic potassium hydroxide. These alcohols were also found by Schneider and Tropsch (24).

Even more work has been done on the acidic portion of the montan wax. As early as 1852 Bruckner (8) isolated from German brown coal an acid melting at 82° C. which he called "geoceriac acid" and gave the formula $C_{26}H_{56}O_2$. Hell (17) obtained the acid from refined montan wax. He determined the melting point of 83–84° C. and not higher than 84.5° C. and his calculations led to the formula $C_{29}H_{58}O_2$. The term "montanic acid" was first applied to the acid occurring in the montan wax by von Boyen (7). Eisenreich (12) found an acid of melting point 82.5° C. and confirmed the formula $C_{28}H_{56}O_2$.

Some later investigators gave the formula $C_{28}H_{56}O_2$. Ryan and Dillion (23) extracted a yellowish wax from Irish peat and from it obtained an acid melting at 83° C. and determined this formula. Easterfield and Taylor (11) obtained from montan wax an acid melting at 82.5° C. and corresponding to the formula $C_{28}H_{56}O_2$. Meyer and Brod (20), investigating montanic acid, arrived at the same formula and the melting point 83–84° C.

Tropsch and Kreutzer (25), however, show that the acid obtained from montan wax is not a single compound but a mixture of acids. By esterifying the acid with ethyl alcohol and sulfuric acid, separating the ethyl ester from the impurities, and distilling the ester in a vacuum, numerous fractions were obtained which were ultimately resolved into three acids—montanic acid, $C_{28}H_{56}O_2$, m. p. 86.5° C.; carboceriac acid, $C_{27}H_{54}O_2$, m. p. 84° C., and an unnamed acid, $C_{25}H_{50}O_2$, m. p. 78° C. A more recent investigation of montan wax by Holde, Bleyberg, and Vohrer (18) indicates that there are several acids present other than those mentioned. They separated numerous fractions by very careful high-vacuum distillation, and found that montanic acid after being freed from the other acids has a melting point of 89° C. (uncor.) and is identical with normal octocosanic acid, $C_{28}H_{56}O_2$.

They contend that montan wax is a mixture of normal fatty acids having chains of an even number of carbon atoms, and have good indications that there is series of acids of 22 up to 32 carbon atoms present. Their investigations are being continued.

The ethyl ester of the acid obtained from the Velva lignite extract melted at 68–70° C. which is a trifle higher than Pschorr and Pfaff's value of 66.5° C. The free acid, however, melts at 80–82° C. and is in fair agreement with their value of 83.5° C. Since the acid does not melt sharply, it seems likely that the acidic portion must be a mixture of acids as found by Tropsch and Kreutzer and by Holde, Bleyberg, and Vohrer. As one will note from the titration values of the molecular weight of 423 and 444, the formula of the acid could be taken as $C_{28}H_{56}O_2$ in the first instance and $C_{29}H_{58}O_2$ in the second. It is therefore quite likely that the benzene extract from Velva lignite consists of a mixture of acids similar to those found in montan wax.

The waxy alcohol obtained from Velva lignite extract is, from its melting point and molecular weight determination, probably largely ceryl alcohol, $C_{28}H_{54}O$. The melting points of the acetate fractions 58–59° C. and 66–67° C., respectively, lead one to suspect some tetracosanol as well, though failure to obtain a sharp melting point for the free alcohol or a good saponification number makes it uncertain. The melting points of the acetates are in good agreement with those of the literature, which gives the acetate of tetracosanol as melting at 59° C. and ceryl acetate at 65° C. Indications of any my-

ricyl alcohol, the acetate of which melts at 70° C., are lacking, since the highest melting point of the acetate obtained was 67° C. As in the case of the acids, it is not improbable that the alcoholic portion may be a mixture of several alcohols.

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Germanium—XXXVI

Extraction of Germanium and Gallium from Germanite—¹

W. I. Patnode and R. W. Work

BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.

GERMANITE is a sulfide ore which was discovered at Tsumeb, South West Africa, in 1920 by Schneiderhöhn (9), and has been made available in large lots by the Otavi Minen-und Eisenbahn Gesellschaft. In addition to about 5 to 6 per cent of germanium, the mineral also contains sulfur, copper, arsenic, iron, lead, silicon, gallium, and lesser quantities of eighteen other elements. Analyses of the ore have been made by Pufahl (7), Lunt (6), and Kriesel (5), while methods for the extraction of the germanium have been reported by Thomas and Pugh (10), Keil (4), Dede and Russ (1), and Pugh (8). The procedures followed in every case were more or less involved, and in no case was more than 0.5 kg. of ore treated at one time. The total weight of germanium extracted was therefore small.

The process described herein has been developed from some unpublished work carried on by N. A. Skow at this laboratory during the summer of 1929.² He found that dry, powdered, germanite heated to 350° C. was attacked by chlorine with the formation of the volatile chlorides of

Various methods have been proposed for the extraction of the rare element germanium from natural sources. This process differs from its predecessors, not only in the type of chemical treatment, but also in the scale of operation. Particular attention has been paid to the technology of the process, with the result that it has been successfully applied to the problem of producing, in a relatively simple and inexpensive manner, comparatively large amounts of the element in a high state of purity.

germanium, arsenic, silicon, sulfur, and lesser amounts of others, which, of course, distilled out of the vessel in which the chlorination was carried out. These chlorides were then further treated in order to separate the germanium. A number of difficulties, particularly with the handling of ma-

terials, in Skow's original process have been eliminated by further work, although the basic chemical treatment remains the same.

Description of Process

The process may be divided into three stages:

- (1) The direct chlorination of the dry ore and collection of the distillate of anhydrous chlorides.
- (2) The fractional distillation of the anhydrous chlorides and subsequent hydrolysis of the distillate.
- (3) The distillation of germanium tetrachloride from the products of hydrolysis and subsequent conversion of the tetrachloride to the dioxide.

Stage One

APPARATUS—The first stage is carried out in the apparatus shown in Figure 1. The flanged cast-iron pot, A, has an internal diameter of 5½ inches (14 cm.) at the top, and a

¹ Received October 30, 1930.

² This work was included in his thesis presented to the faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of doctor of philosophy.

depth of 9 inches (23 cm.). The wall is $\frac{5}{8}$ inch (16 mm.) thick and the weight about 40 pounds (18 kg.) It is supported on a piece of 8-inch (20-cm.) iron pipe 12 inches (30 cm.) long, with ports for the entrance and egress of air at top and bottom. The lid for the pot is also of cast iron, $\frac{3}{4}$ inch (19 mm.) thick, and it is drilled with two $\frac{5}{8}$ -inch (16-mm.) holes for the admission of chlorine and the stem of a 400° C. thermometer. The outlet for the vapors is of 1-inch (2.5-cm.) iron pipe. The center of the lid carries a brass stuffing box through which the stem, a $\frac{3}{8}$ -inch (15-mm.) steel drill rod, of the stirrer passes. Asbestos cord is used as stuffing material. The stirrer, *B*, is also of iron, cast flat in the shape shown, and $\frac{3}{8}$ inch (10 mm.) thick. It is drilled at the top to receive the end of the stem and is held in place by a small set screw. The weight of the stirrer is carried by an angle iron, *C*, bolted to the lid, and the stirrer is turned at 20 r. p. m. by means of a belt around the wooden pulley, *D*, which is 12 inches (30 cm.) in diameter and is attached to the stem by a set screw. Power for the stirrer is supplied by a $\frac{1}{4}$ -horsepower motor connected to a worm-and-pinion speed reducer. This motor will operate two stirrers. The pot is heated by a triple burner, *E*, the heat from which is distributed by an iron plate on a tripod 1 inch (2.5 cm.) below the bottom of the pot. This distribution is necessary since otherwise the pot corrodes very rapidly at the point of overheating. The vapors are condensed in a glass, water-cooled condenser connected to the outlet tube by a glass adapter and rubber tube. It discharges into a 500-cc., 2-necked flask, which is in turn connected by a short length of glass tubing to a 1-liter suction flask containing 500 cc. of water for the hydrolysis of any vapor not condensed in the receiver. These two vessels are cooled in ice water.

PROCEDURE OF A TYPICAL RUN—The burner and tripod are placed in the center of the support and then the empty pot is placed in position. The machined face of the top flange is coated with a thin layer of ordinary cup grease, and an asbestos paper gasket is placed on top of it. This is in turn greased, and then the lid, carrying the stirrer, is set loosely on top. The lid and stirrer are moved about so that the stirrer just clears the bottom of the pot, and it is kept in this position by fastening the pulley and clamping the lid in place with three small steel clamps. The charge, consisting of 1200 grams of the air-dried (0.5 per cent moisture), roughly ground germanite (60 per cent passed a 15-mesh and 96 per cent an 8-mesh sieve), is placed in the pot through one of the small openings in the lid. The thermometer, chlorine-inlet tube, condenser, and receiver are now connected, the stirrer is started, chlorine is admitted to the pot at about 2.5 liters per minute, and after the air in the pot has been displaced the burner is lighted. The chlorine is led first through a bubbler connected to a special device which gives warning by ringing a bell if the flow is interrupted, and is then dried by passing through a tall (2 foot or 61 cm.) tower of fused calcium chloride. For the first 40 minutes there is no evidence of any reaction except an evolution of gas which escapes through the suction flask containing water and is led to the bottom of a tall (4 foot or 122 cm.) tower of lime. This first gas, however, consists of air which is being replaced in the system by chlorine, and sulfur dioxide, which is evidently a product of slight roasting of the ore before chlorination, although probably some of it may be due to hydrolysis of chlorides of sulfur. At the end of this period the temperature within the pot has risen to about 300° C., and during the next 10 minutes it rises rapidly to about 350° C. During this period the evolution of gas decreases and the distillation of a clear, yellow liquid begins. The ore in the pot also becomes sticky and pasty, as is evidenced by the increased power required to turn the stirrer. The reaction is strongly exothermic, and it may be necessary to turn down the gas

flame or decrease the rate of flow of chlorine in order to keep the temperature down. This is important, since a higher temperature within the pot increases the rate of corrosion of the iron and the ferric chloride that is formed has a tendency to distil into the outlet tube and plug it. After the temperature has remained at 340–360° C. for about 15 minutes, the material in the pot becomes less pasty, as is evidenced by less power required to turn the stirrer. Distillation is rapid (about 4 drops per second) and the evolution of gas ceases. The reaction is allowed to proceed under these conditions for about 3 hours longer, during which time the color of the distillate passes from light yellow through orange to deep red. Toward the end of the period the rate of distillation decreases rapidly, finally falling to zero, and chlorine begins to escape through the trap. This is an indication that the ore has been completely chlorinated. About 1.86 kg. of chlorine are required for one run.

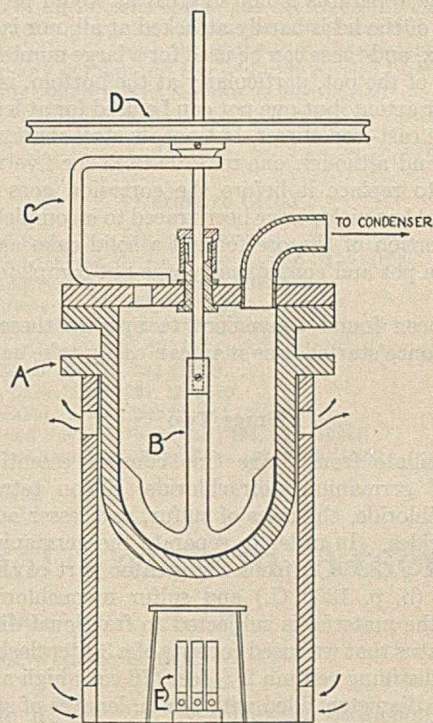


Figure 1—Apparatus for Chlorination of Germanite

The flow of chlorine is now stopped, and air is passed into the apparatus for a few minutes to replace the chlorine in the system. The receiver and trap are then removed, stoppered, and set aside temporarily. If the residue in the pot is allowed to cool, it solidifies (m. p. 310–320° C.) and must be chipped out with a cold chisel. To avoid this labor the lid and stirrer are taken off immediately, care being taken to avoid breathing the fumes, and the pot is placed in a cradle which allows it to be rotated into a horizontal position. The hot liquid residue is now allowed to run out into a shallow sheet-iron container, the sides of the pot being scraped with an iron tool to remove the crystals of ferric chloride which have sublimed up onto the cooler parts. This solid residue is saved for the gallium it contains, the details of which extraction will be published in a later paper.

The distillate is dark red, has a specific gravity of 1.76 at room temperature, and when allowed to stand slowly decomposes with the evolution of bubbles of gas (sulfur dioxide and chlorine) and deposition of sulfur. If this material is allowed to stand in an open vessel, germanium tetrachloride is lost through evaporation. It cannot be stored in a closed container because of the continued evolution of gas.

Therefore, it is advisable to proceed with the second stage of the process without appreciable delay.

YIELD—The average weight of the distillates from seventy runs was 77 per cent of the weight of the ore, although the weights of the individual distillates varied as much as 6 per cent from the mean.

EXAMINATION OF DISTILLATE—In order to trace the germanium and gallium through the process, samples taken from time to time were examined spectroscopically.³ Samples of the distillate, taken 1 and 2 hours after distillation had begun, showed the presence of large amounts of germanium but not gallium. Samples taken 3 hours after distillation had begun showed the presence of not more than 0.1 per cent gallium and less than 0.5 per cent of germanium. Samples of the residue showed considerable gallium but less than 0.05 per cent of germanium.

PRECAUTION AGAINST CORROSION—Corrosion of the metal parts of the apparatus is not so great as would be expected. The inside of the lid is hardly attacked at all, nor is the brass stuffing box, and these can be used for a large number of runs. The inside of the pot, particularly at the bottom, is attacked to a greater extent, but one pot can be used for at least fifteen runs. The cast-iron stirrer, but not its steel shaft, is rapidly attacked, and although one may be used for five runs, it is advisable to replace it before the corrosion goes very far, since several low yields have been traced to incomplete stirring where a portion of the ore formed a solid cake against the walls of the pot and consequently was not completely chlorinated.

It has been found convenient to operate these units in pairs and, once started, one man can easily take care of four units.

Stage Two

The distillate from Stage One consists essentially of a mixture of germanium tetrachloride, silicon tetrachloride, arsenic trichloride, chlorides of sulfur, and lesser amounts of other chlorides. In order to separate the germanium tetrachloride (b. p. 83° C.) from the greater part of the arsenic trichloride (b. p. 130° C.) and sulfur monochloride (b. p. 138° C.), the material is subjected to fractional distillation. The apparatus that was used consists of a 3-liter flask carrying a Hempel distilling column 2½ feet (76 cm.) high and 1 inch (2.5 cm.) in diameter, filled with 5-mm. lengths of small glass tubing. The vapors are condensed in a water-cooled condenser and are discharged into a 2-liter flask immersed in ice water. Any vapors not condensed are led through two Friedrichs spiral gas-washing bottles that contain water and are also cooled in ice water.

FIRST FRACTION (0° TO 120° C.)—It was found convenient to charge the still with the combined distillates from four units of Stage One (3600 to 4000 grams). The still is first heated with the low flame of a triple burner, whereupon a rapid evolution of gas (sulfur dioxide and chlorine) takes place. This gas carries some germanium tetrachloride with it, which is hydrolyzed in the gas-washing bottles. As soon as the evolution of gas has subsided (15 minutes), more heat is applied and distillation begins at about 45° C. The flame is so adjusted that there is twice as much liquid flowing back down the column as is being discharged from the condenser. The temperature rises over a period of about 2 hours to approximately 85° C., after which distillation practically ceases. When more heat is applied, the temperature rises to 132° C. within 10 minutes. All material distilling below 120° C. is taken as a first fraction and is used in Stage Three. This distillate is a clear ruby-red liquid of specific gravity

1.75, that fumes in contact with moist air. It contains all of the germanium tetrachloride (except a small amount caught in the gas-washing bottles) and some silicon tetrachloride, arsenic trichloride, and chlorides of sulfur. About 35 per cent (1200 to 1400 grams) of the charge is obtained in this fraction.

This first fraction is then hydrolyzed by pouring it slowly, with stirring, onto 6 kg. of crushed ice. If insufficient ice is used the heat of reaction is great enough to volatilize some of the germanium tetrachloride. However, when 6 kg. are used, the temperature drops to -18° C. Much agitation is required and when the hydrolysis is complete there results a heavy, light-yellow suspension. This, with the suspensions in the gas-washing bottles, is placed in a 12-liter flask for Stage Three.

SECOND FRACTION (120° TO 138° C.)—The residue left in the still after the first fraction has been removed contains a small amount of gallium trichloride. In order to free it from as much extraneous material as possible, a second fraction is taken. Since the boiling points of arsenic trichloride and sulfur monochloride differ widely from that of gallium trichloride (215-220° C.), the long column is not required for separation. In its place is substituted a simple three-ball Wurtz column containing glass beads. Practically all of the material distills at 132-138° C. This fraction contains neither germanium nor gallium and is discarded.

RESIDUE IN STILL (B. P. ABOVE 138° C.)—Twenty to thirty grams of residue remain in the still after the second fraction is taken. It contains sulfur, rubber from the stoppers, gallium trichloride, and a trace of indium. This material is hydrolyzed with water and is set aside for the recovery of the gallium.

In order to trace the progress of the germanium and other metals through the second stage, portions of the distillate were taken from time to time and were examined spectroscopically. Samples of the first fraction taken at 45° and 75° C. showed the presence of germanium, but no arsenic; at 85° C. both germanium and arsenic were present; at 110° C. arsenic was present but not germanium. Samples of the second fraction taken at 132° and 138° C. showed neither germanium nor gallium. Samples of the residue showed the presence of gallium and indium.

Stage Three

The germanium has been concentrated in the suspension resulting from the hydrolysis of the first fraction of Stage Two. In addition to germanium dioxide the suspension contains hydrochloric acid, sulfur, silicon dioxide, and a small amount of arsenic. To this, which is contained in a 12-liter flask, is added the material in the water traps from Stage One. The flask carries a fractionating apparatus similar to that described by Dennis and Johnson (2), and serves for the final separation of the germanium.

The material in the flask is first saturated with chlorine, which requires about an hour, while the temperature of the liquid rises to approximately 40° C. The flow of chlorine is continued throughout the entire distillation. Heat is applied to the still and distillation of germanium tetrachloride accompanied by a small amount of hydrochloric acid begins at about 68° C. These two liquids form two layers, germanium tetrachloride being the heavier. The forward flow take-off of the Johnson stillhead is so adjusted that half of the total distillate is returned to the column. The remaining germanium tetrachloride is drawn off into a 1-liter Erlenmeyer flask containing 0.5 kg. of crushed ice. As distillation proceeds, the temperature rises slowly and the proportion of germanium tetrachloride condensed in the stillhead decreases. After about 2 hours the temperature has risen

³ These spectrographic analyses were made at this laboratory by Professor J. Papish and his staff, to whom the authors wish to express their sincere appreciation of this assistance.

to 104–107° C. and there is no longer a separate layer of germanium tetrachloride. At this point another flask is substituted for the receiver and the distillate of constant-boiling hydrochloric acid is collected until it no longer gives a test for germanium with hydrogen sulfide. From 200 to 500 cc. of acid are collected over a period of 2 to 4 hours. Distillation is now stopped.

The residue in the still contains a small amount of suspended matter which when investigated was found to be a mixture of 80 to 100 grams of sulfur and 15 to 20 grams of silicon dioxide. The silica was found to carry less than 20 mg. of germanium, and consequently was discarded, it being unprofitable to carry out the difficult separation of such a small quantity.

The germanium tetrachloride collected in the first Erlenmeyer flask is shaken with sufficient crushed ice (about 1 kg.) completely to hydrolyze it to white hydrated germanium dioxide, and is allowed to stand for a few hours in order to facilitate the subsequent filtration. It is then collected on a filter, using suction, washed with a small amount of cold water, dried, and ignited. The germanium dioxide thus obtained is spectroscopically pure and represents 85 to 90 per cent of the total germanium in the ore.

The filtrate and washings are combined with the second part of the distillate, consisting mainly of constant-boiling hydrochloric acid, made 6 normal with respect to this acid, and the germanium is precipitated by hydrogen sulfide as white germanium disulfide. This precipitate represents 5 to 10 per cent of the total element in the ore, bringing the total yield of germanium up to 95 per cent. When running continuously, this precipitation is not carried out until a large quantity of liquid has been collected, and the precipitated sulfide is then converted to the dioxide by the method of Dennis and Papish (3).

If desirable, the dioxide thus obtained may be reduced to

the metal by the very satisfactory method described by Tressler and Dennis (11).

Reasons for Inclusion of Stage Two

Although Stage Two may be omitted and the entire distillate of Stage One be hydrolyzed and distilled as described in Stage Three, it was found expedient to include it for the following reasons:

(1) Most of the arsenic is discarded with the second fraction, thereby making the production of pure germanium dioxide in Stage Three relatively simple. If a large amount of arsenic is present in the material charged into the still at Stage Three, the distillate obtained will contain appreciable amounts of it. This will necessitate at least one redistillation in the presence of water and chlorine completely to separate the germanium from the arsenic.

(2) Most of the sulfur chloride is discarded with the second fraction. The presence of its hydrolytic products (especially sulfur dioxide) in Stage Three is undesirable. In the first place, the presence of an uncondensable gas decreases the efficiency of condensation of the vapors. In the second place, this gas would have to be bubbled through the water in the gas-washing bottles to hydrolyze any germanium tetrachloride carried by it mechanically, and this would retard the rate of distillation.

(3) The volume of material to be handled in Stage Three is reduced to one-third.

(4) It permits a relatively simple concentration of the gallium.

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The Composition of Commercial Calcium Arsenate¹

C. M. Smith and C. W. Murray

INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

IN THE manufacture of the very important agricultural insecticide known as calcium arsenate, it is necessary to use approximately 4 mols of calcium oxide to 1 of arsenic oxide to obtain a product that is insoluble enough to be safe for application to growing foliage. Naturally the question of the state of combination of the calcium and arsenic oxides soon arose, and in the absence of any definite information on the subject it was tacitly assumed that the finished product contained tricalcium arsenate together with calcium hydroxide and calcium carbonate equivalent to the extra mol of calcium oxide. This assumption has persisted to this day. The total arsenic in commercial calcium arsenate is always calculated to $\text{Ca}_3(\text{AsO}_4)_2$ in order to obtain the percentage of active ingredient, the figure so obtained being in the neighborhood of 70 per cent.

However, it has been known for many years that this point of view is probably incorrect, and that, as a matter of fact, the product probably contains a considerable proportion of a basic arsenate. Tartar, Wood, and Hiner (4) reviewed the evidence for this in an article published in 1924 and then presented an account of their own experiments designed to

substantiate it. By the hydrolysis of tricalcium arsenate and of calcium ammonium arsenate with boiling water they produced an end product of fairly fixed composition to which they assigned the formula $3\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$, exactly similar to that of the well-known basic arsenate of lead. These authors were convinced that they were dealing with a definite compound, and not with a mixture of two materials giving a minimum solubility. However, Clifford and Cameron (1) have argued that neither this basic arsenate nor tricalcium arsenate itself exists, but that solid solutions are formed just as they are in the system $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ which had been previously studied by Cameron and others.

One of the present writers undertook several years ago to study the basic region of the system $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$ by means of phase-rule considerations, but obtained such erratic results that the work was never published. He considered that the difficulties arose from a very slow attainment of equilibrium and an attack of the glass flasks by the alkaline solutions during the long standing (as much as 9 months). Some slight evidence was obtained, however, of a compound with a molecular quotient $\text{CaO}/\text{As}_2\text{O}_5$ of 4—that is, one considerably more basic than the compound reported by Tartar, Wood, and Hiner.

No attempt seems to have been made to prove directly the presence of basic arsenate in commercial calcium arsenate.

¹ Received October 9, 1930. Presented as a part of the Insecticide Symposium before the Division of Agricultural and Food Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

It is customary in the analysis of this insecticide to determine the total CaO and total As_2O_5 . That more than this is necessary to interpret the true composition is self-evident. An estimation of the proportion of calcium carbonate present is possible by a determination of the carbon dioxide content, but even then there remains some calcium oxide to be accounted for. With this point in mind Smith and Hendricks (3) developed a method for the estimation of free calcium hydroxide in calcium arsenate. This method is based on the reaction of the free calcium hydroxide with an alcoholic solution of benzoic acid, which medium does not attack either calcium carbonate or tricalcium arsenate, and it was shown that quite accurate results could be obtained on known mixtures of tricalcium arsenate and calcium hydroxide.

Analyses

The present authors have applied this method to sixteen brands of recently manufactured commercial calcium arsenate that are being studied in relation to foliage injury in the hope that there might be a correlation between injury and degree of basicity. Complete detailed analyses were made, but all the results are not given here because they are too voluminous. In general they differ in no marked degree from those quoted by McDonnell, Smith, and Coad (2) for a group of products manufactured about 1921, showing that, as far as gross composition goes, commercial calcium arsenate has become a well-standardized product.

The average values obtained in the analyses of these materials are shown in Table I. It is seen that the total As_2O_5 ranges only from 40.3 to 44.4 per cent, with an average of 42.4 per cent. If, as is frequently the case, this were the only determination made (aside from water-soluble arsenic), a false idea of the similarity of various brands might be obtained. The total CaO has a somewhat wider range, and very marked differences are seen in the figures for calcium carbonate and calcium hydroxide, the former ranging between 1.2 and 11.7 per cent with an average of 6.4 per cent, the latter from 1.5 to 12.7 per cent with an average of 6.6 per cent. A close inspection of the individual figures for calcium carbonate and calcium hydroxide (not given here) will show that they are somewhat complementary to each other, which merely reflects the fact that one is formed at the expense of the other when carbon dioxide is absorbed from the air during storage.

Table I—Average Analyses of Sixteen Commercial Calcium Arsenates

	MAXIMUM	MINIMUM	AVERAGE
	%	%	%
Moisture	3.22	0.74	1.94
Insoluble in HCl	0.97	0.27	0.57
Loss on ignition	12.72	6.94	9.3
Total CaO	47.70	40.42	43.91
CaCO ₃	11.73	1.21	6.37
Ca(OH) ₂	12.66	1.52	6.63
CaO as arsenate	40.59	31.49	35.34
R ₂ O ₃	1.14	0.22	0.39
MgO	1.14	0.13	0.52
PbO	2.49	None	...
Total As ₂ O ₅	44.39	40.32	42.42
As ₂ O ₃	0.52	Trace	0.18
SO ₂	0.78	Trace	...
Cl	0.39	Trace	...
N ₂ O ₅	1.81	Trace	...
Water-soluble As ₂ O	2.37	0.06	...

Little need be said concerning the minor impurities, most of which are to be expected from the nature of the raw materials used. The presence of lead in a few samples is probably due to the use of the same machinery for the manufacture of both lead arsenate and calcium arsenate. The high content of nitrogen pentoxide in three of the samples is rather surprising, but the presence of this impurity is probably explained by the failure to remove from the arsenic acid all the nitric acid used in its preparation. Some of these con-

stituents were not determined in all the samples, which explains the absence of an average value in the table.

Molecular Quotients

The principal interest for our present consideration attaches to the values given in Table II for "molecular quotient." These figures were obtained as follows: It was assumed that the smaller impurities could be neglected, which is partly justified by the fact that the acidic and basic ones tend to offset each other; the percentages of CaO equivalent to both the calcium carbonate and the calcium hydroxide present were then subtracted from the total CaO, the remainders converted to mols, and these figures divided by the mols of As_2O_5 to which the percentages of that component are equivalent. A quotient of 3.0 thus obtained represents tricalcium arsenate, one below 3.0 an acid compound, and one above 3.0 a basic component. It will be seen that all but one of the figures are higher than 3.0; in other words, fifteen samples show evidence of containing some basic compound.

MOLECULAR QUOTIENT		MOLECULAR QUOTIENT	
SAMPLE	CaO/As ₂ O ₅	SAMPLE	CaO/As ₂ O ₅
1	4.1	8	3.3
2	3.4	9	3.7
3	3.4	10	3.4
4	3.6	11	3.7
5	3.3	12	3.6
6	3.3	13	3.2
7	3.2	14	3.1
		15	3.0
		16	3.4
	Maximum.....		4.1
	Minimum.....		3.0
	Average.....		3.4

It is quite impossible to determine from these figures just what basic compound is present. Several of the figures approximate closely the value 3.33, which would be characteristic of the compound $3Ca_3(AsO_4)_2 \cdot Ca(OH)_2$ reported by Tartar, Wood, and Hiner, but since nearly half are appreciably higher the evidence for its existence is not very conclusive. Since no value is less than 3.0 and only one slightly above 4.0, perhaps the best guess is that these samples consist of mixtures of $3CaO \cdot As_2O_5$ and $4CaO \cdot As_2O_5$. The latter, as said before, was also suggested by some of the senior author's earlier work.

It is thus demonstrated that the arsenic in commercial calcium arsenate practically never exists solely as tricalcium arsenate, but that a considerable portion, and perhaps in some cases all of it, is present in the form of a basic arsenate of undetermined composition. It is quite possible that the nature of the basic compound might be more fully revealed by similar work on laboratory samples made from pure constituents under controlled conditions.

Summary and Conclusions

Sixteen brands of recently manufactured calcium arsenate were analyzed in detail, the results tabulated, and the average composition of this important agricultural insecticide thus revealed. The presence of a basic arsenate of undetermined composition is definitely established. The average product contains 80 to 85 per cent of what is probably a mixture of tricalcium arsenate and this basic arsenate, together with about 6.5 per cent each of calcium hydroxide and calcium carbonate and small amounts of incidental impurities. The individual products may, however, differ rather widely from these average figures.

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Technic of Stream-Pollution Investigations¹

F. W. Mohlman, T. L. Herrick, and H. Gladys Swope

THE SANITARY DISTRICT OF CHICAGO, 845 WABASH AVE., CHICAGO, ILL.

EXTENSIVE studies of the pollution of the Illinois River have been made by the Sanitary District of Chicago prior to and since the opening of the Drainage Canal in 1900. A survey was made by the U. S. Public Health Service in 1921 and 1922 (1), and the data collected were used by the Engineering Board of Review of the Sanitary District of Chicago as a basis for extensive calculations concerning the present and future dilution requirements of this river. The Board of Review recommended that further and more extensive studies be made. These studies were started in 1925 and are still in progress. Attention has been directed primarily to a study of the oxygen balance as measured by the relation of dissolved oxygen and biochemical oxygen demand. In the course of the studies many points of special interest have been investigated and improvements in the technic of sampling, analysis, and compilation have been made. It is the writers' intention, therefore, not to present any summarized average results showing conditions from month to month or year to year, but rather to select topics of more general interest, the discussion of which will be applicable to similar investigations of other streams. This discussion may serve to draw attention to certain factors which may have been overlooked in other investigations and, furthermore, the technic that has been adopted may be of some general interest.

luted stream an hourly variation in concentration may occur similar to the well-known variation in concentration of sewage throughout the 24 hours. In the lower reaches of the same stream the same, if not greater, variation may be found in the dissolved-oxygen content due to the presence of green and blue-green algae which give off large amounts of oxygen in the presence of sunlight.

The great width of streams as compared with sewers and conduits makes it necessary to consider the advisability of taking samples at various points across the stream. The sampler then has to decide whether to take top samples or bottom samples, a single sample in the channel, or three or more samples across the stream. After selecting the proper sampling location he must decide whether the hourly variation is large enough to require more than one sample during the 24 hours. The writers have found it necessary to take more samples than one per day in order to obtain a true picture of the oxygen conditions of the Illinois River, although this may not be necessary in other streams.

In selecting the sampling points a cross-sectional survey has been made at practically all of the stations similar to the one reported here for Wesley City, just below Peoria. Current-meter tests were made at various points across the stream and samples were taken at the same points. These samples were analyzed for dissolved oxygen and biochemical

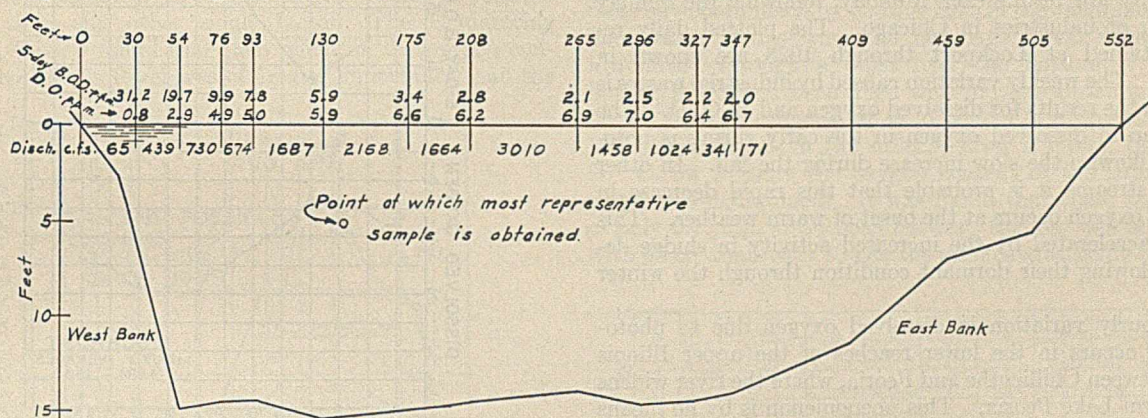


Figure 1—Selection of Sampling Point at Wesley City, Illinois River Investigations

With the exception of the studies made by the U. S. Public Health Service and the Engineering Board of Review, stream pollution surveys are usually of a somewhat qualitative nature, consisting of chemical, biological, and hydraulic observations which show the condition of a river at various points, but which are not complete enough to serve as a basis for computation of oxygen balance, dilution ratios, or re-aeration coefficients. Since facilities were available for making a complete study of oxygen relations by use of a large number of samplers, the writers have been enabled to obtain hourly samples of dissolved oxygen at sixteen stations for a period of a year or more and at ten stations for the last five years.

Sampling

The sampling of a large river presents more difficulties than the sampling of sewage or effluents. In a highly pol-

oxygen demand and weighted averages were computed in order to determine the proper location of a single sampling point. The results of this survey at Wesley City are shown in Figure 1. It will be noted that there would be an appreciable error at this location if a sample were taken at three points across the stream and averaged. Likewise it was necessary to take a weighted rather than a straight average, as shown in Table I. The gagings have been checked several times and, while there is some change between low and high water, the actual distance the point has had to be moved has not been great.

With regard to surface and bottom sampling, there may be more danger in this procedure than value. Unless the exact depth is known, the sampling can may approach too closely the beds of sludge deposits which are known to occur in the Illinois River. A deep sample will show a lower dissolved oxygen and higher biochemical oxygen demand than a surface sample, but it is a question whether this represents the condition of the flowing stream or merely a local condition.

¹ Received November 20, 1930. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

If the samples are taken too close to the bottom a very low dissolved oxygen may be obtained at practically all places where sludge deposits are known to exist.

Table I—Stream Survey at Wesley City

STATION FROM WEST BANK	DISCHARGE Cu. ft./sec.	5-DAY B. O. D.		DISSOLVED OXYGEN		WEIGHTED B. O. D.		WEIGHTED DISSOLVED OXYGEN	
		P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
1	285	31.2	0.8	8892	228				
2	585	19.7	2.8	11524	1638				
3	702	9.9	4.9	6950	3440				
4	1180	7.8	5.0	9204	5900				
5	1928	5.9	5.9	11375	11380				
6	1916	3.4	6.6	6514	12640				
7	2337	2.8	6.2	6544	14500				
8	2234	2.1	6.8	4691	15180				
9	1241	2.5	7.0	3103	8678				
10	682	2.2	6.4	1500	4360				
11	341	2.0	6.7	682	2285				
Total	13431	89.5	59.1	70979	80229				
Average		8.14	5.37	5.28 p. p. m.	5.97 p. p. m.				

Hourly Variations

The extent of hourly variations at Lockport is shown in Figure 2. These results indicate the magnitude of variation in the upper highly polluted part of the river. The U. S. Public Health Service (1) attempted to correct results of a single daily determination for the hourly variation in concentration and flow. For the past several years the hourly variation in flow has not been nearly so great as in 1921 and 1922, but the variation in dissolved oxygen and B. O. D. has been large at certain periods of the year. In addition to the hourly variation at Lockport, a very marked daily variation has been noted throughout the week, with particularly low results each Monday, following the Sunday shutdown of industries in Chicago. The plotted daily results obtained at Lockport through 1928 are shown in Figure 3. The weekly variation caused by industrial wastes is shown by the results for dissolved oxygen and B. O. D. The rapid drop in dissolved oxygen in the early spring is noteworthy, likewise the slow increase during the fall. In other polluted streams it is probable that this rapid decrease in dissolved oxygen occurs at the onset of warm weather. This effect is accelerated by the increased activity in sludge deposits following their dormant condition through the winter months.

The hourly variation in dissolved oxygen due to photosynthesis occurs in the lower reaches of the upper Illinois River, between Chillicothe and Peoria, where the river widens out to form Lake Peoria. This phenomenon is by no means new, but was studied and reported by Professor Palmer in his classic studies of the Illinois River prior to and following the opening of the Drainage Canal in 1900. Typical results for two days in midsummer of 1927 at Averyville are shown in Figure 4. The difference between a sunny day and a cloudy day is quite marked.

The examples given above indicate that one must be very cautious in accepting a single daily sample at a sampling station as representing the average conditions at that point in the Illinois River. The differences are usually not great enough to warrant discarding analyses of single samples, particularly when they are reinforced by biological observations and field investigations, but the large differences found at times from hour to hour make it advisable to recommend that such hourly variations be studied in all surveys of stream pollution. In our control of large sewage treatment works we would be unlikely to give much weight to analyses of a single catch sample. The collection of composite samples is of fundamental importance in sewage sampling. Composite samples may frequently be of equal necessity in stream surveys.

Biochemical Oxygen Demand

The 5-day 20° C. B. O. D. test was used throughout these studies, but it was early recognized that it would be necessary to obtain information for rates of B. O. D. on longer periods of incubation. In a previous publication (3) it was shown that, for Illinois River samples, no constant relation existed between the 5-day demand and either the complete first-stage demand or in fact any longer period of incubation. The 5-day demand may, as it were, be "lifted" off the B. O. D. curve at almost any stage of oxidation; consequently, it is unsafe to use any fixed factor for calculation of longer or shorter periods of incubation. With this precaution in mind for several years weekly tests have been made at each sampling station of rates of B. O. D. with incubation at 20° C. from 1 to 40 days. These curves indicate the degree of oxidation according to the point of inflection between the first and second stages. This occurs after 12 to 14 days at 20° C. with freshly polluted water; increasing stabilization may be noted by the shortening of the first stage. Entrance of fresh pollution again extends the transitional period between the first and second stages. For example, the average of weekly 40-day demands extending over a year are shown for Averyville and Peoria in Figure 5. The transition occurs after 5 or 6 days above Peoria, but the influx of fresh pollution brings this up to 7 or 8 days at Peoria. The writers

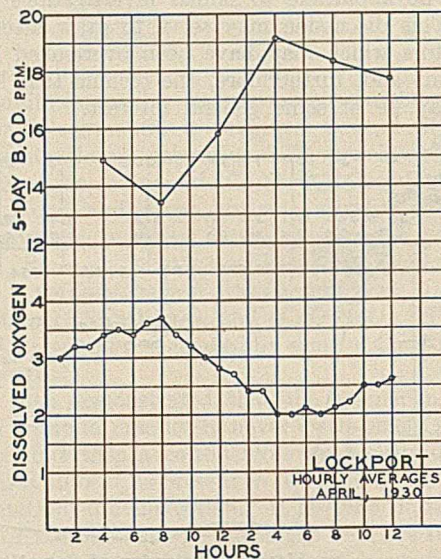


Figure 2—Hourly Variations in Dissolved Oxygen and Oxygen Demand, Lockport

have records far downstream which indicate that for samples far distant from fresh pollution the rates of B. O. D. may approximate a straight line or the curve appears to be in the second stage, that of nitrogen oxidation. Curves at Chillicothe for summer and winter conditions are shown in Figure 6. The first stage is extended to 12 days in winter owing to the slower rate of oxidation, while in summer the more rapid oxidation shortens it to 5 days.

While the information with regard to long-time rates of B. O. D. has been considerably extended, it is still somewhat difficult to use these curves in a precise mathematical relationship. With more knowledge concerning the exact state of oxidation of the organic matter, it might be possible to use these curves with more confidence. The writers believe, however, that it is necessary to go beyond a mere consideration of the 5-day demand in studies of stream pollution.

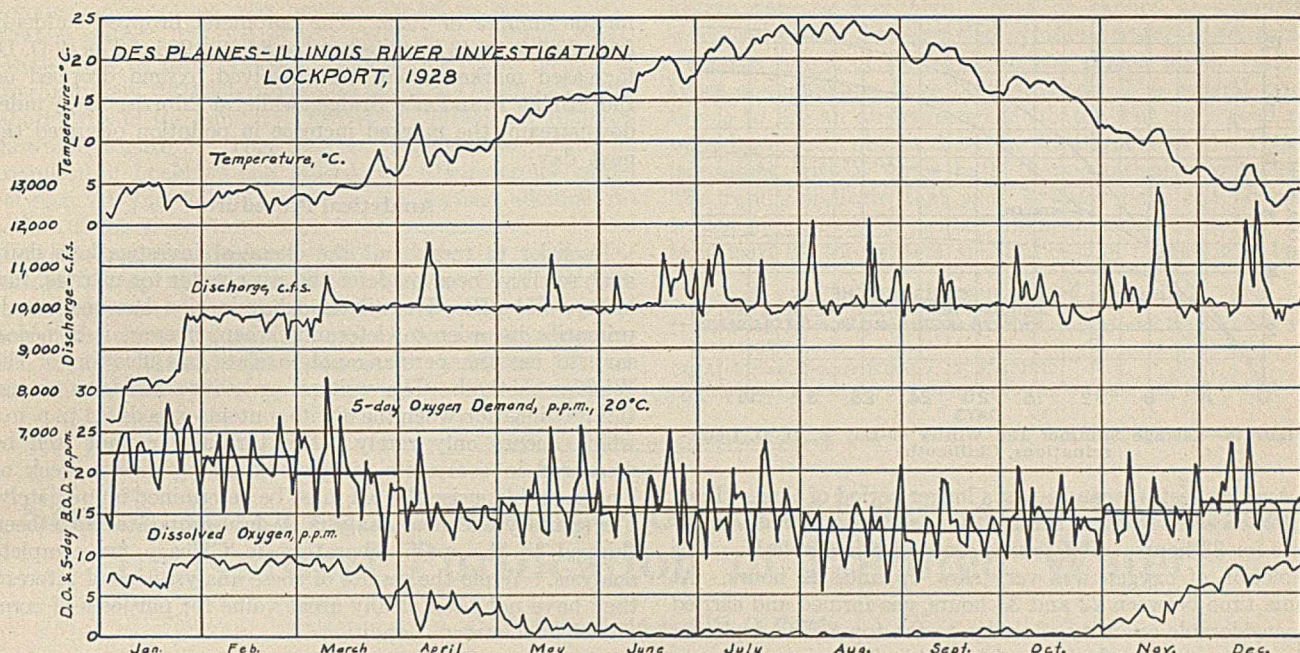


Figure 3—Average Daily Results, Lockport, 1928

Effect of Sludge Deposits

The solids from untreated or partially treated sewage that accumulate in a stream settle to the bottom, there to form sludge deposits of more or less thickness and greater or less putrescibility. These sludge deposits are probably of more importance with regard to conditions of nuisance in polluted streams than any other single factor. The Engineering Board of Review found that their effect on the oxygen content of the Illinois River was of greater importance than the

sludge throughout the flowing river by ebullition of gas. As long as the sludge remains quiescent on the bottom of the river it probably has no great demand for oxygen, but as soon as the solids are carried up by discharge of gas a very rapid demand for oxygen occurs.

A few simple laboratory experiments to illustrate these facts have been made by C. L. Adams in the Joliet laboratory. Samples of sludge from the Drainage Canal were quietly introduced through a pipet over the bottom of 8-ounce bottles which had been filled with oxygen-containing water. In the first experiment 10 cc. of sludge were placed in one bottle and 25 cc. in the other. After standing quietly at 20° C. for 2 hours the oxygen content of the supernatant water was determined. It was found that there was a loss of only 0.2 p. p. m. in both bottles; the loss was no greater with 25 cc. than with 10 cc., the surface area being the same

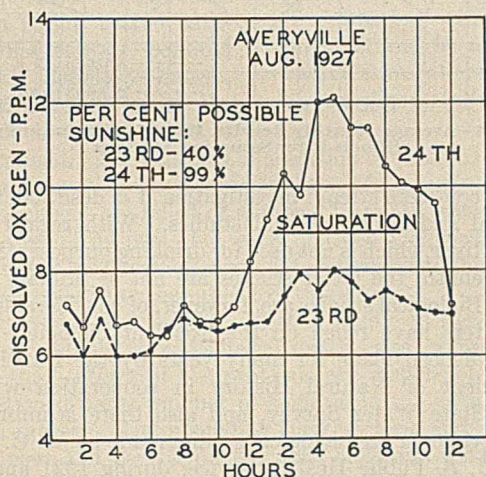


Figure 4—Effect of Sunlight on Dissolved Oxygen, Averyville, August, 1927

effect of the current discharge of sewage, practically all untreated. During July and August, 1922, sludge deposits between Chicago and Chillicothe consumed 1,270,000 pounds of oxygen per 24 hours, while the current flow of sewage consumed only 741,000 pounds per 24 hours. The study of sludge deposits is therefore one of the most important requirements of a stream survey. These sludge deposits may be mapped, classified, and analyzed, but it is difficult to utilize the results in any satisfactory manner, because the relative importance of depth and area is not known. The writers' observations indicate that the depth of the deposits is not very important, but that the factors of most importance are the area of the deposits and the rate of dispersion of solid

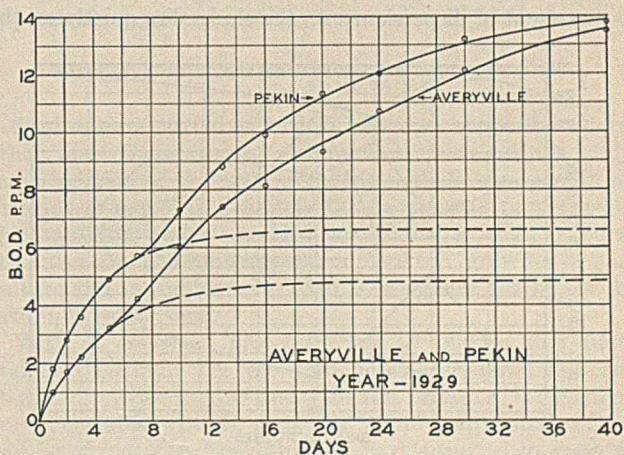


Figure 5—Average Results, Year 1929, of Weekly 40-Day B. O. D. Determinations, Averyville and Pekin

in both cases. In two more bottles, however, which were inverted every 15 minutes for the first half-hour and at intervals of 30 minutes thereafter, the sample containing 25 cc. of sludge had lost 6.5 p. p. m. while the one containing 10 cc. had lost only 3.5 p. p. m. These results show the great difference between quiescent and dispersed sludge.

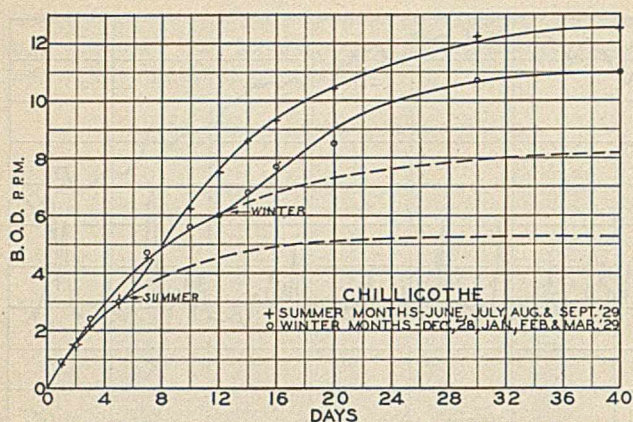


Figure 6—Average Summer and Winter 40-Day B. O. D. Determinations, Chilllicothe

Another test was made over a longer period of time. Each bottle received 25 cc. of sludge. One set was allowed to incubate for 33 hours. The results are shown in Table II. The depletion of oxygen was very slow until 22 hours. At some time between 22 and 33 hours, gas formed and carried a considerable quantity of sludge to the top. The depletion of oxygen was greatly increased by this dispersion, as shown by a loss of 3.6 p. p. m. from 22 to 33 hours, whereas only 2.6 p. p. m. had been lost during the first 22 hours of incubation, while the sludge remained quiescent on the bottom of the bottle. By way of comparison, one bottle under the same conditions as above was inverted once every half-hour. The oxygen was practically depleted in 3 hours, with only 0.4 p. p. m. remaining.

Table II—Consumption of Oxygen by Quiescent Sludge

DISSOLVED OXYGEN	3 HOURS		6 HOURS		10 HOURS		22 HOURS		33 HOURS		3 HOURS MIXED
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	
Initial	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4	8.4
Remaining	8.3	7.5	6.4	5.8	5.8	2.2	0.4				
Consumed	0.1	0.9	2.0	2.6	2.6	6.2	8.0				

^a Sludge at top of bottle.

It thus appears that the oxygen demand of sludge deposits is greatly intensified when the solids are gas-lifted. In a practical way this phenomenon has been noted in the upper part of the Illinois River, with a falling barometer serving as the agent of dispersion. As the sludge lies quietly on the

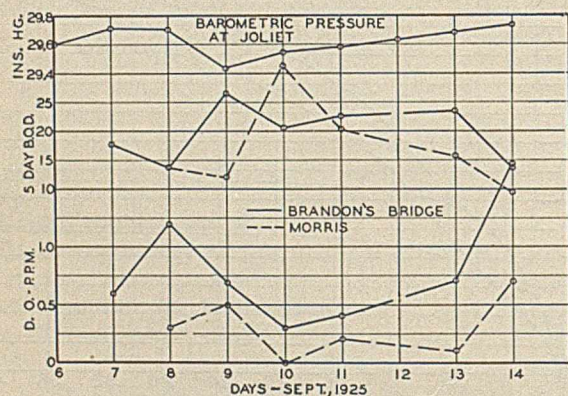


Figure 7—Effect of Falling Barometer on Dispersion of Sludge through Flowing River

bottom of the river it is filled with gas and is under a delicate equilibrium with respect to gravity. A rapidly falling barometer will permit the gas to expand, thus bringing large volumes of sludge to the surface. The results of such occurrences have been noticed in sudden waves of gas attacks at Morris, shortly below the polluted Lake Joliet in the upper part of the river. A typical example is shown in Figure 7

for the summer of 1925. The barometer dropped suddenly from 29.7 to 28.43 from September 8 to 9, 1925. The B. O. D. increased markedly and the dissolved oxygen dropped on the 9th at Brandon's Bridge, while at Morris, 22½ miles downstream, the marked increase in pollution occurred the next day.

Analytical Procedures

In order to round out the chemical investigations daily analyses have been made of the river water for nitrites, turbidity, and pH. The nitrite determination has been made primarily in order to determine when, if ever, it is necessary to use the permanganate-oxalate modification of the Winkler method. The writers' procedure has been to use this modification when the nitrite content exceeds 0.1 p. p. m., which occurs only rarely. The turbidity cannot well be measured in composite samples extending over a week or longer, and likewise the pH must be determined immediately. For sanitary chemical analysis 10-day composites have been shipped to the main laboratory in Chicago for complete analysis. While the results of these analyses are of interest, they have not been of any great value for purposes of computation of stream conditions.

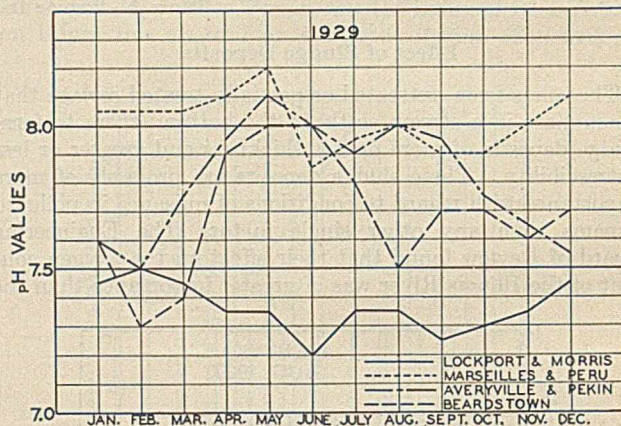


Figure 8—Average Monthly Results, 1929, of pH Value at Various Illinois River Sampling Stations

For a complete stream investigation it is desirable to have biological and bacteriological studies. With regard to the Illinois River, which is not used for drinking purposes throughout its length, the latter studies are not of primary importance. Biological studies are, however, of considerable value. The writers have relied on the excellent biological studies that have been made for many years by the Illinois State Department of Natural History in cooperation with the Illinois State Water Survey, and also there is information of great value in the biological studies made by W. C. Purdy, of the U. S. Public Health Service, during 1921 and 1922.

In studies of dilution water for B. O. D. determinations some preliminary results obtained with synthetic dilution water consisting of distilled water to which has been added 500 p. p. m. sodium bicarbonate have been reported in a former article (3). It was found necessary to develop such a synthetic water on account of the great variety of waters available in the cities where the branch laboratories of the Sanitary District were established. These tap waters were mostly from deep wells, some containing iron, others containing comparatively large amounts of ammonia and nitrate nitrogen, and others containing a variable amount of organic matter. In view of the excellent results with the sodium bicarbonate water this has been used for the past three or four years, at first with 500 p. p. m. sodium bicarbonate and more recently with 300 p. p. m. The reduc-

tion in concentration was made in order to obtain a less alkaline water. The pH of the 300 p. p. m. sodium bicarbonate was usually between 7.7 and 8.3. The results of approximately 1900 determinations of pH in the Illinois River laboratories of the Sanitary District of Chicago for 1929 are shown in Figure 8. These curves indicate that, with the exception of Lockport and Morris, the pH generally varied between 7.5 and 8.2. In view of this rather alkaline reaction of the river water it has been concluded that the use of the sodium bicarbonate water is preferable to that of distilled or tap water. Proposed improvement of this synthetic water has been discussed elsewhere (2). The selection of the dilution water for B. O. D. tests in stream-pollution studies depends upon many local conditions, particularly the suitability of the available tap water. Where such

waters vary or give high blanks or cannot be stabilized successfully, it is our belief that synthetic water is preferable.

In the course of the work on the Illinois River various types of incubators have been studied. The general practice is to use an air-tempered incubator, but very good results have been obtained by G. R. Barnett at the Peoria laboratory with a water bath thermostatically controlled. The results indicate that such a water bath can be controlled much more accurately than an air incubator of the type used by the writers and the cost of operation is less.

Literature Cited

- (1) Hoskins, Ruchhoft, and Williams, U. S. Pub. Health Service, *Bull.* **171** (1927).
- (2) Mohlman, *Sewage Works J.*, **2**, 375 (1930).
- (3) Mohlman, Edwards, and Swope, *IND. ENG. CHEM.*, **19**, 242 (1928).

Some Interrelationships of Plankton and Bacteria in Natural Purification of Polluted Water¹

C. T. Butterfield and W. C. Purdy

U. S. PUBLIC HEALTH SERVICE, CINCINNATI, OHIO

THE abstraction of dissolved oxygen from polluted water during the natural purification process is a well-known phenomenon. It is also well known that the amount of dissolved oxygen used up is definitely related to the amount of pollution present. While these facts in regard to the natural purification of polluted water are definitely known, the mechanism by which the oxidation is accomplished is only assumed. For instance, if a portion of polluted water is examined many bacteria and plankton are found. If all of these organisms are killed or removed from the water, oxidation ceases. The part that each of these biological factors plays in the progress of events, together with their inter-reactions, constitute the subject of this study.

Purdy and Butterfield (3), in their study on the effect of plankton animals upon bacterial death rates, showed quite clearly that certain of the protozoa are responsible for the destruction of large number of bacteria in the natural purification process. Unfortunately their bacteria and plankton results were not complemented with collateral data on the chemical changes produced.

In the present work preliminary studies were made with heterogeneous combinations of bacteria and plankton. These studies, while instructive, presented too many variables to be of real value.

Further studies, with adequate control, were next undertaken to determine oxygen depletion in a medium containing no living organisms; oxygen depletion when bacteria only are present, in pure culture and in mixed culture; oxygen depletion when no bacteria, but plankton only, are present; and oxygen depletion when bacteria and plankton are both present, in pure culture and in mixed culture.

Based on the results of a series of biological and chemical experiments, the theory is advanced that the chief function of certain plankton in the biochemical oxidation process is to keep the bacterial population reduced below the saturation point and thus to provide conditions suitable for continuous bacterial multiplication and as a result provide for more complete oxidation.

Support is given to this theory of the function of the plankton by the results obtained in experiments where the limiting numbers of bacteria were reduced by physical and by chemical means. Such reductions in bacterial numbers were invariably followed by renewed bacterial multiplication and oxidation.

A preceding paper (1) has described the preparation and characteristics of a simple reproducible dextrose-peptone solution. Unless otherwise stated, this standard medium was used in the studies here reported.

Oxygen Depletion in Absence of All Living Organisms

Suitable tests were made to determine the extent of oxygen depletion in the dilute medium: (a) in the absence of all biological forms, and (b) in the presence of dead cells of *B. aerogenes*. No appreciable oxygen depletions were observed in 10 days.

Oxygen Depletion in Presence of Bacteria Only

Studies were carried on with *B. aerogenes* and with bacteria other than *B. aerogenes*. All were in pure culture. The major portion of the work was done with *B. aerogenes* in an attempt to establish definitely the deoxidizing properties of this organism under standard conditions, so that, in turn, the effect and the function of the plankton, growing in pure culture and in combination with *B. aerogenes*, might also be definitely established.

With *B. aerogenes*, procedure was as follows: The dilute standard medium was prepared in 10-liter quantities, and sterilized. After cooling and vigorous agitation, the medium was inoculated with *B. aerogenes*. The temperature of the carboy of inoculated medium was next adjusted to approximately 20° C., the contents thoroughly mixed, then allowed to stand quiescent a few minutes to permit escape of entrained air. The inoculated medium was siphoned to sterile dissolved oxygen bottles with elaborate precautions to prevent contamination.

The dissolved oxygen bottles filled in this procedure were numbered in consecutive order. Initial determinations were made of the bacterial and dissolved oxygen contents of some

¹ Received September 20, 1930. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Table I—Bacterial Counts and Oxygen Depletions Observed in Dilute Dextrose-Peptide Solution Inoculated with Pure Culture of Bacteria

TIME	EXPERIMENT									AVERAGE
	4	5	6	7	8	14	15	16	17	
A— <i>B. aerogenes</i> PER CC.										
Days										
0	48,000	4,250,000	88,000	239,000	1,000,000	37,700	640,000	370,000	85,000	753,000
1	2,700,000	11,400,000	5,000,000	6,650,000	6,700,000	5,400,000	5,200,000	6,700,000	4,100,000	6,130,000
2	6,200,000	12,300,000	7,800,000	6,350,000	7,500,000	5,600,000	6,800,000	7,200,000	4,500,000	7,630,000
3	6,800,000	13,400,000	6,200,000	7,000,000	6,900,000	5,900,000 ^a	6,800,000	8,250,000	7,400,000	7,600,000
4	5,500,000	12,900,000 ^a	7,000,000	6,100,000	6,750,000	6,400,000	6,550,000	9,050,000	7,200,000	7,410,000
5	6,100,000	12,400,000	5,600,000	5,800,000	6,700,000	6,200,000	6,290,000 ^a	8,800,000	7,800,000	7,150,000
6	6,250,000	12,700,000	6,650,000	6,300,000	6,050,000	4,480,000 ^a	5,800,000	9,100,000	7,160,000 ^a	7,430,000
7	7,800,000	10,800,000	5,800,000	5,550,000	7,300,000	4,200,000	6,500,000	9,000,000	6,600,000	7,060,000
8	5,450,000	11,200,000	5,700,000	6,900,000	6,550,000	6,300,000	6,300,000	7,900,000	8,150,000	7,160,000
10	5,800,000	10,800,000	5,800,000	6,900,000	6,800,000	4,900,000	6,170,000	7,500,000	7,000,000	6,850,000
15 ^b		7,650,000	4,200,000	4,150,000	4,350,000	4,100,000	6,200,000	6,100,000		5,250,000 ^b
B—OXYGEN LOSS										
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
1	1.96	..	2.33	2.57	2.49	2.06	2.05	2.83	2.23	2.24
2	3.07	2.83	2.50	2.75	2.44	1.92	1.88	2.06	2.09	
3	2.63	2.94	2.58	2.61	2.54	2.48 ^a	3.12	3.17	3.30	2.77
4	2.76	3.08 ^a	2.50	2.91	2.74	2.28	2.28	2.63	3.30	
5	2.79	3.23	2.56	3.13	3.69	3.01	2.56 ^a	2.69	3.35	2.75
6	2.81	3.64	2.89	3.20	2.53	2.94	2.44	2.47	3.36	
7	2.80	3.21	2.55	2.86	3.17	2.95	2.37	2.64	3.45 ^a	2.83
8	2.60	2.80	2.56	2.89	3.03	3.13	2.45	3.01	3.58	3.05
10	3.07	2.89	2.66	3.64	3.41	3.17 ^a	2.30	2.47	3.50	
15 ^b		3.01	3.32	3.48	2.32	3.37	2.37	4.00	3.63	3.02

^a Calculated figure; mean of preceding and following results.^b Includes results obtained at 13 to 16 days.

Table II—Colpidium Counts and Oxygen Depletions Observed in Dextrose-Peptide Solutions Inoculated with Colpidium in Pure Bacteria-Free Culture

TIME OF INCUBATION	CONCENTRATION OF DEXTROSE AND PEPTONE	COLPIDIUM PER CC.	OXYGEN DEPLETION
Days	<i>Mg. per liter</i>	<i>Cubic standard units</i>	<i>P. p. m.</i>
5	5000	10,350	3.17
5	500	906	1.01
15	500	1,780	2.23
20	500	4,830	5.68

Table III—Colpidium Counts and Oxygen Depletions Observed in a Solution Containing 5000 mg. of Dextrose and of Peptone per Liter Inoculated with a Pure Culture of Colpidium

TIME	OXYGEN DEPLETION	COLPIDIUM PER CC.		BACTERIA PER CC.
		Individuals	Cubic standard units	
Days	<i>P. p. m.</i>			
0	..	3	6	None
1	7.0	4	9	None
2	9.5	13	26	None
4	9.0	83	224	None
5	9.2	190	570	None
7	11.8	755	2,643	None
8	11.5	1,410	5,076	None
9	13.5	2,730	12,285	None
11	34.0	6,230	23,674	None
12	57.0	8,300	29,880	None
13	78.7	10,280	39,064	None
14	95.4	12,260	47,814	None
15	130.5	14,000	67,200	None
16	148.3	15,000	72,000	None
18	175.7	12,700	50,800	None
19	190.9	13,650	54,600	None
21	226.4	14,150	62,260	None
23	244.8	15,600	67,080	None
25	265.4	14,200	55,380	None
27	297.5	13,750	59,125	None

of the first and the last bottles filled. No appreciable differences in the results of these initial analyses were observed at any time. All bottles were incubated at 20° C. Examinations were made at appropriate time intervals thereafter to determine the number of *B. aerogenes* per cubic centimeter, the residual dissolved oxygen content, and any extraneous bac-

teria or plankton that might have gained entrance to the bottles. In these subsequent examinations two or more bottles were usually analyzed at each period. The results secured from duplicate bottles were always in good agreement.

The results obtained from nine such experiments are presented in Table I. The A and B sections of the table contain the bacteriological and chemical results, respectively.

The results obtained in this series of experiments are in good agreement and permit the following deductions: (1) The medium, when inoculated with *B. aerogenes*, seems to favor their growth and the total count increased rapidly to a limiting figure which is fairly constant and is reached by 48 hours. After the limiting number has been reached, growth of the bacteria appears to cease. (2) This maximum count is sustained for several days. (3) While the bacteria were in a state of active multiplication, oxygen was absorbed at a rapid rate. (4) This absorption of oxygen practically ceased after the limiting number of bacteria had been reached although the living bacterial population remained quite high (ten million cells per cubic centimeter in some experiments). This makes it necessary to conclude that, at least under the conditions of these experiments, the oxygen requirements of resting bacterial cells are negligibly small (less than 0.01 part per million of oxygen daily per million bacteria). In a like manner the deduction that biochemical oxidation is effected only by growing cells is apparently warranted.

Similar experiments were conducted with three other species of bacteria in pure culture and with various combinations of mixed cultures of bacteria free from plankton. The results obtained with *B. aerogenes* in pure culture and with the most heterogeneous mixture of bacteria free from plankton are presented in the lower two curves of Figure III. The results with other pure cultures and with other mixed cultures were essentially the same as those obtained with *B. aerogenes*. The only difference noted was that during the first 3 or 4 days the amount of oxygen absorbed by mixed cultures was greater than with pure cultures.

Table IV—Bacteria and Colpidium Counts and Oxygen Depletions Observed in Dilute Dextrose-Peptide Solutions Inoculated with *B. aerogenes* and Colpidium in Pure Culture

TIME	EXPERIMENT										AVERAGE
	5	6	7	8	15	16	17	23A	23B	23C	
Days	A— <i>B. aerogenes</i> PER CC.										
0	4,300,000	92,000	240,000	1,030,000	622,000	422,000	90,000	350,000	350,000	350,000	781,000
1	15,000,000	4,900,000	6,800,000	6,100,000	6,700,000	7,750,000	4,250,000	6,800,000	6,400,000	5,100,000	6,940,000
2	9,650,000	6,200,000	6,400,000	7,000,000	6,900,000	8,800,000	5,700,000	6,100,000	6,900,000	5,300,000	6,050,000
3	1,080,000	6,250,000	6,150,000	4,500,000	4,800,000	9,200,000	6,600,000	6,500,000	5,900,000	6,200,000	6,050,000
4	2,080,000	6,700,000	7,350,000	3,760,000	6,900,000	10,100,000	6,900,000	7,400,000	6,800,000	5,900,000	6,050,000
5	650,000	5,900,000	5,700,000	270,000	5,850,000 ^a	8,700,000	10,700,000	670,000	4,200,000	4,650,000	4,522,000
6	350,000	5,700,000	4,800,000	220,000	6,200,000	9,200,000	8,300,000	520,000	2,500,000	5,700,000	4,522,000
7	565,000 ^a	5,400,000	4,500,000	365,000	6,200,000	5,700,000	5,120,000 ^a	190,000	260,000	6,500,000	3,170,000
8	570,000	730,000	3,280,000	354,000	5,500,000	890,000	130,000	132,000 ^a	90,000	4,100,000	1,640,000
9	690,000	2,450,000	700,000	315,000	3,640,000	585,000	159,000	176,000	480,000	2,880,000 ^a	1,640,000
10	845,000	780,000	1,210,000	500,000	870,000	5,000,000 ^a	1,280,000	48,000	115,000	420,000	1,060,000
11	805,000 ^a	370,000	1,140,000	350,000	420,000	660,000	238,000	238,000	149,000	690,000	873,000
12	480,000	380,000	1,380,000	194,000	560,000	4,300,000	760,000	238,000	247,000	390,000	873,000
13	219,000	415,000	795,000	266,000	720,000	3,600,000	680,000	47,000	129,000	530,000	793,000
14	635,000	475,000	485,000	175,000	980,000	8,600,000	680,000	39,000	41,000	470,000	793,000
15	570,000	660,000	865,000	210,000	331,000	700,000	2,770,000	39,000	41,000	470,000	793,000
16	450,000	810,000	930,000	331,000	700,000	2,770,000	520,000	218,000	340,000	339,090	705,000 ^b
17	510,000	510,000	490,000	347,000	805,000	2,100,000	63,500	158,000	330,000	545,000 ^c
18	366,000	372,000	476,000	237,000	805,000	2,100,000	63,500	158,000	330,000	545,000 ^c
	B—COLPIDIUM PER CC. IN CUBIC STANDARD UNITS										
0	7.0	10.0	10.0	10.0	40	6	5	0.5	1	2	9.2
1	71.0	6.0	4.0	14.0	..	0	0	7	7	1	12.4
2	443.0	9.0	22.3	423.0	3	8	24	36	30	68	108.7
3	804.0	48.0	156.0	720.0	78 ^a	158	220	3367	320	320	511.8
4	404.0 ^a	93.0	456.0	102.0	164	65	380	1116	472	204	538.2
5	3.0	438.0	440.0	72.0	144	360	700 ^a	1120	1410	660	538.2
6	7.5	459.0	456.0	92.0	304	685	960	830	1485	420	535.0
7	7.5	414.0	552.0	51.0	152	1242	817 ^a	817 ^a	944 ^a	560 ^a	535.0
8	48.0	240.0	512.0	498.0	290	461 ^a	384	762	382	614	358.8
9	48.0	50.0	288.0	9.0	214	237	56	556	500	548	358.8
10	37.0	12.0	176.0	344.0	10	237	56	268	216	392	149.6
11	37.0	6.0	204.0	8.0	8	248	108	268	216	392	149.6
12	37.0	15.0	12.0	64.0	8 ^a	248	108	102	24	98	83.0
13	19.0	22.0	20.0	54.0	5	191	0	294	50	124	33.1 ^b
14	19.0	6.0	12.0	6.0	5	191	0	27	30	26	33.1 ^b
15	74.0	27.0	12.0	4.0	1	85	15	15	4	15	30.0 ^c
16	74.0	19.0	51.0	6.0	1	85	15	15	4	15	30.0 ^c
	C—OXYGEN LOSS IN:										
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
1	...	2.37	2.64	2.32	...	2.80	2.77	2.24	2.19	2.27	2.42
2	3.95	2.82	2.60	2.67	...	2.53	2.79	2.21	2.27	2.03	3.15
3	4.32	2.69	2.63	3.40	...	3.78	4.22	2.40	2.68	3.67	3.76
4	4.48 ^a	3.13	2.88	3.35	...	3.64	4.33	2.40	2.67	3.27	3.76
5	4.65	4.99	3.27	3.48	...	3.89	5.11	4.14	3.78	4.31	4.33
6	4.47	3.21	3.53	3.66	...	3.79	5.64	4.11	4.20	4.47	4.33
7	4.52	3.54	3.30	5.51	...	4.29	6.54 ^a	5.54	5.11	4.83	4.33
8	5.05	4.50	4.93	3.82	...	5.34 ^a	7.69	5.46	5.48	5.12	4.85
9	4.65	3.21	3.53	3.66	...	3.10	7.79	5.89 ^a	5.78 ^a	5.56 ^a	4.85
10	4.47	3.54	3.30	5.51	...	5.34 ^a	7.69	6.29	6.09	5.85	5.24
11	4.47	4.50	4.93	3.82	...	3.40	7.69	6.27	6.44	6.44	5.24
12	4.52	3.38	3.16	5.32	...	3.51	5.90	8.48	6.50	6.63	5.38
13	5.05	3.38	3.69	3.59	...	3.50	5.90	8.48	6.50	6.63	5.38
14	5.05	3.43	4.05	4.99	...	3.76	6.24	8.39	7.05	6.84	5.74
15	4.58	5.04	3.78	5.21	...	3.56	6.91	8.40	7.57	6.61	5.74
16	5.02	3.19	3.54	3.62	...	3.56	6.91	8.40	6.90	6.84	5.59 ^b
17	5.02	3.90	3.75	5.08	...	3.88	7.47	8.52	6.98	7.32	5.59 ^b
18	5.02	3.89	3.75	5.08	...	3.88	7.47	8.52	7.25	6.93	5.89 ^c

^a Calculated figure mean of preceding and following results.^b Includes results of 9th to 11th days.^c Includes results of 13th to 16th days.

Thus these four significant facts regarding bacterial growth and oxygen demand in the absence of plankton have been established for certain bacteria growing in pure culture and also in fairly heterogeneous mixtures. In this connection it might be noted that in a few experiments the bacterial counts and oxygen depletions have been followed for 30 to 40 days without observing any marked change in the existing conditions.

Oxygen Depletion in Presence of Plankton Only

The isolation of certain kinds of plankton is a fairly easy procedure. The freeing of individual organisms even from bacteria can be accomplished. Then comes the real problem of finding a suitable medium in which the bacteria-free plankton will live and multiply. Numerous attempts on our part to accomplish this final result have failed, but very recent

work not included within the scope of this paper has apparently been successful. The one plankton organism available to us in pure culture, bacteria-free, was the ciliate colpidium.²

It was found by numerous trials that colpidium would live and multiply, in the absence of bacteria (although it will not live in the dilute medium, unless bacteria are present also), if placed in a concentrated medium containing 500 mg. or more each of dextrose and peptone per liter. Four preliminary experiments to determine the amount of oxidation in these colpidium-only set-ups gave the results presented in Table II.

The experiments were repeated, using a concentration of 5000 mg. of dextrose and of peptone per liter. Frequent examinations were made for 27 days to determine the col-

² Through the skill and kindness of M. A. Barber, U. S. Public Health Service.

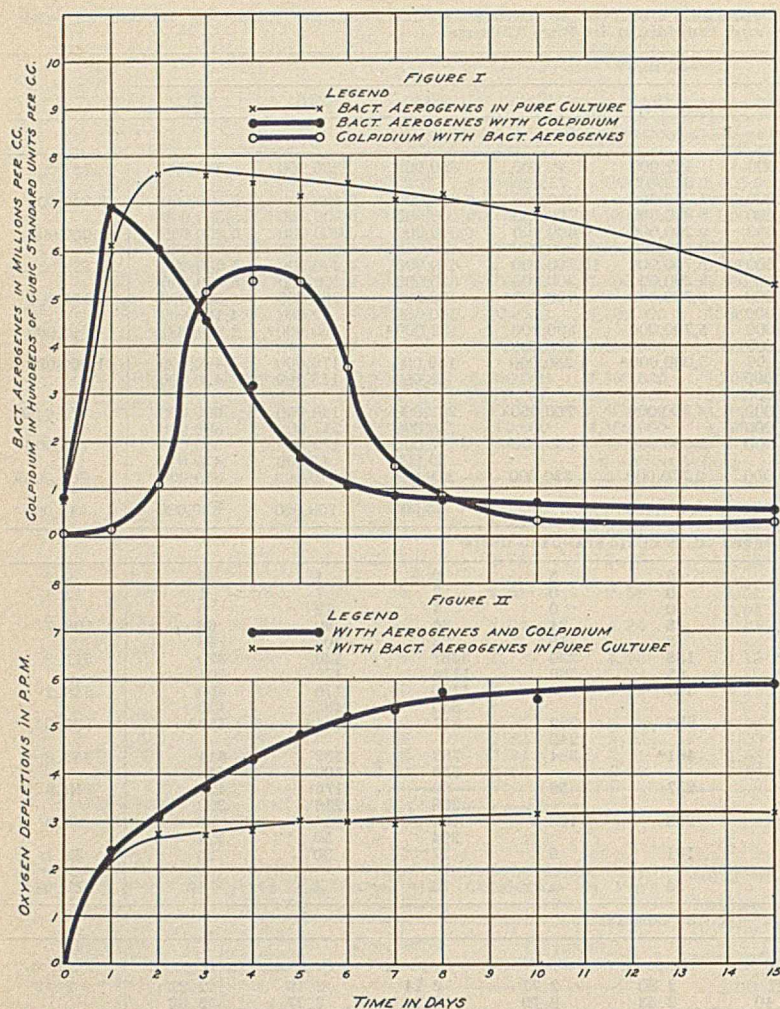


Figure I—Bacteria and Colpidium Counts in Dilute Dextrose-Peptone Solution Inoculated with (1) *B. aerogenes* in Pure Culture and (2) *B. aerogenes* and Colpidium Growing Together in Pure Culture. Average of 10 Experiments

Figure II—Oxygen Depletions Observed in Dilute Dextrose-Peptone Solution Inoculated with (1) *B. aerogenes* in Pure Culture and (2) *B. aerogenes* and Colpidium Each in Pure Culture. Average of 10 Experiments

pidium content, the oxygen depletion, and the absence of bacterial contamination, with results presented in Table III.

Colpidium growth reached its maximum about the 16th day, at which time oxygen depletion was 148.3 parts per million. This high content of colpidium remained nearly stationary up to the 27th day, and during this interval oxygen depletion slowly increased to 297.5 parts per million.

A portion of this medium in which colpidium had been growing for 27 days was now inoculated with river water, thus introducing bacteria and some few plankton. In 5 days an additional oxygen depletion of 6880 parts per million was observed, and 8350 parts per million in 10 days, a very large increase over that observed when colpidium only were present.

Oxygen Depletion in Presence of Both Bacteria and Plankton

EACH IN PURE CULTURE—Since the deoxidizing effects of *B. aerogenes* and of the plankton organism colpidium were studied when each organism was grown in pure culture, these two organisms were now combined in pure culture, and, with the same technic and medium as were employed in the preceding experiments, further study was made of the oxygen depletion and related phenomena of the combined cultures.

Usually two exactly duplicate portions of the standard

dilute medium were inoculated with the same amount of bacterial suspension, one portion being also seeded with a definite amount of active colpidium culture. In order that no question might arise as to the exact duplication of the oxidizable material present in the two series, a similar amount of the colpidium culture was killed by heat and added to the portion of culture containing bacteria only. Thereafter each of the two portions was thoroughly mixed and distributed to sterile dissolved oxygen bottles for subsequent study at regular intervals, noting the content per cubic centimeter of *B. aerogenes* and of colpidium, the extent of oxygen depletion, and the possible presence of organisms other than those introduced.

The results of ten such experiments are presented in Table IV. These results seem to warrant the following deductions:

- (1) In the bacteria-plus-colpidium cultures the bacteria increase very rapidly to a limiting figure (about 7 millions) in 24 hours, then decrease.
- (2) The colpidium increase slowly, requiring 3 to 6 days to reach the maximum. The incidence of the colpidium increase is apparently influenced by the initial bacterial density.
- (3) Coincident with or immediately following the increase of the colpidium, the observed bacterial count begins to decrease. By the time the colpidium have reached their limiting number the bacteria have been reduced about one-half and thereafter both the bacteria and the colpidium decrease.
- (4) The absorption of oxygen proceeds at a rapid rate while the bacteria are in an observed state of active increase.
- (5) In the bacteria-only series the absorption of oxygen practically ceases when the limiting number of bacteria has been reached.
- (6) In the bacteria-plus-colpidium series the absorption of oxygen continues after the limiting number of bacteria has been reached and also after the limiting volume of plankton (colpidium) was observed.

The relationships of these results are indicated by Figures I and II.

If biochemical oxidation be effected only by growing cells, it is necessary to conclude that actual multiplication of the bacteria occurred continuously in these experiments although the apparent bacterial content was continuously decreasing.

Since colpidium fail to grow in a very dilute medium which contains no bacteria, but grow well in this same medium when bacteria are present, and since marked decrease in this bacterial content coincides with the increase of the colpidium, it seems reasonable to conclude that the bacteria, by absorbing the dilute food and thus concentrating it in their own bodies, become a sufficient food in themselves to stimulate colpidium growth. The bacteria are thus "concentrators" or "condensers" of the dilute food material, and under such conditions the colpidium feed chiefly on bacterial cells.

Under existing conditions, the colpidium were apparently responsible for the marked decrease in bacterial numbers in the bacteria-plus-plankton series. Earlier studies by Purdy and Butterfield (3), who found that certain plankton forms feed largely on bacteria, support the above assumption.

On the basis of these considerations the function of the plankton in the biochemical oxidation process is to maintain the bacterial population below its limiting value. As a result it may be said that compensatory bacterial multiplication is stimulated and a continuation of the oxidation phenomenon is obtained. Since the limiting number of organisms decreases with the food supply, the actual numbers of *B.*

aerogenes and colpidium in these experiments decreased as the residual food supply was continuously lessened by their continuous growth.

Bacteria and Plankton Growing Together in Mixed Culture

Tests were made in a similar manner with:

- (1) Mixed cultures of bacteria and pure culture of colpidium.
- (2) Mixed cultures of bacteria and a small flagellate.
- (3) Mixed cultures of bacteria and paramoecium.

The results were in good agreement with those obtained with the combination *B. aerogenes* and colpidium. The only exception noted was that the extent of deoxygenation increased as the complexity of the bacterial flora was increased.

Influence of Variations in Complexity of Biological Factors on Observed Oxygen Depletion in Polluted Water

The summary chart, Figure III, tends to show that the complexity of the inoculation used has little or no effect on the rate of oxidation during the first day or two, that the most simple inoculation (a pure culture of bacteria) produced the smallest oxygen demand, and that the most complex inoculation produced the greatest oxygen demand.

Experiments Bearing on Validity of Proposed Theory of Plankton Activity

If it be true that, as previously stated, plankton activity operates to maintain the bacterial population below its saturation point by feeding upon the bacterial cells, thus encouraging continuous oxidation, then other methods of reducing the bacterial count below the saturation point should produce a similar effect. Such methods as filtration through a Berkefeld filter, chlorination, and partial sterilization by heat were tried and were found to be effective, substantially as follows:

FILTRATION THROUGH A BERKEFELD FILTER—The standard medium, inoculated with *B. aerogenes*, was bottled and incubated at 20° C. until the limiting number of bacteria had been reached. Several bottles were then removed and filtered through a sterile Berkefeld filter into a sterile container. This filtrate was reinoculated by adding a small amount of

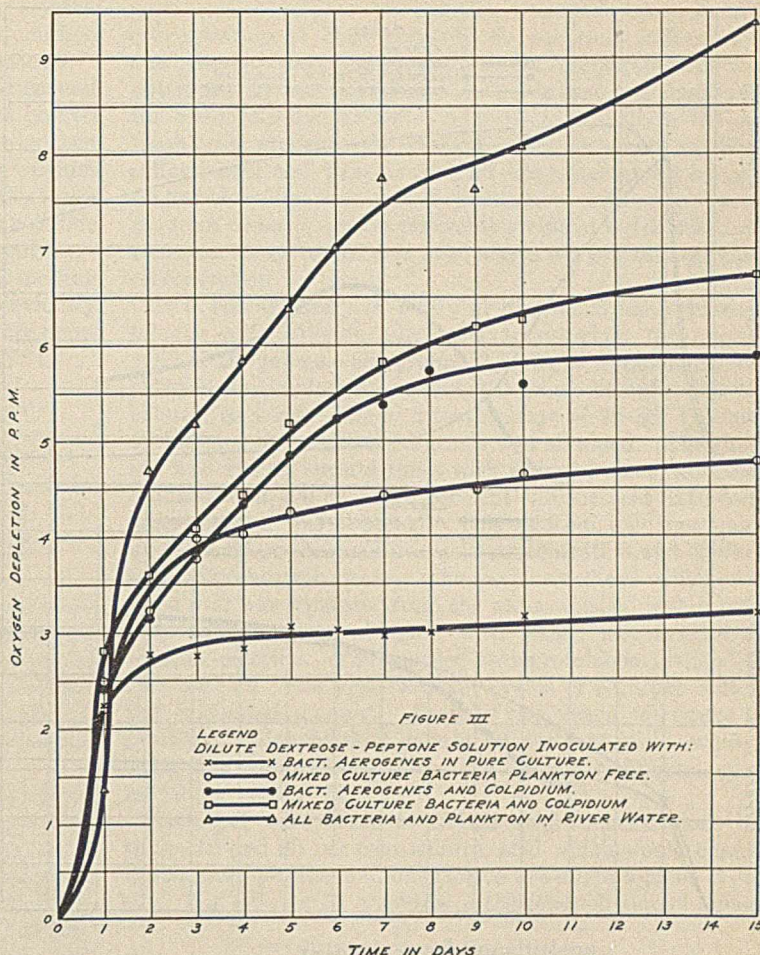


Figure III—Oxygen Depletions Observed at 20° C. When the Dilute Dextrose-Peptone Solution Was Seeded with Inoculations Varying in Biological Complexity

the unfiltered sample, was shaken vigorously, and was again siphoned to sterile dissolved oxygen bottles and returned to storage at 20° C. New initial determinations were made for the bacterial and dissolved oxygen content of the samples.

Eight such experiments furnished the data recorded in Table V and Figure IV.

These results indicate that the reinoculated Berkefeld

Table V—Bacterial Counts and Oxygen Depletions Observed in Dilute Dextrose-Peptone Solution Inoculated with Pure Culture of *B. aerogenes* after Partial Filtration and Attainment of Limiting Number

TIME AFTER FILTRATION	EXPERIMENT								AVERAGE
	4	5	6	7	8	14	19A	19B	
Days	A—BACTERIA PER CC. AFTER FILTRATION								
0	17,400	13,100	7,850	8,800	21,100	248,000	2,100	2,400	39,800
1	610,000	980,000	208,000	420,000	1,090,000	245,000	740,000	220,000	595,000
2	720,000	1,270,000	410,000	230,000	1,730,000	490,000	4,900,000	7,800,000	2,230,000
5	3,500,000	2,590,000	1,680,000	245,000	3,490,000	770,000	5,750,000	5,700,000	4,190,000
7 ^a		2,750,000	980,000	430,000	3,010,000	7,900,000	4,300,000	890,000	2,890,000
10 ^b		2,640,000	960,000	230,000	1,760,000	6,500,000	2,330,000	680,000	2,140,000
							2,280,000	520,000	
	B—OXYGEN LOSS AFTER FILTRATION								
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
0	2.81	3.23	2.50	2.75	2.54	2.98	2.32	2.24	2.67 ^c
1	3.27	3.77	2.58	2.94	3.05	3.32	3.11	2.92	3.12
2	4.01	5.37	3.14	3.12	3.68	4.10	3.83	5.63	4.11
5		8.02	7.86	3.28	5.38	5.69	4.85	5.99	5.87
7 ^a		8.24	7.43	3.92	5.31	5.89	5.27	6.04	5.01
10 ^b		8.30	7.00+	4.50	5.65	6.47	5.45	6.32	6.24

^a Includes results obtained at 6th to 8th days.
^b Includes results obtained at 9th to 12th days.
^c Oxygen demand observed prior to filtration.

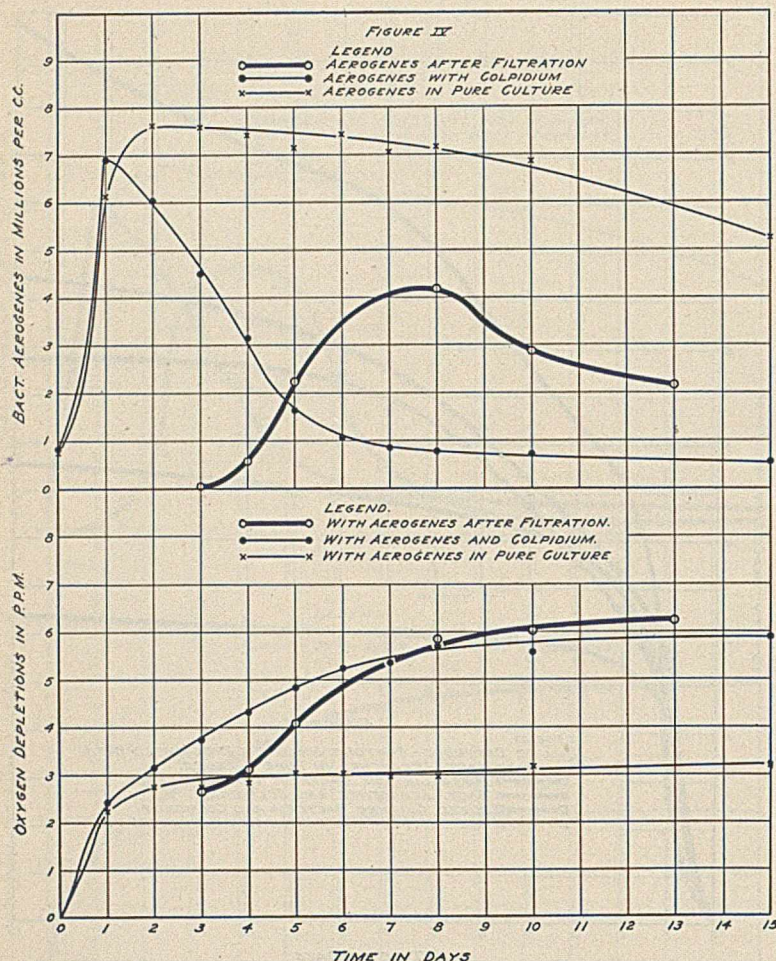


Figure IV—Bacterial Counts and Oxygen Depletions in Reinoculated Berkefeld Filtrate of *B. aerogenes* Culture. Light Lines Give Like Data of Unfiltered Culture

filtrate showed an additional period of bacterial multiplication, and that oxygen depletion was effected, meantime, in a manner very similar to these respective effects obtained previously in plankton-and-bacteria cultures.

Control tests indicated that suction alone, similar in intensity to that applied to the Berkefeld filter, did not stimulate further bacterial growth, so that detrimental volatile substances cannot be responsible for the cessation of growth.

oxidation process is to reduce the bacterial population below the saturation point and provide conditions suitable for continuous bacterial multiplication.

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- (1) Butterfield, C. T., U. S. Pub. Health Service, *Pub. Health Repts.*, **44**, 2647 (1929).
- (2) Butterfield, C. T., *Ibid.*, **44**, 2865 (1929).
- (3) Purdy, W. C., and Butterfield, C. T., *Am. J. Pub. Health*, **8**, 499 (1918).

Preparation of *o*-Chlorotoluene from *p*-Toluene Sulfonchloride¹

L. McMaster and J. Carol

CHEMISTRY DEPARTMENT, WASHINGTON UNIVERSITY, ST. LOUIS, MO.

Preparation of *o*-Chloro-*p*-Toluene Sulfonchloride

THE *p*-toluene sulfonchloride used in this work was supplied by the Monsanto Chemical Works. It was melted and mixed with a small quantity of antimony trichloride. This mixture was warmed to about 70° C. and dry chlorine passed into it slowly, with stirring, until there was an increase in weight corresponding to 1 mol of

chlorine for 1 mol of *p*-toluene sulfonchloride. Allowance was made for the amount of chlorine used to change the antimony trichloride to pentachloride. The temperature, in all but one run, was maintained at 70–80° C. to prevent the formation of higher chlorinated derivatives. At 120° C. such derivatives begin to be formed. About 3 hours were required to chlorinate the mixture, after which it was poured into ice water, whereupon *o*-chloro-*p*-toluene sulfonchloride separated as a solid, and not as an oil as described by Limpricht and Paysan (2). Davies (1) also obtained the compound as a solid, which, on distillation, gave an oil that

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solidified upon cooling. It melted at 37–38° C., after crystallization from petroleum ether. Thus far this is the method described in D. R. P. 133,000 with slight modifications.

The *o*-chloro-*p*-toluene sulfonchloride was washed several times with dilute caustic soda solution, which was poured off with the suspended antimony oxychloride. It was then washed with water, dissolved in ether, and dried over calcium chloride. After the ether was evaporated, the product was obtained as crystals of melting point 37° C. The amide obtained from it melted at 137.5° C. Limpricht and Paysan (2) converted their oily product into an amide of melting point 135° C., while Wynne and Bruce (3) had previously found that *o*-chloro-*p*-toluene sulfonamide has a melting point of 134° C. Davies (1) gives the melting point as 137° C.

Table I—Yields of *o*-Chloro-*p*-Toluene Sulfonchloride

<i>p</i> -TOLUENE SULFONCHLORIDE	SbCl ₃	TEMPERATURE	YIELD
Grams	Grams	° C.	%
190.5	4	70–80	94.2
190.5	2	70–80	90.0
190.5	1	70–80	88.0
190.5	4	80–90	92.0
381.0	10	70–80	94.0

The best conditions for the preparation of *o*-chloro-*p*-toluene sulfonchloride by chlorinating *p*-toluene sulfonchloride are thus shown to be that for each 190.5 grams (1 mol) of the *p*-toluene sulfonchloride, 4 grams of antimony trichloride should be added and the mixture chlorinated at 70–80° C. with constant stirring. Slightly higher temperatures may be used.

An attempt was made to replace the antimony trichloride by powdered iron. One mol of *p*-toluene sulfonchloride was melted, 0.5 gram of powdered iron added, and the mixture chlorinated. In earlier attempts larger amounts (2 to 5 grams) of iron were used, but each gave a very thick, tarry mass. Contrary to the conditions given in D. R. P. 133,000, the chlorination took place, not between 70° and 80° C., but between 120° and 140° C. It was continued until an increase in weight of 38 grams occurred. The chlorinated mixture was poured into a mixture of ice and diluted hydrochloric acid and washed free from iron chloride. The mixture would not solidify, but remained as a thick paste. It is quite probable that a mixture of chlorinated products was obtained, as no *o*-chlorotoluene was obtained from it when treated by the method to be described later.

o-Chlorotoluene from *o*-Chloro-*p*-Toluene Sulfonchloride

One mol (225 grams) of the *o*-chloro-*p*-toluene sulfonchloride was mixed with 500 grams of 80 per cent sulfuric acid and distilled with steam. The *o*-chloro-*p*-toluene sulfonchloride distilled over unchanged. Sulfuric acid solutions of various concentrations were tried—10, 40, 50, and 60 per cent. With only the 50 per cent solution was a small amount of *o*-chlorotoluene obtained.

An attempt was made to split off the sulfonchloride group by water under pressure. One-tenth mol (22.5 grams) of the material was mixed with 50 cc. of water, sealed in a glass tube, and heated in an autoclave for 5 hours at 200° C. The *o*-chloro-*p*-toluene sulfonchloride was not changed to *o*-chlorotoluene, but to *o*-chloro-*p*-toluene sulfonic acid. This solution was made up to an 80 per cent sulfuric acid concentration and distilled with superheated steam. A 90 per cent yield of *o*-chlorotoluene was obtained.

It was found that the *o*-chloro-*p*-toluene sulfonchloride could be changed to the corresponding sulfonic acid by refluxing it with water and sulfuric acid. Sulfuric acid concentrations of 10, 50, and 85 per cent were used, but the hydrolysis was found to take place most rapidly in the 10 per

cent solution. When this solution was made up to an acid concentration of approximately 80 per cent sulfuric acid and distilled with superheated steam, *o*-chlorotoluene was obtained. It was thus shown that it is first necessary, with the *o*-chloro-*p*-toluene sulfonchloride, to hydrolyze the sulfonchloride group to the sulfoxyl group by means of dilute sulfuric acid and then to split off the latter group by concentrated sulfuric acid and distillation with superheated steam in order to obtain favorable yields of *o*-chlorotoluene. Concentrations of sulfuric acid above 85 per cent produce carbonization.

It is not necessary to purify or dry the crude *o*-chloro-*p*-toluene sulfonchloride. In order to ascertain the over-all yield of the process, 381 grams (2 mols) of *p*-toluene sulfonchloride were chlorinated, using 10 grams of antimony trichloride as a catalyst and a temperature of 70–80° C., until an increase in weight of 75 grams was obtained. The product was washed several times with water, drained, and then refluxed with 400 cc. of 10 per cent sulfuric acid until complete solution was obtained. This solution was then made up to an 80 per cent sulfuric acid concentration and distilled with superheated steam. The *o*-chlorotoluene which distilled over was separated from the water, washed with caustic soda solution, washed again with water, and dried over calcium chloride. The purified *o*-chlorotoluene distilled at 157–159° C. The yield was 224 grams or 88.5 per cent of the calculated amount. Another run, using 95 grams of *p*-toluene sulfonchloride, gave a 90 per cent yield, while a third one, using 381 grams of the original compound, gave an 89 per cent yield.

Attempts were made to obtain acid concentrations between 10 and 80 per cent sulfuric acid which would change the *o*-chloro-*p*-toluene sulfonchloride to *o*-chlorotoluene in one step, but only small amounts of the product were obtained.

Summary and Conclusions

1—*o*-Chlorotoluene may be prepared from *p*-toluene sulfonchloride with 90 per cent yield by chlorination of the latter to *o*-chloro-*p*-toluene sulfonchloride and subsequent hydrolysis. The chlorination takes place, using antimony trichloride as a catalyst, at a temperature from 70° to 80° C.

2—The *o*-chloro-*p*-toluene sulfonchloride must first be hydrolyzed to *o*-chloro-*p*-toluene sulfonic acid with 10 per cent sulfuric acid, which is then hydrolyzed to *o*-chlorotoluene by increasing the acid to 80 per cent concentration and using superheated steam.

3—Iron proved unsatisfactory as a chlorine carrier in place of antimony trichloride.

4—The presence of chlorine in the ring of an aromatic sulfonchloride appears to hinder the splitting off of the sulfonchloride group by sulfuric acid.

Acknowledgment

The writers wish to thank Jules Bebie for some valuable suggestions concerning this investigation, and the Monsanto Chemical Works for the *p*-toluene sulfonchloride.

Literature Cited

- (1) Davies, *J. Chem. Soc.*, **119**, 860 (1921).
- (2) Limpricht and Paysan, *Ann.*, **221**, 212 (1883).
- (3) Wynne and Bruce, *J. Chem. Soc.*, **73**, 764 (1898).

Correction

An error has been found in literature reference (16) in the article entitled "Studies in the Development of Dakota Lignite—III," by Lavine, Gauger, and Mann, *IND. ENG. CHEM.*, **22**, 1347 (1930). This reference should read: Sterne, U. S. Patent 838,281 (December 11, 1906).

Unfired Pressure Vessels¹

W. Spraragen

AMERICAN BUREAU OF WELDING, 33 WEST 39TH ST., NEW YORK, N. Y.

THE application of fusion welding to the fabrication of pressure vessels and tanks of all kinds has been a gradual development. Unfortunately, in the beginning good design and construction were at times sacrificed in favor of cheapness, which has resulted in tremendous damage to the prestige of the industry and has caused legislative bodies to place severe restrictions on its use.

As a matter of fact, welding is admirably adapted to the fabrication of vessels of all kinds. When properly applied, a vessel may be made oil- and gas-tight practically up to pressures that would cause rupture of the material itself. We therefore find welding used for the fabrication of vessels from the very light gages and small sizes to huge vessels required in chemical processes where the contents are subjected to great heat and pressure and the thickness of steel is as great as 4 inches.

In 1923 there were reported the results of a series of investigations made under the auspices of the American Bureau of Welding with the coöperation of the U. S. Bureau of Standards (1), which gave a wealth of valuable information on the design and construction of unfired pressure vessels and which enabled the Boiler Code Committee of the American Society of Mechanical Engineers in time to promulgate a code which removed some of the restrictions placed against welding.

This paper is based in a measure on the results of these tests, the Unfired Pressure Vessel Code of the A. S. M. E., the writings of the late S. W. Miller, and the experience of a number of engineers. The latest edition of the A. S. M. E. Code for Unfired Pressure Vessels should be consulted for the design of any welded vessel subjected to pressure.

As in other important construction work, the fundamental factors to be considered are: (1) selection of material of good welding quality and the use of good welding wire; (2) correct design of vessel and welded joints; (3) use of qualified welders; (4) proper preparation of the material for welding; (5) employment of proper technic; and (6) testing of the completed vessel.

Material

An excellent résumé of the requirements of good materials is given in the Recommended Procedure for Fusion Welding of Pressure Vessels, which is an appendix to the latest edition of the Unfired Pressure Vessel Code of the A. S. M. E.

Well-made steel is largely dependent for its physical properties on its carbon content and this is the first consideration in deciding what chemical analysis should be followed. Other things being equal, the higher the carbon the more difficult is the welding and less satisfactory is the weld. The difference in welding qualities is not very great between 0.10 and 0.20 per cent carbon, but there is a marked difference between 0.20 and 0.30 per cent carbon. There is a corresponding difference in the physical properties, 0.15 per cent carbon having probably 50,000 pounds tensile strength while 0.30 carbon will have about 65,000 pounds. These figures apply to plates of ordinary thickness made in the usual way.

Steel plate of not over 0.20 per cent carbon is therefore recommended because the lower the carbon the less injury is done to the steel by any method of heating or by hot- or cold-working. The lower the carbon the less the yield point and

a lower yield point allows the welding strains to be absorbed by the plate rather than concentrated in the weld. For plates more than $\frac{3}{4}$ inch thick a slightly higher carbon content (0.22 per cent) is permissible.

There is no point in having a steel of high tensile strength if the welding wire is such that the weld produced therein has an average tensile strength of 50,000 pounds per square inch.

Steel to be used in the welding of pressure vessels should be of good quality and free from impurities. The quality is dependent on the care with which the steel was made. Impurities, together with any such defects as segregations and laminations, may seriously affect the weldability of the plate. Steel is made in four usual qualities—firebox, flange, ship, and tank. Of these, firebox is the best. Therefore, for use in welded pressure vessels firebox plate of low carbon content, and consequently low strength, should be specified. A welded joint in this material, properly made and reinforced, will always be stronger than the plate material.

Particular attention is called to the specifications for filler material as given in the Recommended Procedure for Fusion Welding of Pressure Vessels cited above.

Design of Shell

The Unfired Pressure Vessel Code requires that the minimum thickness of shell plates, heads, and dome plates after flanging shall be as follows:

DIAMETER OF SHELL Inches	THICKNESS OF SHELL Inches
16 and under	$\frac{1}{8}$
Over 16 to 24	$\frac{3}{16}$
Over 24 to 36	$\frac{1}{4}$
Over 36 to 54	$\frac{5}{16}$
Over 54 to 72	$\frac{3}{8}$
Over 72	$\frac{1}{2}$

The thicknesses of the smaller vessels were probably designed to allow for some corrosion. The maximum allowable working pressure on the shell of a pressure vessel, subjected to internal pressure, is computed from the formula:

$$\text{Maximum working pressure, in pounds per square inch} = \frac{S \times t}{R}$$

where S = maximum allowable fiber stress in pounds per square inch

t = minimum thickness of shell plates in weakest course, inches

R = inside radius of the weakest course of the shell, inches, provided the thickness of the shell does not exceed 10 per cent of the radius. If the thickness is over 10 per cent of the radius, the outer radius shall be used.

Where the vessels are fabricated in accordance with the recommended procedure for fusion welding of pressure vessels, the Unfired Pressure Vessel Code specifies a working maximum unit working stress, S , at right angles to the direction of the joint.

	Lbs. per sq. in.
For butt double-V longitudinal welds.....	8000
For butt single-V girth or head welds.....	6500
For double full fillet lap or girth welds.....	7000
For spot or intermittent girth or head welds.....	5600

For plates $\frac{1}{4}$ inch or more thick the author is of the opinion that longitudinal seams should be of the double-V type—that

¹ Received September 22, 1930.

is, welded from each side half-way through the sheet. The double V is favored for hand operation, as any irregularities will occur at the bottom of the V, which in a double-V joint is in the center. Improperly fused material may be chipped out before welding the V on the other side. However, a single-V weld is permissible if the improperly fused material is chipped out from the inside and filled in with an additional layer of metal properly reinforced (Figure 1). In automatic machine welding the weld is deposited in one or more layers in a single V or U-shaped groove. Sometimes a backing-up strip is used to insure a perfect weld at the bottom of the V or U. Where this is not done the same precautions should be followed as in hand welding. Although not specifically stated in the Boiler Code, the author believes that the double-fillet lap joint or the double-fillet joggled lap joint should not be used for longitudinal seams when the shell plate exceeds $\frac{3}{8}$ inch. The load is probably unevenly distributed between the two fillet joints except where the plates are thin.

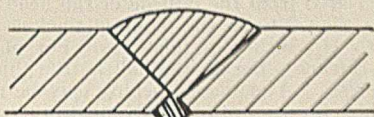


Figure 1—Single-V Weld with Incompletely Fused Filler Material Chipped Out and Filled In from Opposite Side of Plate

In the series of vessels designed for 250 pounds pressure and tested at the Bureau of Standards, the average bursting fiber stress of the double-V butt joints was 97 per cent and the minimum 90 per cent. The average strength of the steel used in these tests was 50,000 pounds per square inch. With a factor of safety of 5 and a weld value of 80 per cent this would give a design fiber stress at the working pressure of 8000 pounds based on the nominal plate thickness.

A comprehensive investigation on the subject of weld pressure vessels has recently been described by L. W. Schuster, of the British Engine Boiler and Insurance Company (19). Various types of joints and head construction, both theoretical and practical, are discussed in detail, and special forms of strap reinforcement are analyzed. However, the present author's experience leads him to believe that the double-V joint, properly reinforced, is the best type for the construction of longitudinal seams for pressure vessels. Paragraphs U-71 and U-72 of the Unfired Pressure Vessel Code give pertinent information which should be carefully followed.

Design of Heads, Manholes, and Threaded Openings

The appropriate sections of the Boiler Code should be carefully studied and followed, as they are based upon safe practices. The author believes, however, that it may be advantageous to discuss the results of tests and general experience that are available on this subject. Approved designs of nozzles and heads as given in this code are reproduced herewith as Figure 2. In a suggested code proposed by Miller slightly different types of construction are proposed, which are reproduced in Figures 3, 4, and 5, which meet with the author's approval except for Figure 5, which shows a head construction with intermittent spot welds. In a number of tests made on full-size pipe sections with a similar type of construction, it has been found that these spots are a source of weakness.

HEAD DESIGN—Heads inserted in a shell should be well fitted. The minimum length of head flanges, either convex or concave, should be as follows:

Dished heads convex to the pressure should have a flange not less than $1\frac{1}{2}$ inches long. Dished heads concave to the pressure should have a length of flange not less than 1 inch for shells not

over 24 inches in diameter. For vessels over 24 inches in diameter this length should not be less than $1\frac{1}{2}$ inches.

Attention is called to the desirability of reducing the thickness of the head at the edges to be welded to approximate that of the shell thickness. Attention is also called to the section on recommended procedure of this code dealing with construction. The greatest objection to the usual design of welded inserted heads concave to the pressure is that it is not possible to prevent some bending strains on the weld because of the distortion of the head under pressure and because a perfect fit cannot be had. This led Miller to propose the designs shown in Figure 5 using spot or tack welds at the end of the flange to avoid this bending. However, the author believes that the design shown in Figure 2-J, approved by the Boiler Code Committee, is safer.

For thin material ($\frac{3}{8}$ inch or less) and for small-diameter tanks (about 24 inches) the author believes that the designs assembled in Figure 6 are entirely safe, provided the dimensions and location of the welds shown in the illustrations are followed.

It is somewhat interesting to note that the experience of British investigators in head design differs from that of the United States (19). While they concede the head construction shown in Figure 2-J to have a high rating, par-

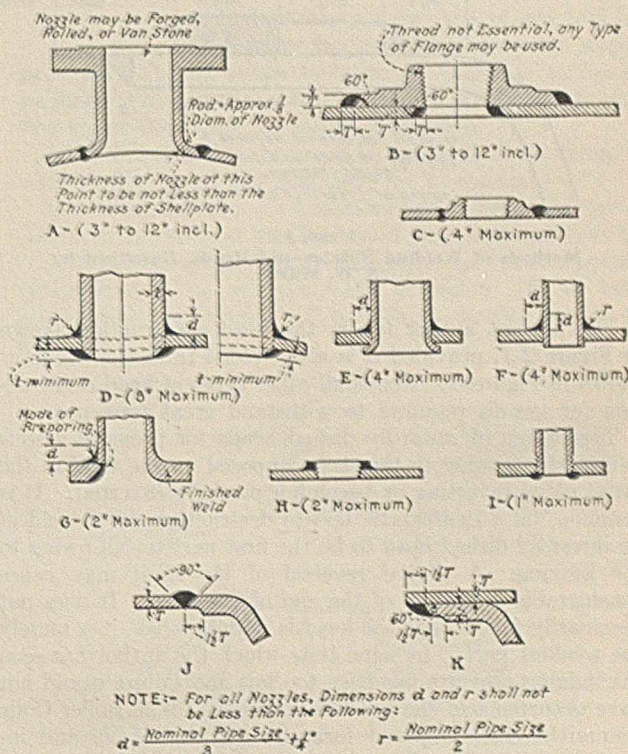


Figure 2—Methods of Autogenously Welding Nozzles and Heads, Specified by A. S. M. E. Code

ticularly if the V-joint is welded both inside and out, they regard it as somewhat dangerous because of bending at the end. In fact, they look more favorably upon a double fillet lap joint, with proper length of flange, as a somewhat superior type of construction. Schuster recommends some crimping method to increase the safety of the head construction. In a series of tests made at the Bureau of Standards crimping was not found to increase the safety of a vessel materially. On the other hand, Schuster does not look favorably upon the head construction shown in Figure 2-K. He maintains that this type of construction is subjected to an out-of-line pull, although he admits that the primary bending action is reduced because the part is circular.

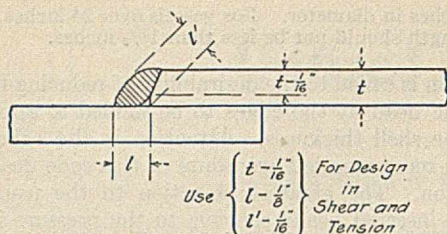


Figure 3

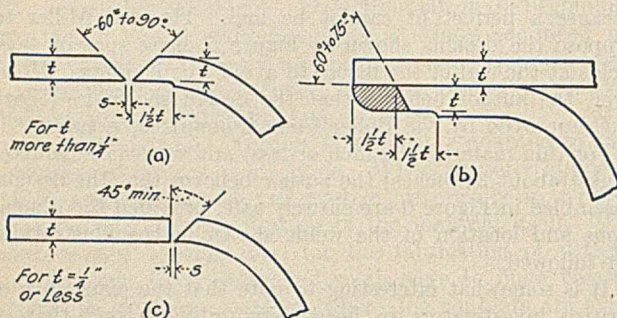


Figure 4

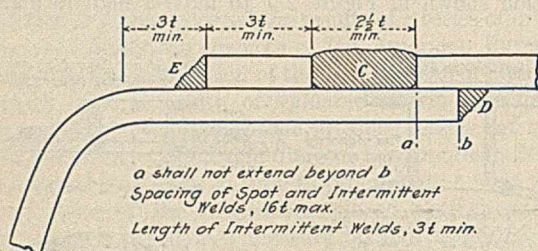


Figure 5

Methods of Welding Nozzles and Heads, Described by S. W. Miller

The present author favors the head construction shown in Figure 2-J, provided it is also welded from the inside as shown in Figure 6-F, above all other types of head construction for vessels required to withstand great pressures.

The design of inwardly dished heads for pressure vessels is important owing to the stress imposed on the weld in the event of its inverting or becoming partially inverted. It is common, on a hydrostatic test to destruction, for a weld of an inwardly dished head to be the first part to fail owing to the bulging. A partial reversal of the head may cause considerable distortion of the end of the shell. It does not necessarily follow that the head is unduly weak, it is merely the weakest part. In some tests which the author has seen the bulging pressure has been too low and failure would not have occurred had the head been convex. The Boiler Code Committee has prepared formulas for the design and insertion of dished head construction which are given in paragraphs U-36 to U-39 and U-74 to U-76 of the Unfired Pressure Vessel Code. These paragraphs also discuss openings in the head.

Welded construction has permitted the testing of vessels at hydrostatic pressure several times the working pressure. As a result it has been possible to determine experimentally the exact behavior of vessels at high pressures. In such a series of investigations made in the laboratories of one or two companies, zones of unexpected weakness were found in several important points, notably at the knuckle of dished heads, manhole openings, and at nozzles. The stresses at the knuckle when ordinary dished heads are used are entirely out of proportion to those in the shell and are of sufficient magnitude to give considerable concern, even where the shell design is based on the factor of safety of 5 or more.

Investigations show that the correct design for eliminating high local stresses is an ellipsoid with a ratio of 2 to 1 between the major and minor axes.

The Boiler Code Committee states:

A blank head of a semi-elliptical form, in which the minor axis of the ellipse is at least one-half the diameter of the shell, shall be made at least as thick as the required thickness of a seamless shell of the same diameter. If a flanged-in manhole, which meets the code requirements, is placed in an elliptical head, the thickness shall be the same as for an ordinary dished head with a radius equal to 0.8 the diameter of the shell and with the added thickness for the manhole.

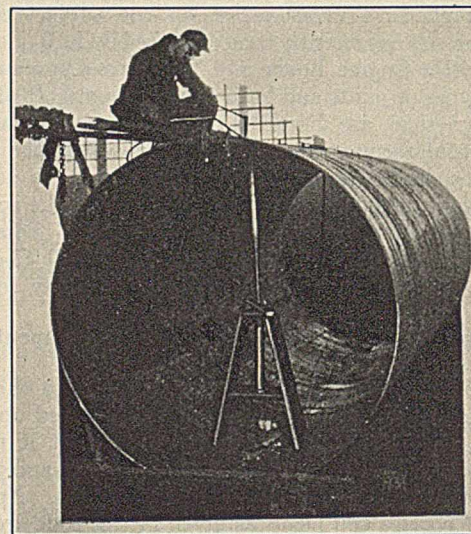
This allows a very much lighter head construction than would be permitted with any other form of dished head.

MANHOLE OPENINGS—Paragraph U-39 of the Unfired Pressure Vessel Code states:

A flanged manhole opening in a dished head shall be flanged to a depth measured from the outside of the head at the major axis of not less than 3 times the required thickness of the head for plate up to 1 1/2 inches in thickness. For plate exceeding 1 1/2 inches in thickness the depth shall be the thickness of the plate plus 3 inches. A manhole opening may be reinforced by a riveted manhole frame or other attachment in place of flanging.

At first it may seem that the Boiler Code Committee has been unduly conservative in regard to these flange requirements. However, as stated above, the results of a series of tests to destruction indicated that the former requirements were not stringent enough.

In 1927 Rockefeller (17) proposed a design of manhole reinforcement ring which reduces the stresses at the opening to normal. The salient features of this design are illustrated in Figure 7.



Oxyacetylene Welding Longitudinal Seams on Large Pressure Vessel

NOZZLES—Nozzles in heads or shell are limited by the Boiler Code Committee to 12 inches nominal diameter and are to be made of forged or rolled steel. Methods of insertion are indicated in Figure 2. The committee prescribes that threaded connections shall be not less than extra-heavy pipe size and shall fit snugly when inserted into the shell plate. The nominal diameter of threaded connections shall not exceed one-third the nominal diameter of the shell.

The procedure for lining up outlets varies somewhat with the different types. Nozzles that require butt welds are usually accurately aligned with a space about 25 per cent

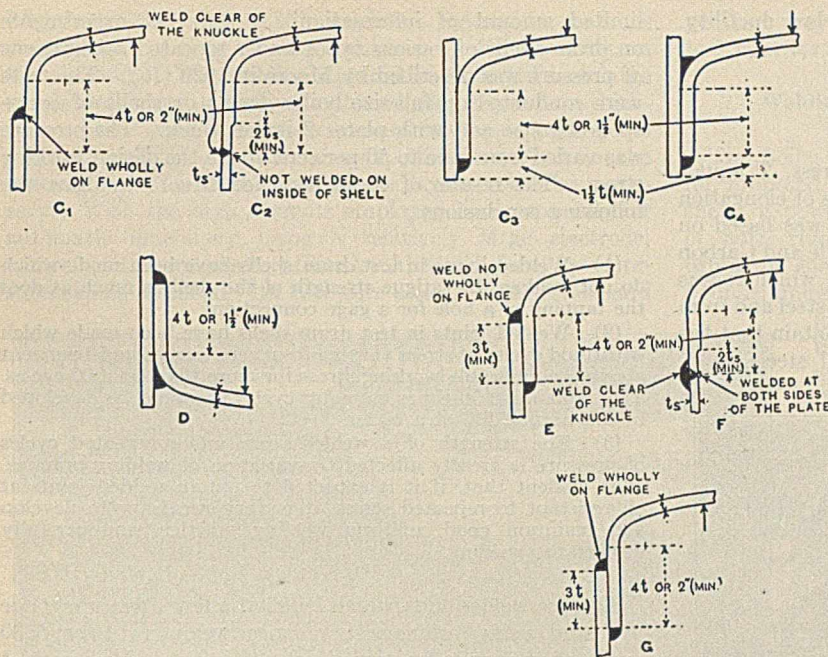


Figure 6—Head Designs for Thin Material and Small-Diameter Tubes Preferred designs are F and G.

of the plate thickness separating the abutting edges and tacked at the quarter points.

In welding outlets the position of the tank is such that the welding takes place downward—i. e., in a flat position. Where this is not possible, shell nozzles are welded in somewhat the same way as the position weld in pipe. The shell is turned so that the axis of the nozzle is horizontal. The weld is started at the bottom and continued up one side. The shell is then rotated 180 degrees and the weld continued.

Qualifications of Welders

Although no welder should be employed on any construction work unless it is known that he is competent, this is particularly important in the case of the welding of unfired pressure vessels. All welders engaged in this class of work should be tested carefully.

In the Recommended Procedure for Fusion Welding of Pressure Vessels qualification tests for welders are covered in detail. Essentially these requirements are that the welder shall make up two test plates of the same material and thickness that are to be used in the tank construction. Butt welds made in the flat position are specified. If, however, other forms of joint or positions of welding are required in the tank construction he must also qualify by making up specimens under these conditions. After the weld is completed, the test plates are cut up into test specimens and the reinforcement at the weld is ground off. For a welder to qualify, the tensile strength results should average at least 45,000 pounds per square inch with no one test piece giving less than 42,000 pounds. If these results are not reached, the welder may be given a duplicate test.

Inspection

The same recommended procedure for fusion welding of pressure vessels covers the requirements for inspection. These rules relate more particularly to the duties of the inspector and stamping rather than to detailed instructions for determining the quality of welds from a visual inspection. The importance of supervision and local inspection in a shop is, however, stressed.

The Boiler Code rules, however, do require that during the process of the manufacture of a vessel the inspector shall inspect the material for surface defects, cracks, blisters, pit marks, blow holes, or any other defects liable to develop in fabrication, and for excessive hammer marks. Plates that are found laminated are required to be rejected, as are also plates having a depression greater than 15 per cent of its thickness and exceeding 4 inches in its greatest length. Low spots in or at the sides of the welds must be filled up.

Testing

A finished tank is tested to find out if it has been properly made and if it will with reasonable assurance stand the service for which it has been designed. For welded tanks the Boiler Code has accepted the recommendations of the American Bureau of Welding (1). This test requires that the sheets on both sides of the welded seam be given a hammer or impact test while under a hydrostatic pressure test of one and one-half times the maximum allowable working

pressure. The blows are to be struck with a 2- to 6-pound hammer 2 to 3 inches apart as hard as possible without indenting or distorting the metal of the sheet.

After this test the pressure is raised to three times the working fiber stress and held there for 3 minutes.

This requirement is for fusion-welded vessels only, but the results of the tests at the Bureau of Standards indicate that these requirements are not to be feared if the vessel is properly constructed. The recommended procedure (2) is rather rigid in its requirements if any leaks develop under this test.

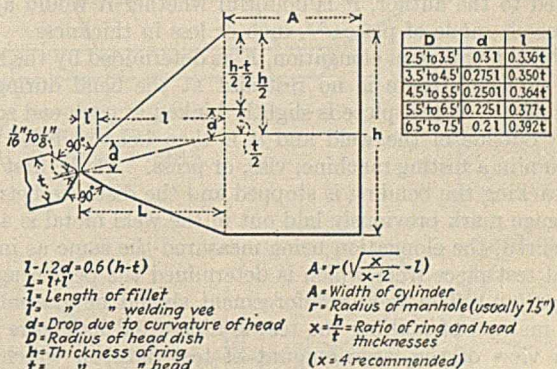


Figure 7—Design of Reinforced Manhole

It is interesting to note that Schuster (19), in recommending a code for pressure vessels for use in Great Britain, places the requirements for the hydrostatic test at least twice the working pressure at which the pressure hammer tests are administered. The pressure is then reduced by at least 50 per cent of its value and then raised to the original value for 3 minutes.

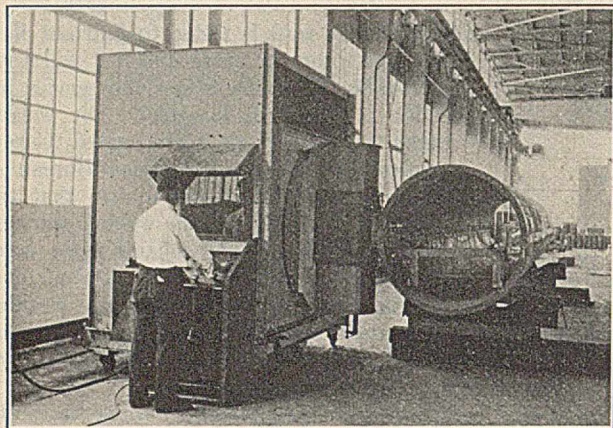
Kinzel-Miller Formula

A formula for safe working fiber stress in the design of pressure vessels was developed by A. B. Kinzel and S. W. Miller. This formula takes in account the ductility of the weld metal in such a way that the lower working fiber stress

would be allowed where the weld metal has low ductility. The formula is

$$S = \frac{T}{7.15} \sqrt[3]{\frac{E}{10}}$$

in which S is the allowable working fiber stress, T equals ultimate tensile strength, and E the percentage of elongation as determined by a bend test. This formula was based on a large series of tests made by the Union Carbide and Carbon Company. While most of the test results on which it was based were derived from welds made in firebox steel and from medium and low-carbon steels, the authors maintain that the formula would also be safe for other special steels. The



X-Ray Apparatus for the Production Examination of Welded Pressure Vessels

formula is intended to apply to arc and gas welding. It is held by some to place undue emphasis on the ductility of the weld metal. The proper range of applicability of the formula has not yet been determined. From evidence submitted to the author, it is doubtful whether it would apply to vessels made of plates $\frac{1}{4}$ inch or less in thickness.

The percentage of elongation, E , is determined by the bend test in which there is no restraint at the bend during its making. The test piece is slightly kinked at each end somewhat outside of the weld and it is then bent endwise as a column in a testing machine, vise, or press. At the first sign of cracking the bending is stopped and the distance between the gage mark previously laid out in the weld metal is again measured, the elongation being measured the same as in the usual test piece from which is determined the percentage of elongation. The weld reinforcement should be ground off. The method of making the test is illustrated in Figure 8.

In view of the large amount of test data on which the formula is based, the author recommends its use as a checking formula in the design of important pressure vessels. In some instances, however, the formula will give the design values greater than that permissible in the present A. S. M. E. Boiler Code, although the author believes they would be safe. However, the apparent lack of applicability to thin-walled vessels should be noted.

Fatigue Tests on Drums and Shells

The advent of high pressure in steam boilers has necessitated the use of plate material of increased thickness for the shells. This has appreciably affected the design of boiler drums. For pressures ranging between 800 and 1500 pounds per square inch, forged drums, or welded seams are necessary in the heavy plates. Competent authorities feel that the ordinary static pressure test to destruction gives only a

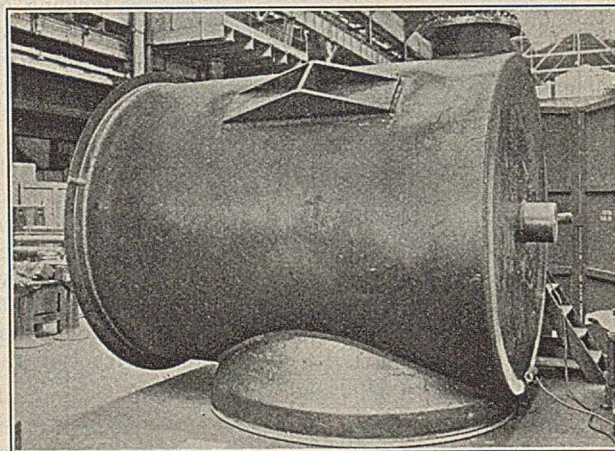
limited amount of information. A series of experiments on drum shells of various types under repeated applications of pressure was described by Moore in 1929 (16). The tests were conducted on full-size boiler drums or shells of corresponding size and with plates 2 inches thick. The pressure was varied from zero to 50 per cent above the design working stress. The results of these tests led Moore to draw the following conclusions:

- (1) Welded joints in test drum shells have been made which do not weaken the fatigue strength of the shell as much as does the tapping of a hole for a gage connection.
- (2) Welded joints in test drum shells have been made which withstood cycles of stress varying from zero to a value 50 per cent above the allowable working stress for more than 400,000 cycles. This is at least 50 times as many cycles as would be developed in the normal life of a boiler.
- (3) The strength of a welded seam under repeated cycles of pressure is greatly affected by variation of welding practice. It is evident that, if it is expected to obtain welded joints at all resistant to repeated stress, it is very necessary to develop and maintain good, uniform welding practice, and carefully inspect the welding.

The one welded tank which failed at a low stress was made by hand using ordinary bare wire welding. After 5530 cycles of pressure a fracture developed in the welded seam at the junction of the base and weld metal. The other vessels, which were made by special technic using a flux-covered electrode, fractured at cycles varying from 417,000 to 565,000, the fracture occurring at the taphole in the gages and not in the weld. This undoubtedly led Moore to conclusion (3).

Ductility of Welded Joints

The importance of ductility of the welded joints in the construction of pressure vessels has already been emphasized. The question of ductility is also, in a measure, tied up with "locked-up stresses." A number of important and practical methods have been developed to secure greater ductility where this seems to be desirable. Several of the larger companies that are welding vessels for the oil and chemical industries regard their processes as more or less secret. However, the generally recognized procedures for obtaining increased ductility are outlined below.



Courtesy General Electric Co.
Special Condenser Boiler Shell. All Seams Electric Arc Welded

ARC WELDING—This method is applicable with automatic or hand operations. A flux-covered wire which has a suitable covering to protect it from the oxygen of the air is generally employed. High current values are generally used. The metal is kept in a molten or puddled state as

long as possible, but in this condition the molten metal is protected by a slag coating furnished by the covering on the electrode. The welding material is deposited in a large number of layers, each layer not exceeding $\frac{3}{16}$ inch in thickness. Each layer is carefully cleaned before depositing the succeeding layer. It can be seen, therefore, that in the welding of 2-inch steel ten or twelve layers would be necessary. With the high currents employed, and especially for automatic machinery using a relatively large electrode, control of the arc is also utilized. Although fairly good results can be obtained with bare wire using a high current and

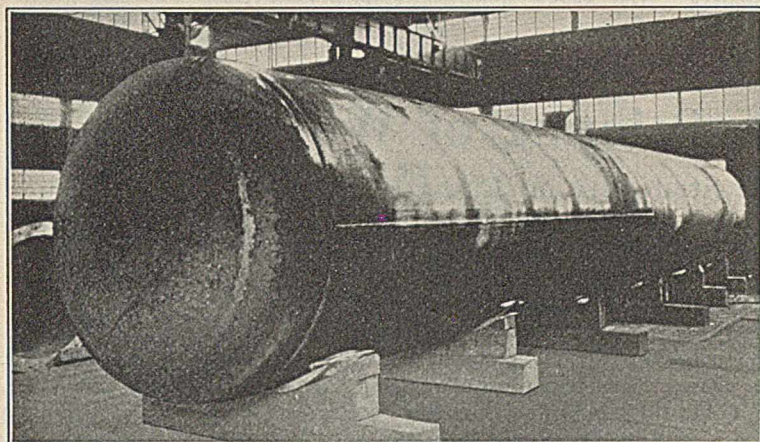
perature may vary from 4 to 5 hours for the thicker vessels to 1 hour for vessels of 1 inch in thickness.

Welding of Drums or Shells of Power Boilers

The Boiler Code Committee is now considering suggestions for proposed specifications for fusion welding of drums or shells of power boilers. This is a result of the inadequacy of both riveted and forge-welded construction for such drums or shells for boilers to operate at from 900 to 1500 pounds, unless the diameters are kept down to impracticable limits. On the other hand, recent refinements in the application of fusion welding have made practical the welding of drums and shells of plate thicknesses up to 3 inches or more, and vessels constructed in this manner have been successfully used in large numbers in connection with petroleum refinery equipment.

Proposed specifications issued as a basis for discussion (3) called for stress relieving and sample test specimens from which tension, impact, and bend tests may be made, as well as macroscopic and microscopic examinations. Chemical analyses are required as well as non-destructive tests of the vessels. A modified fatigue test of the vessel is proposed in that the annealed vessels are required to be subject to 10,000 cycles of pressure, each cycle varying from zero to one and one-half times the working pressure. Welding vessels for such severe service conditions will require more careful selection of

material and perhaps steel of different composition than that ordinarily used and careful rolling of the plates and preparation for welding as well as testing of the finished product.



Oxyacetylene Welded Tank, 7 X 50 Feet, Designed for 200 Pounds Working Pressure

a large number of layers, nevertheless, for the best results a flux coating on the wire which affords protection from oxidation is necessary.

GAS WELDING—A vessel constructed under rigid procedure specifications by the gas-welding method will be entirely safe and the weld metal possesses excellent ductility and tensile strength. Special wires may be used to obtain greater strength or ductility of the welded metal deposit where this is desirable.

ELECTRIC TORNADO WELDING—This method is used to designate the automatic carbon-arc process, where the arc is magnetically controlled and confined, the electrode given a rotary motion, and the arc surrounded by a reducing atmosphere. The metal is also kept puddled for a somewhat greater length of time. The filler material is added by placing the rod or strip on or between the edges to be joined. Excellent physical properties of the welded joint have been obtained by this process.

ATOMIC HYDROGEN AND SHIELDED ARC METHODS—Ductility of the welded joints in either of these methods is dependent on the exclusion of oxygen by a surrounding atmosphere of hydrogen gas, although in the shielded arc other gases have been used successfully. Keeping the metal in a molten or puddled condition while at the same time excluding the oxygen of the air has also been found helpful.

STRAIN RELIEF—Almost all the important heavy-plate vessels of which the author has knowledge have been given a stress-relief annealing treatment and he recommends such treatment for all vessels with plates of 1 inch or more in thickness. The vessels should be brought up to at least 1200° F. maintained at this temperature for a certain length of time dependent upon the thickness, and then slowly cooled. The time that the vessel is left to "soak" at the above tem-

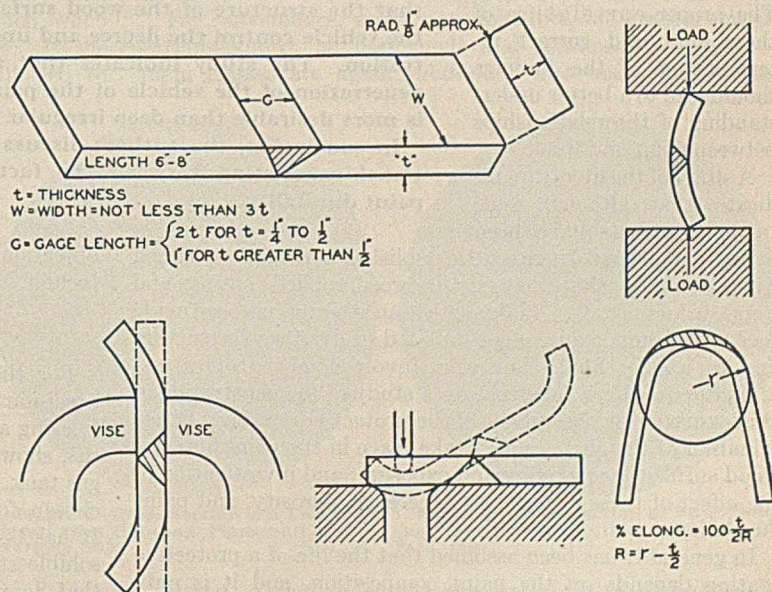


Figure 8—Making Bend Test to Determine Ductility of Welded Joints

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Studies in the Painting of Wood

I—Influence of Wood Structure on Paint Behavior¹

J. H. Haslam and S. Werthan

THE NEW JERSEY ZINC COMPANY, PALMERTON, PA.

THE paint industry, in its effort to improve protective coatings, has made considerable progress in paint technology. At the same time institutions such as the Forest Products Laboratory and universities have carried out many investigations of wood structure. The proper correlation of these data and correct interpretation of the findings should lead to a better understanding of the relationships between paint and wood.

A study of the literature indicates that, although some investigations have been carried out abroad, there is little published information dealing with the relationships that exist between applied coatings and wood surfaces (2, 4). In this article an attempt has been made to show the importance of a correlated study of wood structure and the applied film. This work involved microscopical examination of the wood structure; study of the penetration of this structure by the vehicle of the protective coating; determination of the changes that take place in the paint film and wood surface during aging and exposure; and investigation of the effect of these changes on adherence, porosity, and paint durability.

In general it has been assumed that the life of a protective coating depends on the paint composition, and it is only recently that the microstructure of wood has been considered an important factor in paint durability. Unquestionably, long life depends on proper formulation, but proper formulation should provide a well-adhering film of the best pigment-binder combination after the paint has been applied to the wood and the vehicle adsorption by the wood satisfied.

One method suggested in the literature for the study of paint films and their behavior on wood is the use of dyed vehicles in the paints to be examined. There are, however,

A new method for studying the structure of wood with relation to paint films is presented. The method involves a microscopic examination of sections stained by selective dyes.

A brief description of the wood structure is followed by a discussion of the effect of wood upon the protective coating, including data on the changes occurring in spring and summer wood under the influence of moisture.

Photographs and information are given, showing that the structure of the wood surface and nature of the vehicle control the degree and uniformity of penetration. The study indicates that a slight uniform penetration of the vehicle of the paint into the wood is more desirable than deep irregular penetration.

In conclusion, the authors discuss the several relationships existing between the factors studied and paint durability.

several objections to this procedure. The dye is often absorbed by the dense wood structure or upon the surface of the pigment, rendering it useless in the study of oil penetration. Also, the presence of the dye may cause a retardation of the oxidation of the oil, altering the period of penetration. Observation of the penetration of a dyed oil under low magnification has shown a layer of clear liquid just in advance of the colored oil, suggesting that a measure of the penetration of the color is not a measure of the total penetration. These

objections have been overcome in the development of a new technic in which the specimens are stained after being cut.

Apparatus and Technic

For the preparation of the mounts, a Minot automatic precision microtome with modification in the form of a freezing attachment is used. Figure 1 illustrates the apparatus, showing the adaptable freezing unit and carbon dioxide gas tank. The dyes used for staining the sections have been chosen for their ability selectively to stain wood and oil. It has been found that brilliant green,² a water- or alcohol-soluble stain, is entirely satisfactory for staining wood and that Soudan III or IV³ and scarlet R⁴ are quite effective in the oil. This gives a green and red contrast which is more satisfactory for microscopic examination than if other preferential stains for wood, such as hematoxylin or safranin, are used.

² A 1 per cent aqueous solution of brilliant green, a sulfate or double zinc chloride of tetraethyldiaminotriphenyl carbinol, also known as emerald green, malachite green, or ethyl green.

³ Soudan III is benzeneazobenzene-azo- β -naphthol, an oil soluble stain that is made up in 1 per cent strength in alcohol and diluted with 50 per cent water.

⁴ Scarlet R is the sodium salt of xylene-azo- β -naphthol disulfonic acid, an oil-soluble stain, a deeper red than Soudan III. This stain is also prepared by dissolving 1 per cent in alcohol and diluting 50 per cent with water.

¹ Received September 19, 1930. Presented before the Division of Paint and Varnish Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

The sections are cut from a specimen about $\frac{1}{2}$ inch (1.3 cm.) square of the panel under examination. It is not necessary to freeze the specimens if the paint is on wood and is to be examined for penetration of the oil. A drop of water on the end of the block or edge of the knife of the microtome facilitates the cutting, giving a more uniform section. For most purposes sections 10 to 15 microns in thickness are satisfactory. It is, however, necessary to use sections 1 to 2

successfully cut with a cold knife. Cold toluene is used to remove the beeswax and rosin and has so far shown no indication of affecting the film. The sectioned films if not stained may be mounted in balsam.

Figure 2 illustrates the type of sections that may be secured by this method and that are used in the study of pigment concentrations in the film. Figure 3 is a highly magnified (1500 \times) section of the upper surface of a paint film. It is possible to observe the distribution of the pigment throughout the film. In investigations of this sort great care must be exercised in choosing representative sections, as the area actually photographed is indeed quite small in comparison with the total paint surface. These sections nevertheless offer a means of studying changes that take place in the film during aging and failure. Preliminary investigation shows that there is a vast amount of information that can be derived from this source.

Structure of Wood

By selectively staining sections of painted blocks of wood, it has been possible to get an insight into the complex structure of wood and obtain some explanations for certain paint failures. Although two pieces of different woods having received the same treatment may appear uniform and equally satisfactory for painting, the same paint applied on the two pieces often behaves quite differently. Figure 4 shows actual-size photographs of flat-grain surfaces of white pine, redwood, fir, and cypress. These surfaces were all prepared in the same manner and appear quite uniform for painting. Figure 5 is a portion of the same white pine, redwood, fir, and cypress surfaces magnified 50 \times . Each surface is quite different structurally and these fundamental differences exert an effect upon the life of the paint film applied to them and often cause variations in failure of the same paint.

For convenience, wood is grouped into two general classifications known as hardwoods and softwoods. These two main classes are again subdivided into many species and

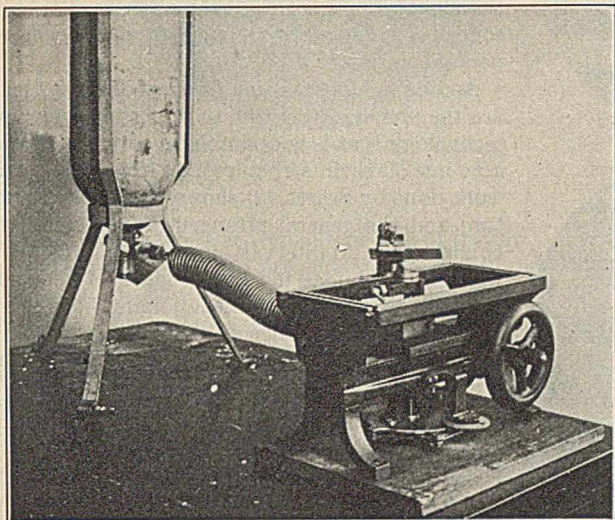


Figure 1—Minot Automatic Microtome with CO₂ Freezing Attachment Used to Obtain Microsections

microns thick for the study of film structure, and approximately 5 microns for observations of pigment concentrations. The sections are placed on slides which have previously been cleaned and covered with a film of egg albumin, which, when dry, serves to attach the specimens to the slide. If the sections are of freshly applied paint, they are allowed to oxidize for 8 to 10 hours.

The slide bearing a section is then placed in the solution of brilliant green for 1 to 2 minutes, which stains only the wood fibers. If the wood is too deeply stained, it may be decolorized with dilute alcohol and then washed in water. The slide is then placed for 2 minutes in the solution of Soudan III or IV or scarlet R, which stains the oil red. Passing the specimen through hydrochloric acid fumes and then washing clear with water tends to intensify the red color.⁵ For permanent preservation the specimen may be mounted in Allen's medium⁶ and protected with a cover glass. Balsam was found to be unsatisfactory. The Euscope as described by Exton (3), has proved to be a valuable instrument in observing and photographing the sections.

When it is desirable to prepare sections of paint films for a study of the structure of the film, a somewhat different technic must be used. These films may be soft and contain unoxidized oil and when sectioned smear or become greatly distorted. To avoid this and keep the film intact it is imbedded in a combination of beeswax and rosin (2:1) and the entire block frozen to the point at which the wax can no longer be dented with the finger nail. The specimens can then be

⁵ In the presentation of the paper autochrome plates were used which cannot be reproduced in the written paper.

⁶ Allen's medium consists of a strained solution of gum arabic of the consistency of glycerol, to which $\frac{1}{3}$ volume of glycerol and $\frac{1}{20}$ volume of formaldehyde has been gradually incorporated. This medium sets hard.

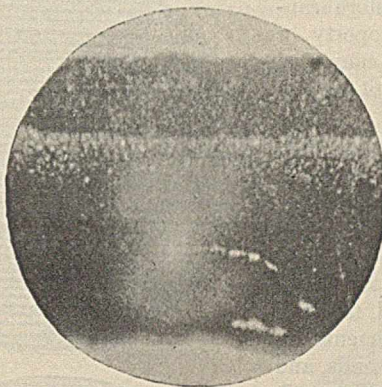


Figure 2—Cross Section of a Two-Coat Paint Film Showing Pigment Concentrations. 40 \times

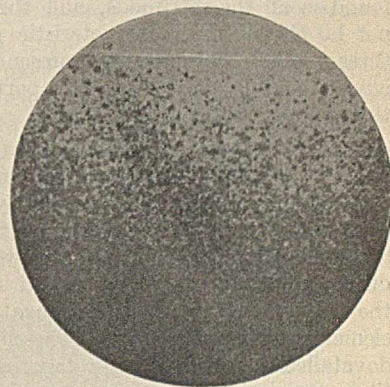


Figure 3—Cross Section of Film Showing Pigment Distribution at Upper Surface. 1500 \times

varieties. The two large classes may readily be identified by microscopic examination, but it is sometimes difficult to differentiate between species.

Oak, a typical representative of the hardwoods, as seen in Figure 6, exhibits a very complicated structure of the wood elements and a complex system of tissue which serves very often as a means of identification. Hardwoods have not been considered in this work because they are not generally used in outside construction.

The woods used in the exterior of buildings are generally the softwoods, and it has been necessary to limit this investigation to the more common of these. The cells of the softwoods bear a more or less simple relationship to one

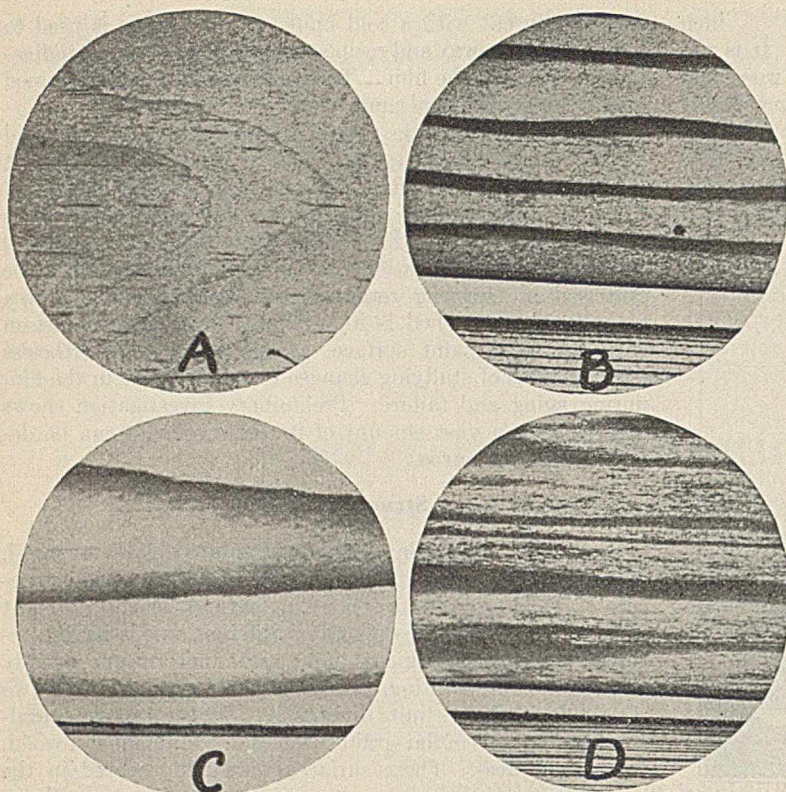


Figure 4—Actual Size, Flat-Grain Surfaces Showing Apparent Uniformity for Painting

A—white pine; B—redwood; C—fir; D—cypress

another and lack entirely the complexity and specialized character exhibited by the hardwoods. The structure of the softwoods has been thoroughly covered by botanists. There are three types of cells that are of major interest to the paint industry—the tracheids, the medullary rays, and the resin ducts. The resin ducts are not found in all the softwoods, and therefore cannot be classed as a characteristic property of these woods. However, their presence cannot be ignored because they play an important part in the woods in which they occur.

TRACHEIDS—According to Jeffrey (5) and Penhallow (8), the tissue of softwoods consists chiefly of tracheids or fibers. This primary tissue may be divided into two groups on a basis of their formation in growth. The spring wood, formed during the rapidly growing period in the life of the tree, is made up of large, elongated, tapering elements with bordered pits. These elements are dovetailed together at their tapering ends and their arrangement may be seen in Figure 7. These spring-wood fibers have thin walls, the radial walls being covered with bordered pits.

The other group of fibers makes up the summer-wood tissue, which is formed during the more or less quiet period in the life of the tree. These fibers are also tapered and are dovetailed together, but their walls are considerably thicker and the bordered pits are confined to the tangential wall. Figure 8 pictures the summer-wood fibers, showing the absence of pits on the radial surface of the fiber. Figure 9 is a cross section of white pine at the point of transition from the summer wood to spring wood. There it is easy to see the location of the pits, the difference in thickness of the cell wall, and the relative void space in the

two groups of fibers. It will be noted that the transition from summer wood to spring wood in white pine is very abrupt, but as shown in Figure 10, the change from spring wood to summer wood is a gradual one. This characteristic varies tremendously with different woods. Figure 11 shows representative sections of fir, redwood, and cypress. These variations or changes from one type of wood to another coupled with the variations in thickness of the fiber walls have been a source of trouble to the paint trade, as will be pointed out later.

Among the outstanding features of these fibers are the pits, and they are so important in paint technology that it is desirable to give a detailed account of their structure and function. The work done by Scarth (9) shows clearly the structure and the general arrangement of these pits (Figure 12). At intervals along the cell wall there will be found bulges toward the inside of the fiber, and directly opposite in the adjoining fiber there is a corresponding bulge so that these structures resemble saucers, one inverted upon the other. At the apex of these convex surfaces there is a small orifice. Thus far the structure is quite simple and would remain so were it not for a membrane which is stretched laterally across the center. This membrane is a continuation of the lignin matrix, which serves to cement the fibers together. However, according to Bailey (1) this membrane is so constructed that it allows the passage of liquids and gases. The center portion, or torus, of this membrane is solid, but around it, radiating as the spokes of a wheel, there are narrow slits through which very fine colloidal material may pass. The diffusion of gases may take place quite readily provided the torus of these

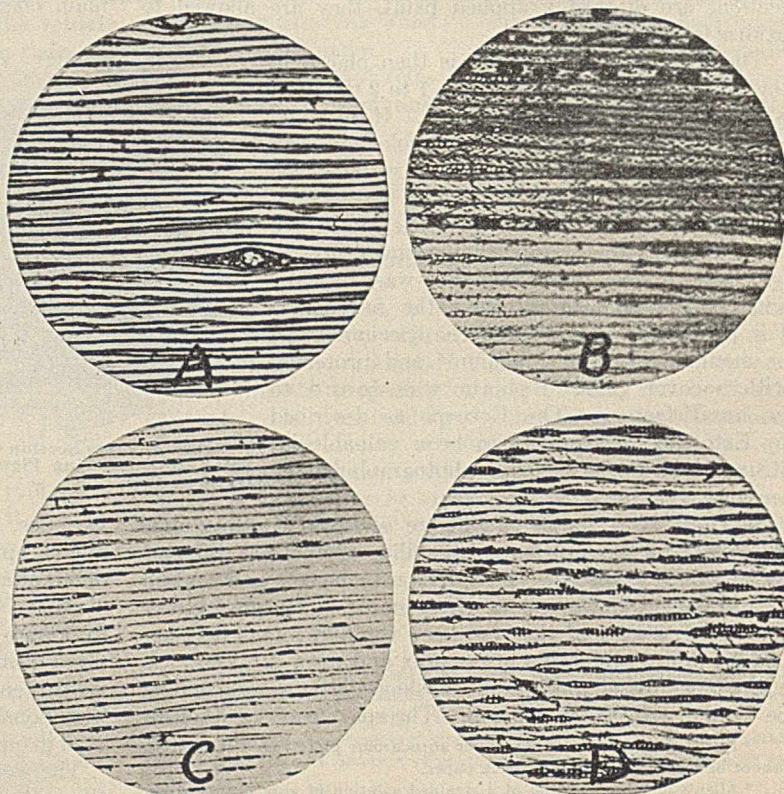


Figure 5—Magnified Surface (50 X) of Flat-Grain Wood Showing Irregularities and Variation in Surface to Be Painted

A—white pine; B—redwood; C—fir; D—cypress

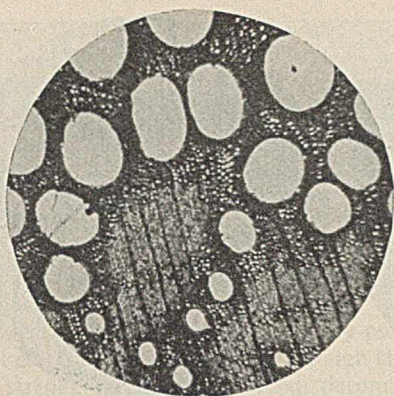


Figure 6—Cross Section of Oak Showing Irregularity of Structure Typical of the Hardwoods. 50 X

membranes remains free from either wall of the pit. If gas is applied suddenly under pressure, these membranes will be pushed to one side of the pit, the small orifice closed, and flow stopped. Also, if a liquid is flowing through these pits from one cell to another, the membrane is operative, but by a different force. Wherever there is an air-liquid interface the surface tension forces are great enough to pull the membrane closed, stopping further flow. The natural function of these pits in the life of the tree is to prevent too rapid evaporation of the water at an injury or too rapid diffusion of solutions from one cell to another. It is interesting to note that in nature as the tree ages and forms heartwood the pits are closed and firmly sealed in these fibers. Studies in wood preservation show that great difficulty is encountered when heartwood has to be impregnated, because the pits of the fibers are closed against the penetrating liquid. In fact, deeper penetration is obtained in all types of cells by slow infiltration rather than by using high pressures.

The same forces are at work when vehicles of paints penetrate wood and depth of penetration might be controlled by controlling various physical properties of the vehicles. The higher the surface tension of the vehicle the less deeply will it penetrate, but invariably the penetration will be more uniform.⁵

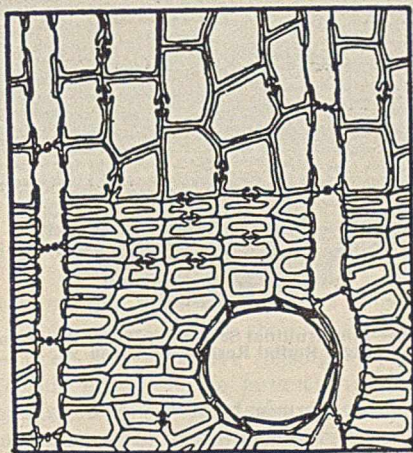


Figure 9—Cross Section of White Pine at the Point of Transition from Spring to Summer Wood (Penhallow)

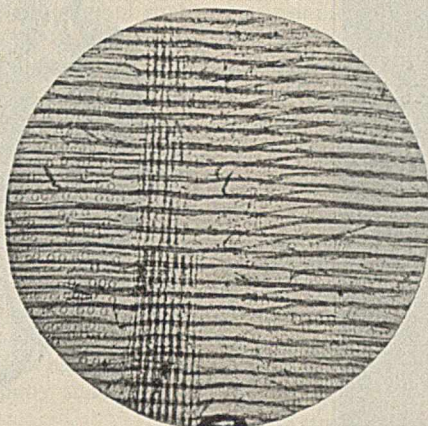


Figure 7—Radial Section of White Pine Showing Elongated Tapered Fibers, with Bordered Pits Dovetailed Together. 50 X approx.

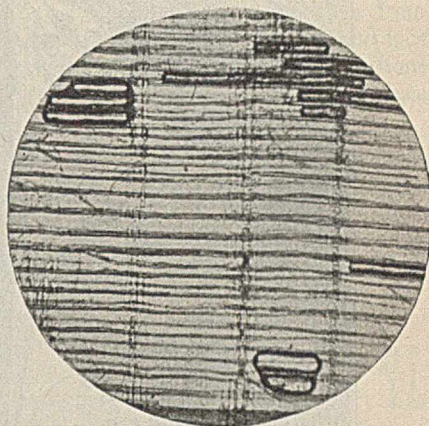


Figure 8—Radial Section of White Pine Showing the Absence of Pits on the Narrower Summer-Wood Fibers. 50 X approx.

MEDULLARY RAYS—The individual elements of the medullary rays are short, cylindrical cells with blunt ends, which lie end on end from the center of the tree to the periphery. The adjoining end walls have what is called a simple pit, so that flow of gases or liquids can be retarded but not stopped, as is the case with the bordered pits. In reality, then, the medullary rays are continuous tubes radiating from the center of the tree and consequently must play some part in the life of the paint film. The position of flat- and edge-grained boards in the log may be seen in Figure 13 which would indicate that the two surfaces are quite different. In the flat-grained board the medullary rays are at right angles to the surface and occupy approximately 20 per cent of the total surface. In the edge-grained board the rays are parallel to the surface and the area occupied varies considerably. From this arrangement of the cells it seems apparent that the flat-grained board offers a greater opportunity for deep and irregular penetration of liquids, although true edge-grained and flat-grained boards are not so common as a mixture of the two types.⁵ This condition is entirely lacking in true edge-grained lumber.

The medullary rays have a peculiar pit structure where the ray cells and tracheids are in communication. These pits are simple on the ray side but are bordered on the tracheid side. This makes them capable of acting as one-way valves; that is, gases and liquids may pass readily from the tracheids into the ray cells, but flow in the other direction is hindered. In this way there is the possibility of building up pressure that may be exerted against the paint film, as these

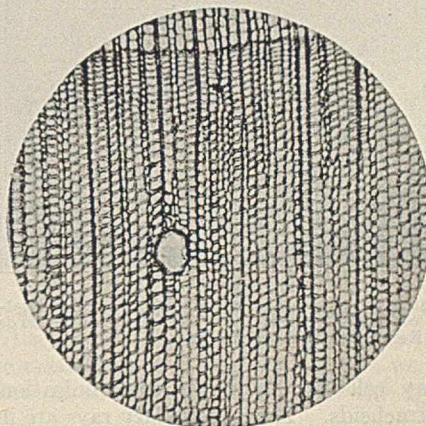


Figure 10—Cross Section of White Pine Showing Gradual Change in Size of Cells from Spring to Summer Wood and Abrupt Change from Summer Wood to Spring Wood

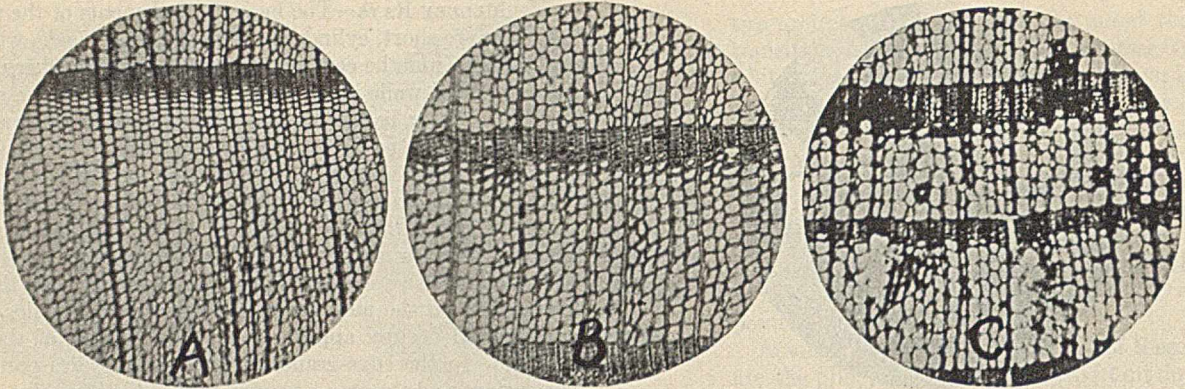


Figure 11—Cross Sections Showing Changes in Size of Cells of Spring and Summer Wood. 50 X approx.
A—fir; B—redwood; C—cypress

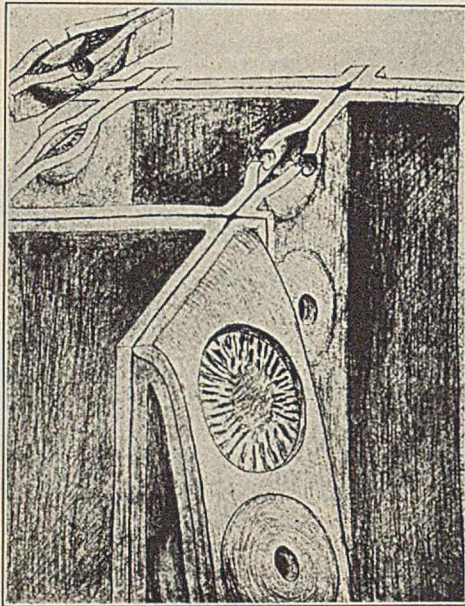


Figure 12—Fibers and Pit Structure as Found in Spruce (Scarff)

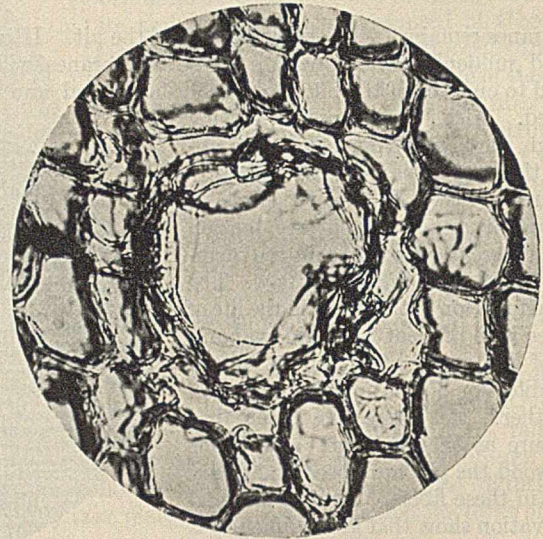


Figure 14—Cross Section of White Pine Showing Size of a Longitudinal Resin Canal with Respect to Surrounding Cells. 270 X

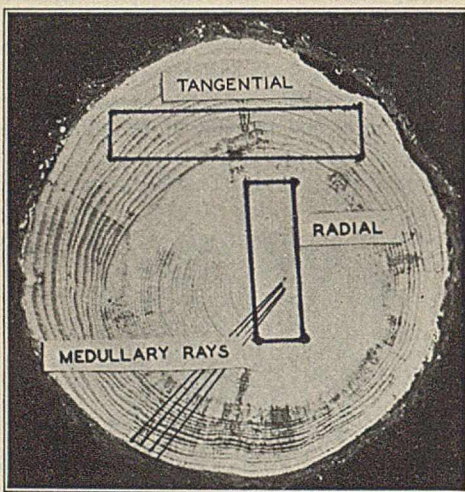


Figure 13—Cross Section of a Log Showing Position of Flat-Grained and Edge-Grained Boards with Respect to Medullary Rays

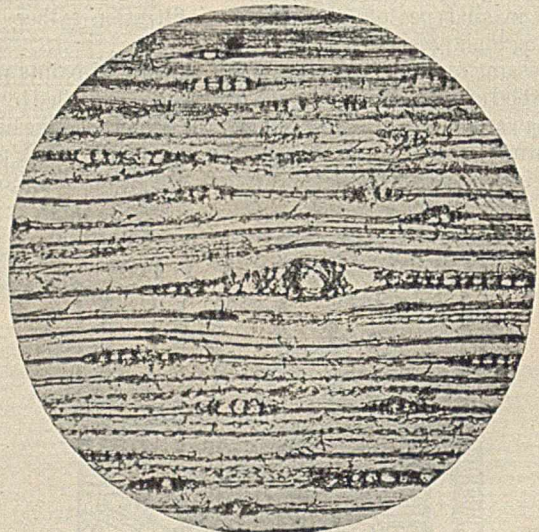


Figure 15—Longitudinal Section of White Pine Showing a Radial Resin Canal. 60 X

medullary ray cells are in direct communication with a great many tracheids. These medullary rays are important in still another way, serving as the easiest and quickest means of transferring gas through a board. Any pressure set up in a board exerts itself along the medullary rays and these, in

flat-grained lumber, terminate at the paint-wood interface. Studies now in progress indicate that these structures are directly related to failure by blistering.

RESIN DUCTS—The last group of cells of importance in softwoods are the resin ducts. Very often, in some species

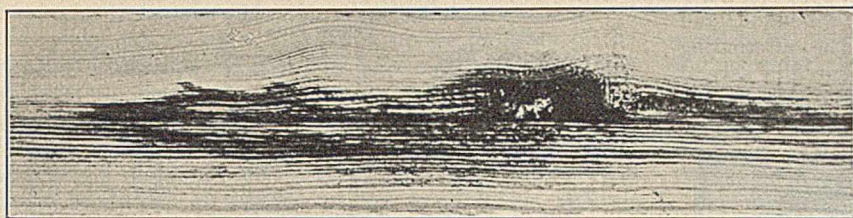


Figure 16—Actual Size Surface of Yellow Pine Showing a Longitudinal Resin Canal That Has Exuded Resin upon the Surface

of wood, the resin is responsible for unsightly paint failures, such as small globules of resin exuding through the film, and dark brown streaks formed as the resin decomposes or as peeling of the film from exposed resin canals in which the resin has become hard and brittle by oxidation. These resin canals are considerably larger than the surrounding cells, as may be seen in Figure 14, which shows the longitudinal resin canals of white pine. The lateral resin ducts (Figure 15) are smaller and often are in communication with resin pockets. These canals are in communication with adjacent fibers and tissue. Solvents or heat make the resinous material of such a consistency that it will flow from the resin canals to the surrounding tissue and to the surface of the board. The radial ducts terminate at the surface of flat-grained lumber, while the longitudinal tubes may be exposed for many inches, as shown in Figure 16, which is a tangential (flat grained) surface of yellow pine. Both the radial and longitudinal canals are responsible for some of the irregular penetration of oils, as the resin is soluble in the oils and thus aids in penetration of the oils from the paint down into the wood. Quite contrary to the general opinion, resinous woods are readily penetrated by oils. For example, yellow pine, a very resinous wood, showed the greatest ease of penetration. The penetration was greatest radially, and passed through the resinous bands of the summer wood more rapidly than in any of the other woods used.

less trouble for the paint industry to overcome.

An extended study covering the expansion of wood when it becomes wet and its shrinkage when it dries out again shows that the over-all expansion and contraction are appreciable (Table I). The swelling of wood caused by the adsorption of water is greatest in a tangential direction, averaging approximately twice that of the radial expansion and perhaps

fifty times that of the longitudinal expansion. This condition is explained by the wood structure. From the general assemblage of the cells in wood the small elongation in a longitudinal direction is perhaps due to the fact that the fibers may slip past each other and their increase in length not result in a direct elongation of the wood. The greatest increase is in a tangential direction because in this direction the fibers have the greatest degree of freedom. In the radial direction the fibers are firmly attached to the medullary rays so that the resultant change is more restricted than the tangential expansion. The swelling of an individual fiber free from restraint will be the same radially and tangentially, and it is the arrangement of the cells that accounts for the variations in the degree of swelling in the different dimensions of a piece of wood.

Table I—Over-All Expansion of Yellow Pine

	(1)	(2)	(3)	(4)	(5)	(6)
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
EXPANSION IN RADIAL DIRECTION						
Over-all wet	76.7	80.0	80.0	80.6	79.8	77.5
Over-all dry	73.6	76.0	75.6	78.0	76.0	74.6
Difference	3.0	4.0	4.4	2.6	3.9	2.9
Increase, %	4.07	5.26	5.82	3.34	5.15	3.9
Average expansion	4.59 %					
EXPANSION IN TANGENTIAL DIRECTION						
Over-all wet	88.0	87.6	90.0	90.7	89.9	89.8
Over-all dry	82.0	81.5	81.6	82.5	82.5	82.4
Difference	6.0	6.1	8.4	8.2	7.4	7.4
Increase, %	7.33	7.48	10.3	9.94	8.97	8.99
Average expansion	8.83 %					

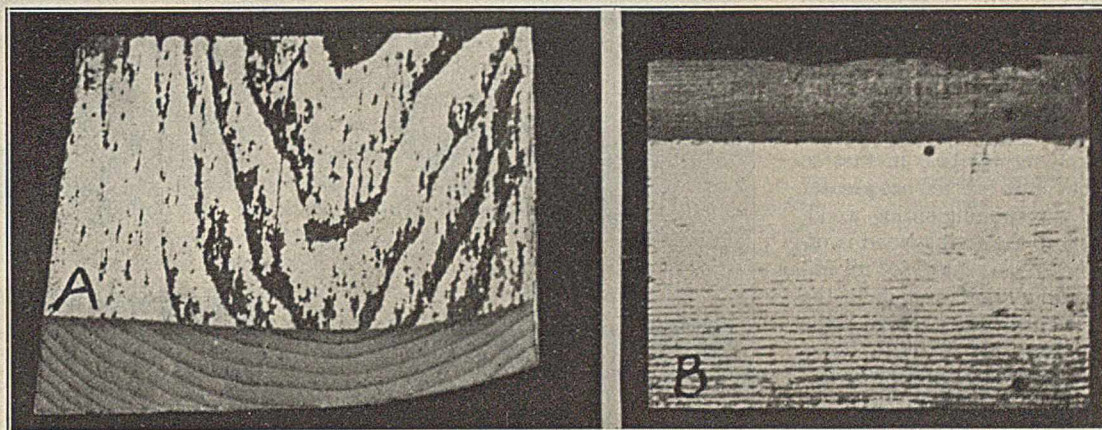


Figure 17—Failure of Paint over Summer Wood as Shown by Beveled Edge of Panel A for Edge-Grained Surface and Panel B for Flat-Grained Surface

Swelling of Wood and Effect on Paint Coatings

Having covered the three main groups of cells found in softwoods, it is now necessary to show how these cells exert an influence upon the protective coatings applied to them. As the tracheids make up the largest amount of surface directly in contact with the paint film, they are perhaps the most important and should be discussed first. Reference was made earlier to the relative thickness of the cell walls of the spring and summer wood. Were these cells of uniform size and thickness of wall, there would undoubtedly be one

A detailed study of the expansion of wood has placed a different aspect upon the behavior of wood under conditions of swelling. It was found by two methods that the expansion of the summer wood is often greater than the over-all expansion of the wood. The methods involved were a direct microscopic measurement of the dry and wet wood and the measurements of enlarged photographs of the dry and wet wood.

When direct measurements were made, samples of wood with carefully prepared surfaces on which the bands of spring and summer wood were plainly visible were used. With a

microcomparator accurate measurements could be made and satisfactory checks could be obtained. The alternating bands of spring and summer wood were measured in several places across the face of the specimen. Table II gives the

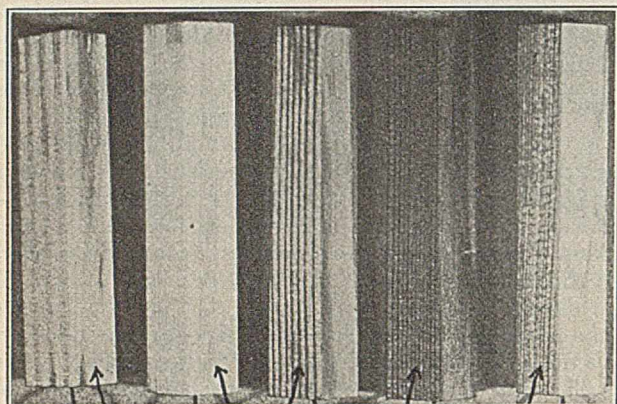


Figure 18—Samples of Yellow Pine, White Pine, Fir, Redwood, and Cypress with Edge- and Flat-Grained Surfaces, Showing Relative Ease of Penetration in Radial Tangential Directions. Arrows Indicate Surface Most Readily Penetrated

data secured by measuring the different bands of spring and summer wood, dry and wet, of a piece of yellow pine.

This table represents the data obtained by measuring numerous specimens of various species of wood, although it has been found that the variation in expansion and contraction is quite appreciable so that even in the same sample of wood the results obtained are not identical. In woods such as white pine difficulty in measuring is encountered owing to the gradual change in the size of the cells and lack of definite boundary lines between spring and summer wood, but when the change is abrupt it is very easy to obtain accurate measurements. Yellow pine, which has very heavy dark-colored summer-wood fibers, offers an excellent wood from which to secure measurements.

The data indicate that the summer wood expands considerably, in fact so much that the forces exerted are greater than those of the swelling spring wood, with a result that the spring wood is often compressed. This must set up uneven stresses and strains throughout the wood, which in turn affect the film of the protective coating. It is quite interesting to picture a paint film on a flat-grained board and investigate the forces at work as the paint-wood swells. Considering first the film on the summer-wood areas, where there may be 12 to 15 per cent expansion, the paint film when fresh according to stress-strain data (6, 7) is capable of being stretched more than this amount without breaking. However, as the film ages this distensibility diminishes so that films 8 months to a year old have only 4 or 5 per cent elongation. Therefore, in the early stages of the life of the paint film it is soft and elastic enough to take care of the swelling of the wood, but later it becomes hard and brittle and can no longer adjust itself to the changes that take place.

Table II—Measurements of Spring and Summer Wood of Yellow Pine

SUMMER WOOD			SPRING WOOD		
Dry wood	Wet wood	Diff.	Dry wood	Wet wood	Diff.
Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
RADIAL MEASUREMENTS					
9.2	9.6	+0.4	12.1	11.0	-1.1
7.6	8.5	+0.9	12.0	11.4	-0.6
7.5	8.0	+0.5	12.0	11.6	-0.4
9.3	10.3	+1.0	11.0	10.5	-0.5
9.6	10.3	+0.9	12.1	11.6	-0.5
7.4	8.3	+0.9	11.6	11.4	-0.2
9.6	10.5	+0.9	12.1	11.8	-0.3
8.0	9.0	+1.0	11.8	11.2	-0.6
9.5	10.3	+0.8	12.0	11.8	-0.2
9.5	10.4	+0.9	14.1	13.5	-0.6
87.2	95.4	+8.2	120.8	115.8	-5.0
9.4 % increase			4.14 % decrease		
TANGENTIAL MEASUREMENTS					
11.1	13.3	+2.2	12.8	12.3	-0.5
11.6	12.8	+1.2	15.4	15.4	0.0
12.0	13.1	+1.1	17.4	18.4	+1.0
11.3	12.8	+1.5	10.3	9.6	-0.7
14.2	15.4	+1.2	9.3	9.6	+0.3
12.3	13.9	+1.6	13.2	12.7	-0.5
11.8	13.1	+1.3	14.1	13.8	-0.3
12.5	13.5	+1.0	11.8	11.0	-0.8
13.1	14.9	+1.8	10.6	10.0	-0.6
11.6	13.5	+1.9	12.6	12.2	-0.4
121.5	136.3	+14.8	127.5	125.0	-2.5
12.2 % increase			1.96 % decrease		

In the paint film over spring wood entirely different conditions exist. There is no evidence in the literature that any work has been done on the compressibility of paint films. Therefore, it is difficult to state the conditions set up at the paint-wood interface when the spring wood is compressed. All that is known is that the paint very seldom chips and flakes from spring wood, indicating that the paint film can adjust itself to the smaller compression changes. This leaves but one other point of interest in the paint-wood interface, and that is the point at which spring and summer wood meet.

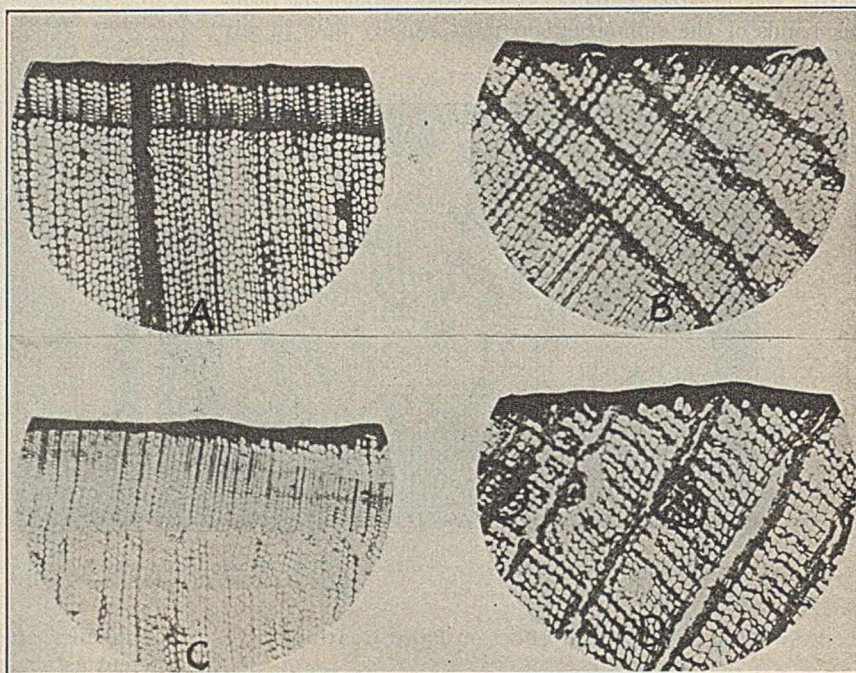


Figure 19—Cross Sections of Wood and Three Coats of 60-30-10 (Lead-Zinc-Inert) Paint, Showing Penetration and Surface Film
A—white pine; B—redwood; C—fir; D—cypress

This point is the most important as it is at this interface that paint films invariably become loosened and begin to lift over the summer wood. Figure 17 illustrates the sharp line of failure of paints at the transition of summer wood to spring wood, accompanied by the characteristic flaking of the

paint over summer wood. Apparently the greatest stresses and strains are set up at this point, or the resultant of the forces of expansion and compression is most effective at the union of summer and spring wood. An analysis has been offered by J. B. Reynolds, of the Mathematics Department of Lehigh University, as far as the data will permit of the mathematics and mechanics of the relationship of paint to wood under conditions of swelling of the wood. This analysis will be refined as data are accumulated and when it is complete will be published.

Effect of Wood Structure on Penetration of Paint

Having considered some of the physical changes that take place in wood, it is advisable to see what effect the wood structure has on the penetration of the liquid of protective coatings. Microscopic examination gives no evidence that penetration occurs directly through the fiber wall, although there is the possibility of adsorption on the cell wall exposed on the surface to be painted. However, examination shows that penetration occurs through the pits located on the cell wall or by a cut fiber. If the fibers are parallel to the surface, there is little danger of excessive penetration by means of cut fibers and penetration is then controlled by the bordered pits. If a true flat-grained surface is painted, excessive penetration can take place at the medullary rays⁵ (Figure 6). In this way large amounts of oil in proportion to the amount available may be withdrawn irregularly from the surface film. This irregular and excessive penetration must leave the film on the surface with areas depleted of oil. Since the entire surface of a paint film is subject to the same oxidizing atmosphere, areas with less oil will in a given time be oxidized more than areas high in oil. This non-uniform oxidation will result in localized "dry spots" or a heterogeneous film. As the porosity of the film is partially dependent on the amount of oil present, the area of the film depleted of oil would also become more porous than the surrounding film and at these points the natural elements could enter the film, producing premature failure. The logical assumption is that the more uniform the retention of sufficient oil and the more homogeneous the oxidation and structure of the film, the longer will be the life of the paint.

Each species of wood seems to have its own peculiar method and degree of ease of penetration. Figure 18 shows five samples of wood with their flat- and edge-grained surfaces exposed. Dyed oil placed in the center and allowed to penetrate showed that yellow pine, which has always been considered a hard wood to penetrate and that extra turpentine is required for good penetration, was penetrated through the alternating bands of spring and summer wood more readily than any of the other specimens. Liquids will penetrate more readily radially in white and yellow pine but more readily in a tangential direction in fir, redwood, and cypress. The ease of penetration of yellow and white pine is due to the large medullary rays and radial resin canals through which the oil flows quite readily.

The addition of turpentine to clear vehicles does increase the depth and irregularity of penetration by decreasing the viscosity of the vehicle. The actual amount of oil penetrated, however, does not vary as the supply of vehicle in a paint is limited so that large amounts of turpentine will tend to make the penetration less uniform, which probably is not as desirable as it may seem. By close examination of films on wood it has been noted that if penetration is uniform, although only one or two cells deep, the surface film is more homogeneous. There is no apparent reason for any advantage in deep penetration except in so far as the vehicle tends to preserve the wood, as the structure of the wood is such that if the two or three surface layers of wood cells are impregnated

with oil additional penetration should have no beneficial effect on the adherence of the film. Observations of the deep and irregular penetration of raw oil, the somewhat more uniform and not so deep penetration of bodied oils⁵ and the very little but very uniform penetration of a varnish, indicate that more thought should be given to this property in paint-vehicle formulation.

Six typical outside paints and numerous clear vehicles on four or five common woods have been investigated. There is very little difference in the average depth of penetration of one paint on several woods, but there is a decided difference in the uniformity of penetration. Figure 19 shows that where the penetration is uniform and not very deep the surface film is heavier and more regular, and that the average depth of penetration is about the same but the uniformity of penetration varies.

Conclusion

The results of this investigation indicate that the method presented can be successfully employed in studying the problems of penetration, adherence, and wood-paint interfacial relationships; that the microstructure of wood, a heretofore ignored component of paint failures, is worthy of detailed study in the endeavor to overcome the failures characteristic of protective coatings. Work of this nature has opened a field for future investigation and studies along this line have been started with the idea of obtaining fundamental knowledge to aid in a better understanding and correction of the failures of protective coatings.

Acknowledgment

Acknowledgment is made of the helpful suggestions and criticism of various members of the Research Department of the New Jersey Zinc Company, and especially to C. H. Hall for his efforts in obtaining some of the microphotographs used.

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Resistance of Chromium-Plated Plug Gages to Wear

Plug gages used for measuring internal diameters are often plated with chromium, because chromium wears at a lower rate than most steels which are used for this purpose. Several types of chromium plate are produced by variations in the control of the electroplating bath, and are designated in the industry as "bright," "milky," and "frosty," according to the appearance of the deposits. In a laboratory study made at the Bureau of Standards, milky and frosty deposits showed better performance than bright deposits, excepting bright deposits which had been heated to 300° C. Lapped chromium plate was more resistant to wear than unlapped plate. In the process of the electro-deposition of chromium, hydrogen is evolved which to some extent is absorbed by the chromium plate. Heating the chromium deposit to about 300° C. was found to improve the quality, probably by driving out the hydrogen. When a thin coating of copper was deposited prior to plating with chromium, the plate exhibited greater resistance to wear than a similar deposit of chromium applied without the copper.

Notes on Hydrogen Sulfide Poisoning¹

Lewis B. Allyn

WESTFIELD TESTING AND RESEARCH LABORATORIES, 102 ELM ST., WESTFIELD, MASS.

SEPTEMBER 26, 1930, was hot and sultry. Shortly after 5 p. m., Walter Swiatek, a boy about fourteen years of age, began to explore a rubbish dump situated about 300 feet north of his home in Chicopee, Mass. This dump occupies a portion of a deep ravine with precipitous sides about 65 feet in height. At the bottom runs a small stream or brook. The location, known as the Lemieux dump, is used exclusively by a large manufacturing firm for rubbish disposal. No regular caretaker is employed at the ravine.

Young Swiatek in the course of his exploration came upon a discarded steel cylinder about 46 inches long and 5¹/₄ inches outside diameter, fitted with a brass valve at one end. It was doubtless his intention to remove the valve and sell it as junk. Since he could not unscrew it, he apparently broke it off with a large stone. The compressed gas rushed out with a loud hiss and, judging from the relative position of the body to the tank, immediately killed him.

A second boy who happened along the bank looked down and saw Swiatek's body lying across the tank. He immediately notified the father, Joseph Swiatek, who at once started up the ravine to rescue his son. The elder Swiatek succeeded in reaching the body, picked it up, then he himself dropped dead.

The police quickly appeared on the scene and later with great difficulty carried the bodies up the bank. The officers were all more or less nauseated and suffered severely from vertigo. The medical examiner himself was partially overcome by the fumes.

The tank was plugged and sent to these laboratories for examination. Since the residual gas in the tank was not under pressure, an L-shaped piece of glass tubing was cemented into the vent left by the broken valve, gentle heat was applied to the opposite end, and sufficient gas collected for a systematic analysis. It proved to be hydrogen sulfide. In a dilution of 1 to 400 it killed in 40 seconds a normal albino rat weighing 164 grams.

The physical setting for the tragedy was ideal; a sultry, still day, a deep ravine about 40 feet across at the bottom, with steep, wooded sides, well sheltered from air currents. The contours formed a pocket or reservoir from which the gas could only slowly escape.

Both bodies were deeply cyanosed and reeked with the offensive smell of the gas.

The tank, said to have had a small crack in one side, was a discarded one originally for use in the manufacturing plant previously mentioned. The company has for some time stored in its factory hydrogen sulfide which it purchases in heavy steel cylinders. It is unknown whether the gas is used exclusively in its laboratory or in some manufacturing process.

An excerpt from the coroner's report is of interest:

While it is customary to return these tanks to the manufacturer, this tank appeared so badly corroded that it was felt it would be useless to try to return it. A company officer ordered it to be loaded onto a truck, and it was taken to the dump and unloaded. Even though some of the officials should at some time have known that this tank contained a dangerous gas, in view of the fact that the official immediately responsible for its transportation to the dump saw this crack and detected

some sort of an odor in the vicinity, I am not convinced that at this particular time he should have known that there was any danger in sending it to the dump along with other worthless junk. Upon all the evidence, I am of the opinion that there was no criminal act upon the part of any person.

Medical Examiner Samuel E. Fletcher states:

On arriving I found the bodies lying face down on the ground with physicians and police applying artificial respiration and friction to the surface of the bodies.

Both bodies were cyanotic and cold and showed no signs of life when the stethoscope was applied to the chests.

The atmosphere for a distance of at least two hundred yards from the spot where the bodies were found was heavily charged with an offensive odor something like sulfuretted hydrogen.

This tragedy again emphasizes the poisonous qualities of hydrogen sulfide, especially when the concentration is high enough.

Lehmann (2) says that:

Hydrogen sulfide kills rabbits and cats within ten minutes in an atmosphere containing as little as one to three parts of hydrogen sulfide per thousand parts of air. Death follows from an inflammatory oedema of the lung, preceded by convulsions; there is also a paralysis of the nerve centers.

The following excerpt from "Noxious Gases" by Henderson and Haggard (1) is of interest:

Death in acute hydrogen sulfide poisoning results from failure of respiration and the consequent asphyxia. This respiratory failure is occasioned through two separate processes depending upon the concentration of the gas inhaled. Concentrations higher than 2000 parts per million cause almost immediate cessation of breathing by paralyzing the respiratory center. Concentrations between 600 and 2000 parts per million cause hyperpnea through stimulation of the respiratory center. The excessive breathing lowers the carbon dioxide content of the blood, the apnea vera results.

The action of hydrogen sulfide upon the nervous system is exerted only during the time the free hydrogen sulfide is in the blood and to a degree depending upon the concentration present. The symptoms of acute poisoning develop immediately on the inhalation of the gas; but because of its rapid oxidation in the blood they pass off when the inhalation ceases. Death in acute poisoning is as rapid as in poisoning by cyanides; a man inhaling a high concentration drops dead. Hydrogen sulfide is in a high degree a non-cumulative poison; thus if the victim is revived there are no systemic sequelae. In less severe poisoning, convulsions and dyspnea are marked symptoms. In subacute or chronic poisoning the main symptoms are those of irritation, particularly of the eyes, and to a less degree of action of the respiratory tract. In some cases the depressing action of the gas is also evidenced in a mild degree of malaise. The limit of danger for prolonged exposure is said to be a concentration of 50 parts per million, or possibly lower.

The treatment of acute hydrogen sulfide poisoning consists in restoring breathing by means of manual artificial respiration, combined with inhalation of oxygen mixed with 5 per cent of carbon dioxide.

Physiological Response to Various Concentrations of Hydrogen Sulfide

	HYDROGEN SULFIDE P. p. m.
Slight symptoms after several hours	100 to 150
Maximum amount that can be inhaled for 1 hour without serious disturbance	200 to 300
Dangerous in 30 minutes to 1 hour	500 to 700
Rapidly fatal	1000 to 3000

Literature Cited

- (1) Henderson and Haggard, "Noxious Gases," p. 190, Chemical Catalog, 1927.
- (2) Lehmann, *Arch. Hyg.*, **14**, 135.

PERKIN MEDAL AWARD

The Perkin Medal for 1931 was presented to Arthur D. Little, president of Arthur D. Little, Inc., Cambridge, Mass., on January 9, at the joint meeting of the American Section of the Society of Chemical Industry, the AMERICAN CHEMICAL SOCIETY, the Société de Chimie Industrielle, and the American Electrochemical Society in New York City.

Frederick G. Keyes, of Massachusetts Institute of Technology, gave an account of the "developments, projects, processes, and enterprises" with which Doctor Little has been identified, which was followed by the presentation of the medal by D. D. Jackson, chairman of the American Section, and the address by the medalist himself.

The Perkin Medal may be awarded annually by the American Section of the Society of Chemical Industry for

the most valuable work in applied chemistry. The award may be made to any chemist residing in the United States of America for work which he has done at any time during his career, whether this work proved successful at the time of execution or publication, or whether it became valuable in subsequent development of the industry. The medalist is chosen by a committee representing this society, the AMERICAN CHEMICAL SOCIETY, the American Electrochemical Society, the American Institute of Chemical Engineers, and the Société de Chimie Industrielle. It was founded in 1906 at the time of the semi-centennial celebration of the discovery of mauve by Sir William H. Perkin, the first medal being presented to Sir William himself.

Perkin Medal Awards

DATE	AWARDED TO	PRINCIPAL ACHIEVEMENTS	DATE	AWARDED TO	PRINCIPAL ACHIEVEMENTS
1906	Sir William H. Perkin	Pioneer work in synthetic dye industry			
1908	J. B. F. Herreshoff	Improvements in chamber process for sulfuric acid; development of the contact process for sulfuric acid, a roasting furnace for pyrites fines, a copper smelting furnace, and electrolytic refining of copper	1922	William M. Burton	alloys, and new apparatus and electric equipment
					High-temperature process of cracking petroleum under pressure
1909	Arno Behr	Work in field of corn products, including grape sugar, crystallized dextrose, mill starch; and utilization of various by-products	1923	Milton C. Whitaker	Achievements in manufacture of alcohol, ethyl acetate, acetone, other solvents, and the utilization of by-products
1910	E. G. Acheson	Development of Carborundum, artificial graphite, graphitized electrodes, soft graphite, deflocculated graphite, Siloxicon, Aquadag, and Oildag	1924	Frederick M. Becket	Processes for extraction of rare metals from ores, manufacture of calcium carbide, and reduction of rare metals and alloys
1911	Charles M. Hall	Development of process for manufacture of aluminum by electrolysis of alumina in fused cryolite bath	1925	Hugh K. Moore	Development of electrolytic processes for chlorine and caustic soda and recovery and utilization of by-products in pulp and paper industry
1912	Herman Frasch	Contributions to refining of Canadian and Ohio petroleum and his method of mining sulfur	1926	R. B. Moore	Achievements in field of helium and radioactive elements
1913	James Gayley	Invention of dry air blast for manufacture of iron	1927	John E. Teeple	Achievement in manufacture of acids, alkalies, chlorine, permanganate, special chemicals; design of plants for same, distillation of hardwoods; utilization of pine oil; and chiefly for recovery of potash and borax at Searles Lake, Calif.
1914	John W. Hyatt	Discovery of celluloid and development of its manufacture	1928	Irving Langmuir	Accomplishments in field of low pressures; conduction, convection, and radiation of heat; vapor pressure of metals; new vacuum pumps and vacuum gages; atomic and crystal structure; electronic and ionic currents; high-power vacuum tubes; theories of absorption, evaporation, and passivity; first to apply argon and nitrogen in tungsten lamps; atomic hydrogen flame for welding; and conception of space charge in thermionic tubes
1915	Edward Weston	Achievements in electrodeposition of metals, electrolytic refining of copper, construction of electric generators and motors, arc and incandescent illumination, electric measuring instruments, and the Weston standard cell	1929	E. C. Sullivan	Development of special glasses for heat resistance, for transmission of certain light rays, and for other purposes
1916	Leo H. Baekeland	Discovery of Velox paper, Bakelite, and of other synthetic resins	1930	Herbert H. Dow	Developments in bromine and electrolytic production of chlorine and alkali; in manufacture of metallic magnesium and its salts; and in introduction of novel processes for phenol, aniline, and other organic chemicals
1917	Ernst Twitchell	Discovery and development of use of organic sulfo acids as catalysts in hydrolysis of oils and fats for production of fatty acids and glycerol	1931	Arthur D. Little	Work as a pioneer in the application of research to industry and development of processes for chrome-tanned leather, chlorate of potash, cellulose acetate, smoke filters, newsprint from southern woods, recovery of naval stores from lumbering wastes, and vapor-phase cracking of petroleum.
1918	Auguste J. Rossi	Achievements in field of titanium steel and other titanium alloys			
1919	F. G. Cottrell	Recovery of helium from natural-gas wells and electrical precipitation of suspended particles			
1920	Charles F. Chandler	Work as educator and expert in field of industrial chemistry, as pioneer in field of sanitary chemistry, and for invention of system of assay weights			
1921	Willis R. Whitney	Achievements as research director of General Electric Company, in development of metallized incandescent filaments of Gem lamps, tungsten lamps, gas-filled lamps, insulating materials,			

Accomplishments of the Medalist

(Abstract)

Frederick G. Keyes

THOSE of us who have had the privilege of a long and intimate acquaintance with Doctor Little's accomplishments, and have worked with him, either as colleague or collaborator, sharing the joys and tribulations characteristic of the paths leading from the naked idea to the perfected and productive process, know that he is a man in whom fine character, sound judgment, intelligent optimism, and abundant humor are combined with scientific imagination in a remarkably agreeable and effective manner.

The young man entered upon his career at a moment when the rapid social and industrial changes following the Civil War had begun to reach a steady state. It was, indeed, about the very beginning of the rational application of scientific methods to industry in this country, a period that at first developed very slowly but which became immensely active during and since the last war.

After leaving the Massachusetts Institute of Technology, our colleague became the chemist and later superintendent of the first sulfite wood pulp mill in the United States, that of the Richmond Paper Company. This was a 10-ton plant at Rumford, R. I., installed in 1884 at a time when organized knowledge of chemical engineering was non-existent. Imagine a digester, with a tissue lining of 5-pound lead crawling away from its shell, cracking, buckling, and adding, for digester repairs, \$15 per ton to the cost of the product, and you will see good reason for the chemist's initial loss of embonpoint at the rate of 4 pounds per week. The process was inherently right, but the young superintendent's task was to make right the engineering, inherently and completely all wrong. The disabilities of the original digester design inspired, incidentally, A. D. Little's first patent.

The period beginning with 1890 saw the introduction into the United States of many new industrial processes. Artificial silk produced by Count Chardonnet from nitrocellulose became known at the Paris exhibition of 1889. The process of Cross, Bevan, and Beadle for artificial silk, now known as the viscose process, was communicated to Doctor Little in 1893. He at once saw the range and importance of the manifold applications of the cellulose thiocarbonates and derived products, and in 1894 reported an extraordinary amount of investigative work resulting in such products as a cellulose glue, dense masses of cellulose, films and various admixtures of the viscose solution with untreated fibers and mineral substances, besides many other applications. "Educated money" was immensely difficult to find thirty-five years ago, and is still sufficiently difficult to find for the development of a new process. Not until about 1900, after extended development abroad, was an American company formed for the exploitation of viscose. By 1927, however, the world's production of artificial silk from viscose was somewhat in excess of 200 million pounds.

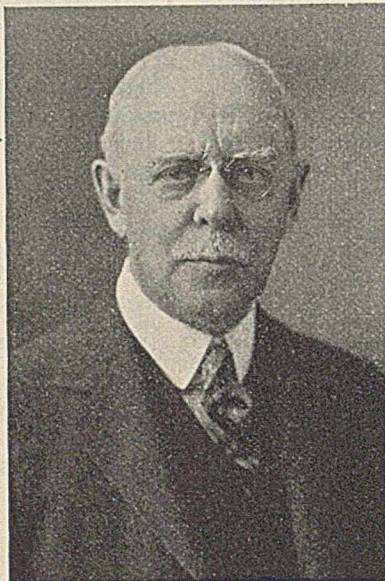
About the same period we find Doctor Little demonstrating the revolutionizing chrome-tanning process of Schultz, and a patent was issued on the process in 1893. The studies with viscose cellulose acetate and like products appeared to be progressing simultaneously, for I find, among others, a patent for carbon filaments from cellulose issued in 1895. Paper-making problems and manufacturing improvements continued to hold a large measure of attention. Patents for waterproofed and waxed papers bear the date 1902. Wood-waste utilization, alcohol production, casein products, electrolytic production of chlorine and soda, hypochlorites, and chlorates constituted the pioneering work for the most part, but at the same time a prodigious amount of thought and effort was expended in carrying on the work of the industrial chemist in checking waste, increasing plant efficiency, and organizing and directing capital along the lines of new enterprises.

Something over twenty years ago about the only company-owned industrial research laboratory was that of the General Electric Company, then but recently organized by Willis R. Whitney.

The industrial leader or business executive at that time who could grasp the significance of persistent research effort over a long period of time was a remarkable rarity. It is easy to imagine that the firm of Griffin and Little, organized in 1886 for industrial research and control, must have somehow found the means of endowing itself with a wonderful self-renewing quality of faith and optimism. The firm prospered, was reorganized in 1900 under the name of Little and Walker, and the scope of its activities enlarged.

At about this period, perhaps much earlier, A. D. Little must have been turning over in his mind the problem of meeting the need in industry for well-educated and thoroughly trained men. He evidently foresaw with clearness the period of rapid acceleration in the application of scientific principles to industry, which was well under way in the United States when the cataclysm of 1914 punctured the peace of the world. The inauguration of the Research Laboratory of Applied Chemistry at M. I. T. took place in 1905 and Doctor Little's partner, William H. Walker, assumed the professorship of industrial chemistry.

Doctor Little's industrial contacts and activities were expanding steadily in the period from 1900 to 1914. By 1909 there had been brought into existence an organization consisting of a number of departments manned by specialists whose activities were correlated and brought to bear on a wide variety of industrial problems. By 1911 the business was eight times what it had been in 1904. In 1914 the present model industrial research laboratory on Charles River Road in Cambridge, "Dedicated to Industrial Progress," was built and placed in full operation. It was an opportune moment, for the enormous expansion of American industry caused by the huge demands for supplies of



A. D. Little

all sorts by England and France immediately emphasized the importance of research and scientific control of operations.

Doctor Little's effort after the American participation in the war, in its immediate and tangible aspects, centered around the development of airplane dopes, acetone production, and smoke filters. I believe his process of setting the smoke-filter fiber on the gas-mask canisters is now the approved process.

That all these very practical results were important may be readily admitted. There was other even more important work to be done, and that of a kind few chemists do well. Some one has remarked that the man of science is the only one in the world with anything really important to say and he doesn't know how to say it. Our colleague is, however, the conspicuous exception, for he always has something important to say and he certainly knows how to say it. I wonder, then, if his greatest contribution from 1915 on, has not lain in the stimulus, impetus, and direction given to industrial research through his well-composed addresses, papers, and essays. The beginning of the war was a moment when, German imports being cut off, the United States was hamstrung for dyestuffs, scientific apparatus, synthetic drugs, and many other necessary products dependent for their production on highly organized and scientifically controlled processes. Certainly the brilliant series of papers during this period constitutes a wonderfully clear statement of the problems to be solved, the useful kinds of organizations to be developed, and the importance of cooperation, not only between the different branches of science, but between the exact sciences and economics and government. The subject of the conservation of natural resources of the country was studied and the facts correlated in an exceptionally clear, logical, and forceful form of expository literary style. The range of topics touches almost every practical problem of the complicated pattern of our industrial and social life. It was the most important kind of service, and needed, to awaken the consciousness of the discerning public to the importance of intelligent, immediate, and concerted action.

It is interesting to observe that, besides being a skilled expositor of the scientific, A. D. Little perceives and presents, with ad-

mirable forcefulness, the dangers of allowing applied science to march out of step with social development.

Interest in educational matters at M. I. T. did not lag during the hectic years of the war. As chairman of the visiting committee of the Department of Chemistry and Chemical Engineering, Doctor Little was the active force that finally induced the adoption of the Chemical Engineering Practice School.

The war, besides bequeathing us life without much joy, gave us a complex variety of evil changes and distressing disasters unparalleled in the aftermath of other wars. An intelligent man of sensitive and acute perceptions must have very uncommon internal sources for the nourishment of the soul to emerge from the experiences attending the conduct and prosecution of a modern war with unimpaired optimism and faith in the future of his civilization. Here we see a man with calm intelligence surveying the post-war problems in a world which still resembles nothing as much as a pot of spiders trying to devour one another. During the period from 1918 to the present A. D. Little found time for some sixty papers and addresses. The stimulus to thought and action in all directions resulting from these admirable essays can probably never be quite fully measured. The sane and objective presentations of fact, the voluminous statistical information, the constructive criticisms of worn-out points of view and procedure, the clear indication of the danger signals with respect to our long misused but dwindling natural resources is a monument to constructive and sane intelligence. A volume containing some twelve essays has recently appeared under the title "The Handwriting on the Wall." It is to be hoped that the remaining essays will ultimately be collected and published in book form.

After 1918 industrial research, new processes, technical investigations and matters pertaining thereto came under the attention of Doctor Little and his organization to an extent which would have been expected in view of the part the industries of the United States were destined to play in world commercial com-

petition. It seems that the vapor-phase cracking of petroleum worked out by A. D. Little and his organization marks an important step in petroleum chemistry. The subsequent small-scale commercial operation of the process at Tiverton, R. I., gave, without carbon deposition, besides high-quality antiknock gasoline, tertiary butyl alcohol and secondary alcohols, propylene, and other unsaturated olefins. It seems clear that the further development of this process and its offshoots may usher in an era of industrial development in which the aliphatic compounds derivable from petroleum may prove as interesting and important as the aromatic compounds from coal tar.

A. D. Little served the AMERICAN CHEMICAL SOCIETY as president for two years (1912-1914). He was president of the Institute of Chemical Engineers in 1919, and president of the Society of Chemical Industry in 1928. The University of Pittsburgh conferred upon him the degree of doctor of chemistry in 1918. The University of Manchester gave evidence of its appreciation in the form of an honorary doctor of science degree in 1929, while the College of Technology of Manchester have him as their honorary associate. He has served as chairman of the Commission on the Economy of Fuel and Raw Materials of the American Section of the International Chamber of Commerce, as vice chairman of the Engineering Foundation Board, as a member of the Division of Engineering and Industrial Research of the National Research Council, besides other national committees. A very important work was that of organizing the National Resources Survey for the Canadian Pacific Railway in 1916 and 1917. He is a life member of the M. I. T. Corporation and has served the Harvard Department of Chemistry as a member of its visiting committee, as well as the Departments of Chemistry and Chemical Engineering at his own Alma Mater. Doctor Little is a member of more scientific and technical societies than any one I have ever known and, what is more remarkable, he finds time to contribute to all of them pretty regularly and effectively.

The Evaluation of Chemical Projects

Arthur D. Little

ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS.

WHEN we search for the fundamental basis upon which our whole industrial structure has been reared, we find, in the last analysis, that it rests upon a bed rock of chemical processes. We practice agriculture only because the growing plant, under the influence of sunlight, transforms by subtle chemical processes its raw materials in soil and air into the starch and sugar and oils and proteins required for our purposes. We have a lumber industry because the tree, by a chemistry which far transcends our own, converts water and carbon dioxide into the cellulose which is the physical basis of its structure. The coal and oil and gas upon which our civilization is so definitely founded are themselves the products of chemical processes operating in ages long since past, and neither coal, nor oil, nor gas would be of interest or value to us except for the typically chemical process of combustion. The ores we mine are what they are because of a long succession of chemical changes which had their remote beginnings even before the earth was formed. We obtain them by the aid of chemical explosives and we win their values by methods which are largely chemical. In short, we go back to chemistry for all our basic raw materials.

Chemistry similarly pervades that second line of industry in which these raw materials are converted into things of higher value and more immediate usefulness. It would be difficult indeed to find a manufacture which is without some chemical aspect. Many, like the smelting of iron and the making of steel, are as chemical as a sulfuric acid plant, although not commonly so regarded.

Impossible though it may be to draw any strict line of demarcation, there is a large and highly important group of manufacturing activities which constitutes what are generally accepted as the chemical industries. It includes those con-

cerned with the making of acids, alkalies, and salts, dyes and synthetic products, solvents, explosives, and the multitude of compounds utilized by others for producing chemical effects. It may, although with less general acceptance, be extended to include many specific industries where the product, like celluloid or cellophane or rayon, is the result of processes which are predominantly chemical. Sulfur, although obtained by methods in which chemistry is not involved, is so vitally essential to the chemical industries that the companies producing it are naturally associated with the group.

Taken as a whole, the chemical industry presents characteristics which, from the point of view of the investor, differentiate its members from industry in general, and which invite and well repay his serious study.

Financial Considerations

The importance of the chemical industries, both in the financial sense and from the investor's standpoint, may be gaged from the brief summary of significant items which follows.

At the end of 1928 the total tangible assets of fifty American chemical companies were in the neighborhood of \$1,800,000,000. About 40 per cent of this must be credited to three companies—Allied Chemical and Dye, Union Carbide, and du Pont when the du Pont investment in General Motors is excluded, as it was from the grand total. The remainder is distributed among the forty-seven remaining companies in proportions ranging from 5 per cent down.

It is particularly noteworthy that these smaller companies are by no means throttled by the giants. They often show a higher percentage of profit than any of the three, while offering promise of a greater percentage of future expansion.

The average turnover of sales in the chemical industry is about once a year on capital investment, although it varies in some cases from twice a year to once in three years, depending on the type of products made.

During the five-year period from January 1, 1924, to December 31, 1928, the average percentage of net earnings on the net worth of 1929 was as follows in case of the representative non-chemical companies named below:

	%		%
Bethlehem Steel Corporation	3.75	Standard Oil Company of New Jersey	7.85
United States Steel Corporation	5.06	New York Central Railroad	8.02
Southern Pacific Railway	5.96	American Can Company	8.93
Pennsylvania Railroad	6.42	American Telephone & Telegraph Company	9.34
International Harvester Company	6.48	General Electric Company	10.8
Atchison, Topeka & Santa Fé Railway Company	6.96	Sears, Roebuck & Company	12.3
Consolidated Gas Company of New York	7.78	National Biscuit Company	13.43
		F. W. Woolworth Company	18.2

For purposes of comparison the corresponding percentage figures are given for ten representative companies in the chemical field:

	%		%
Union Carbide and Carbon Corporation	9.66	Air Reduction Company	18.2
Allied Chemical and Dye Corporation	9.87	Dow Chemical Company	19.3 ^b
Mathieson Alkali Company	10.41	Commercial Solvents Corporation	28.03
Eastman Kodak Company	14.6	Aluminum Company of America	38.1
International Nickel Company	15.8 ^a	Texas Gulf Sulphur Company	55.15

^a 1929 only.

^b May 31, 1928, to May 31, 1930.

Viewing the situation from another angle, we find that during the five-year period beginning January 1, 1925, the total assets of five chemical companies (Allied Chemical, Union Carbide, Texas Gulf Sulphur, Vanadium, Commercial Solvents) increased from \$582,835,000 to \$814,338,000 and real earnings rose from \$41,902,000 to \$87,397,000. Whereas in most businesses the percentage of earnings falls as the investment increases, we find here that the group as a whole has not yet reached the point where the law of diminishing returns becomes effective, since an increase of about 40 per cent in assets resulted in an increase of 108 per cent in earnings. The ratio is less striking in case of Commercial Solvents, which, nevertheless, shows the very satisfactory increase of 251 per cent in earnings when assets increased 241 per cent.

Again, the market values of half a dozen leading chemical companies at the 1930 lows are still three or four times the market values of the same companies at the 1924 lows, whereas many other leading industrials are now at the same low market value reached in 1924. The stock market appraisal is an indication both of actual increases in value in the chemical stocks during this period and of their future possibilities for growth, whereas the others have taken a roller-coaster ride and are now back where they were.

According to Standard Statistics it also appears that the total profits of thirteen leading chemical companies, excluding du Pont, declined during the first nine months of 1930 by 18.7 per cent from the peak level of the corresponding 1929 period, whereas the decline of aggregate corporate earnings in industry as a whole was 35 per cent. The resilience inherent in the chemical industry is indicated by the fact that whereas the profits of eight leading chemical companies in 1921 declined almost 67 per cent from the profits of 1920, the earnings of these companies so quickly recovered that the final returns for 1922 were only 18 per cent below the record level of 1920, and by the end of 1923 a new profits peak had been established.

It is also interesting to note that, whereas the total net income of the du Pont Company during the first six months of 1930 showed a decline of 26 per cent from that of the first six months of 1929, when the return from General Motors is excluded the decline was only 9.7 per cent.

It would be easy to cite many examples in the chemical industry of remarkably rapid increase in volume of sales and of phenomenal profits. In the five years from 1922 to 1927, for instance, the production of ethylene glycol by the Union Carbide and Carbon Corporation rose from 10,000 pounds to 12,000,000 pounds, while in the first half of 1926 the production of pyroxylin lacquers exceeded 10,000,000 gallons as against less than a million and a half gallons produced during the first half of 1924.

One large chemical company, which turns its capital over once every two and a half years, has shown net profits on sales as high as 80 per cent. The most spectacular example, however, of what is possible in the industry is that given by Courtaulds, Limited, which, in addition to its plants in other countries making rayon, controls The Viscose Company in America. There is reason to believe that about 1902 Courtaulds appropriated £100,000 for developing the viscose rayon process. This development proved so successful that not only was further plant expansion paid for out of profits, but the investment of \$10,000,000 in the American Viscose Company was also made from the profits of the English rayon plant. In 1928 the reported net income of Courtaulds was £5,172,000, and it has been estimated that in some years, when undivided profits of subsidiaries are included, the total profit has exceeded \$50,000,000. From this original moderate investment, supplemented by huge annual profits, Courtaulds has built up in thirty years total asset values close to one-half a billion dollars.

Interest of Investor

Many factors have contributed in recent years to develop among individual investors, banking houses, and investment trusts an active interest in chemical companies and projects. The initial impulse undoubtedly came from the spectacular development of our chemical industry to meet the exigencies of the war. The publicity given to this development revealed the existence of the industry to the multitude who had never heard of it before, and the demands for new capital in vast amounts forced the industry upon the attention of bankers.

As time went on the inherent stability of the stronger companies in the field became apparent, and their demonstrated and exceptional earning power and capacity for growth not only made them favorites on the stock exchange, but fostered the promotion of many other projects which sometimes failed to justify the confidence they aroused. There is thus a definite need for the investor to realize that, as a basis for decision, he requires a competent appraisal which takes into account both the risks peculiar to the chemical industry and the exceptional opportunities it offers.

The term "investor" in this context includes not only the individual seeking a safe and profitable employment for his money, but also the investment trust considering changes in its portfolio, the private banking house invited to float an issue of securities or carry through a reorganization, the national bank from which loans are requested, and finally, the management of going chemical concerns upon whom devolves the consideration of new projects, plant expansion, a suggested merger, or the grant of an appropriation for a major research program. We may with equal propriety include the director of the research laboratory who requests the appropriation, for he is staking his reputation and perhaps ultimately his salary.

Before launching an expensive research program one should clearly visualize the results to be expected from its successful outcome. What will you do with the thing when you get it, and is it worth getting? To answer these questions may require consideration of most of the factors mentioned in this paper.

Since earning power implies operation on the commercial scale, an essential qualification of the person making the type of study under consideration is a sufficient acquaintance with the industry to enable him to formulate the project as a going concern and to foresee the problems that would normally arrive were the project at that stage.

Every investment made in revenue-producing property, whether real estate, securities, or a business enterprise, is essentially a capitalization of earning power. That is, the earning power in dollars per year is multiplied by some factor. The factor used depends both on the risk involved and on the credence given to the prospect that earnings will increase. It was this latter element which led to the acceptance of the absurdly high factors generally in use a year and a half ago.

If the industry is unstable, as, for example, that of wood distillation; if the enterprise is new, like the production of alcohols from petroleum; if obsolescence is rapid, as in the early days of the sulfite pulp manufacture, the risk is high and the factor low. The general rule is clearly illustrated in case of bonds. Where there is no doubt of the security of the principal, the factor is high, and conversely, as with United States Government bonds, the yield is low. Doubt lowers the factor and increases the yield required to attract, as with bonds of companies in precarious or waning industries. The evaluation of a chemical project, therefore, requires, first, an authoritative estimate of its earning power, and second, a comparison of the risks involved with the risks of any other investment promising equal returns.

This evaluation is subject to the same type of analysis that good business men apply to the evaluation of other manufacturing industries. There must be the same consideration of raw material supply, location, capital requirements, cost of manufacture, transportation, markets, and so on. The chemical project presents, however, a distinctive difference in that the layman is rarely capable of rating the technical soundness of the process itself or of accurately visualizing the present and prospective competitive position of its product in the market. To do this requires a rather broad acquaintance with chemical industry as a whole and a keen sense of the trend of impending developments which may either restrict or expand the market.

The future of a company is, from the investor's standpoint, always of greater importance than its past. Although Patrick Henry, in his famous speech, said, "I know of no way of judging the future but by the past," balance sheets and records of past earnings are not the only, and not always the safest basis for a forecast of the future of a chemical enterprise, or in fact of any other that is likely to be affected by the advance in science. Nor do the products of one period always prefigure those of the next. The two tin cans connected by a string and called in my boyhood a lover's telephone did not suggest the Bell system, nor did the zoetrope of my youth suggest the modern motion-picture industry.

Nevertheless, the best possible outline of what is coming is essential to any industrial evaluation, and one may usually be drawn with reasonable accuracy by those who are sufficiently familiar with the industry to enable them to sense trends and who are alive to incipient developments. Since, therefore, one may be called upon to appraise a chemical project at any stage of its development from the initial inspiration or idea to a plant in operation for a long period, the closer the project is to being a going concern the more one has of past history upon which to base his judgment. The same

questions arise at every stage, but guesswork decreases as the basis for opinion broadens.

When the concern has been in operation for a considerable number of years, the record of the company will be available as an aid to judgment. From this record the weaknesses and the strong characteristics of the business can be picked out, the general trend of the company's affairs determined, and an estimate formed of the ability of the management. Whether, during the period, profits have expanded, contracted, or remained stationary will be apparent.

Peculiarities of Chemical Industries

Although chemical industry is necessarily governed by the same sound business principles which apply to industry in general, it nevertheless presents certain peculiarities which require special consideration, and which may modify or extend the usual application of these principles. The following, therefore, deserve attention as factors which tend, in greater or less degree, to differentiate a given chemical project from the more usual types of manufacturing operations.

Whereas many of our most conspicuous industries owe their success to the persistence with which they devote themselves to the making of products of a single general type, perhaps the most significant and distinctive characteristic of chemical industry is its extraordinary power of treelike growth by branching from an original main trunk. A company may undertake the manufacture of a single chemical product requiring two or three other chemicals as raw materials. As the volume of production rises a point is reached where it is cheaper to make these raw materials than to buy them. So their manufacture is begun and usually on a scale beyond the process requirements of the company, which thus has the excess for sale. This new manufacture requires other raw materials. The cycle is repeated, and again the company's list of offerings grows. Meanwhile, by-products appear and are commercialized. Still other products are developed by processes in which the basic, initial product of the company is utilized as raw material, and so on until the original trunk has become a spreading industrial tree with boughs, branches, and twigs of ramified production.

The history of the Dow Chemical Company affords a familiar and typical example of this capacity for growth, and its present plant, making over 150 products in 310 buildings covering 250 acres gridironed with 18 miles of standard railroad track, stands as a monument to the genius of Herbert H. Dow, the Perkin Medalist of 1930. This development is so instructive and so directly to the point that one may be permitted to recall a few of the facts brought out in connection with the award.

Following a careful study of the Michigan brines, which proved them to contain the chlorides of sodium, calcium, and magnesium, with less than 0.2 per cent of bromine in the form of bromides, Doctor Dow began, in 1889, the production of ferric bromide by a process involving the use of bleaching powder. There were near-by sawmills, and from the ashes of their wood waste potash could be extracted. This was done and more bromine was utilized in making potassium bromide. Soon the bleaching powder for the bromine process was made in the plant and bromine itself was sold. In 1900 bleaching powder from an enlarged plant was put upon the market. Other enlargements followed in 1902 and 1904 to provide further supplies of chlorine, which permitted the manufacture of sulfur chloride from which, with carbon disulfide, carbon tetrachloride began to be made.

We hear much of the unearned increment in connection with real estate. To the chemical manufacturer who has placed himself in a position to receive it a similar increment of business and profit often comes from developments in other

lines of industry for which he is not responsible. It was so with Doctor Dow, but the significant thing is that he was ready.

The demand for carbon tetrachloride was greatly stimulated by its use in fire-extinguishing apparatus and as a non-inflammable cleansing agent. His production of the chloride was increased to meet the new demand and to a point which led him to install a plant for making carbon disulfide. He was thus in position to profit by the great demand for this latter commodity which followed the introduction of viscose rayon.

By 1914 the popularity of magnesium oxychloride cements and the call for calcium chloride for refrigeration purposes and for laying dust on roads led the company to separate these salts from its brines, and some years later the production of Epsom salts (magnesium sulfate) naturally followed and soon rose to 100 tons a day.

During the war much of the chlorine produced by the company was employed by it in making various organic compounds essential to the Allies, and the dearth of dyes in our own country stimulated the management to undertake, in 1916, the manufacture of indigo and further to utilize its bromine in the production of brominated indigos of superior fastness and brilliance.

The rapidly expanding demand for synthetic resins derived from phenol, which was a war product of the company, led to the resumption of its manufacture by an improved process in a plant which has since become the largest in the world. From phenol the step to salicylic acid and pharmaceuticals was obvious and short.

Presently, also, a new use for the old product, sulfur chloride, was developed in a process for making acetic anhydride, a basic raw material for cellulose acetate, and here again a great new market was opened by the application of cellulose acetate to the production of non-inflammable movie films and a special type of rayon.

Now we have come to the navigation of the air, with its demand for light metals for the construction of planes and airships. And again the Dow Company has met the situation by producing metallic magnesium from its brines.

My only justification for referring at such length to the development of a single company lies in the fact that it so typically illustrates the possibilities for growth inherent in chemical industry in general. We have seen the company expand its operations, step by step, by the logical, progressive development of the resources latent in a single raw material—the Michigan brines. Other companies have similarly grown, as the du Pont Company from black powder to nitrocellulose with its many applications and near relatives, or Union Carbide and Carbon Corporation from calcium carbide and acetylene. It is the habit of the industry.

Less distinctive, perhaps, but nevertheless important, is the fact that a chemical plant is commonly engaged in making products which are raw materials for industry in general. Its sales are thus, in most cases, to manufacturing consumers rather than to the consuming public, and this, of course, determines its sales organization and policy and its arrangements for distribution. The business rarely lends itself to emotional advertising. Sulfuric acid and liquid chlorine make small appeal to the general public. Intensive advertising may, indeed, create a broad demand for toothpastes, cigarettes, and many other articles of popular consumption, but chemical products, by and large, must be sold on their intrinsic value. They are commonly bought on specification, or at least on a definite presumption of quality, and they go to purchasers equipped to check quality by analysis.

Whereas vast sums may be legitimately spent in advertising many products which go directly to the ultimate consumer, the chemical industry can to greater advantage devote such

appropriations to research directed toward the lowering of costs, the raising of quality, and the development of new and more profitable lines.

One finds also that the individual chemical industry is apt to be highly specialized. It commonly involves greater risk and, when successful, returns greater profit, than industry as a whole. It is peculiarly dependent upon rigid scientific control; highly sensitive to changes in its situation resulting from research by others; and must largely rely, for the continuance of its prosperity, upon the effectiveness of its own research. It is, however, little subject to changes in styles and fashions, though more dependent than many other industries upon patent protection.

There is also in chemical industry a greater gap than in most others between paper work and practice. One cannot go out and rent a building and lease machines and begin manufacture as one can start making shoes.

While it is frequently possible to use standard equipment, chemical processes often require that which is specially designed and which, if the process is a new one, must be developed, sometimes at great expense, as was the case with the high-pressure cracking processes and the ammonia synthesis. Moreover, in the initial stages of process development so many undetermined factors are invariably present that the development must, of necessity, proceed by steps. Even under the most favorable circumstances the bringing into operation of a chemical plant is a much slower and far more complicated matter than that of starting up a cotton mill or a paper mill or a shoe factory, where the performance and capacity of every machine is already known. In a chemical plant, even though it be one in which standard equipment is used throughout, one must still reckon with many variables, as time, temperature, pressure, and the disconcerting idiosyncrasies of the reacting materials.

Important as the yield of a process is for the estimation of its economic value, high yields are sometimes secured at disproportionate cost. A German technician once visited an American electrochemical plant and, during his inspection, asked what the current efficiency of the process was. When told it was only 47 per cent he foresaw bankruptcy for the company and said, "We get 85 per cent in Germany and are still losing money." "Of course you are," the manager replied, "you have wiped out your profits by adding too many refinements."

Many chemical industries are distinguished by the number and importance of their by-products, others by the necessity they are under of making collateral products, as when the electrolysis of salt for chlorine involves a proportionate production of caustic soda. It is as though a cotton mill to make 35 yards of cloth was forced also to turn out forty shoes. The demands for cloth and shoes may not always be in this proportion, and there may also be some difficulty in satisfactorily allocating costs between them.

After a chemical product is made its distribution often involves special problems, or costs which are out of line with those of other industries. Certain types of chemical products—as chlorine, acetylene, and other compressed or liquefied gases, volatile liquids, and corrosive acids—require especially expensive containers in which much capital may be tied up. This is obviously true in case of pressure cylinders, rubber-lined tank cars, or aluminum drums, but sheet steel for making drums may be the heaviest item of raw material expense in some large plants.

Development of a Project

Turning now to the study of the proposition itself, we find that the consideration of any chemical project must proceed in stages. There is first an examination of the ob-

vious facts in the situation, and these are often sufficient to cause the immediate rejection of the proposition. One would not undertake the manufacture of alcohol from waste sulfite liquor when molasses could be had for 4 cents a gallon, nor that of synthetic rubber with plantation rubber selling at 8 cents a pound.

Thus the relation of a process to contemporaneous developments is of the first importance in estimating its value. In 1851 Charles Watt described, in a remarkably comprehensive British patent, methods for the production of hypochlorites, chlorine, and alkali, and chlorates by the electrolysis of common salt. Had this patent appeared thirty years later it would have had great value. In 1851 it was of no industrial interest because the only current then available was that from expensive primary batteries.

If the preliminary review fails to disclose anything seriously adverse to its prospects, one may make the tentative assumption that the project is sound and proceed directly to the study of the economics of the situation. This will either reveal such unfavorable conditions as to make further consideration unnecessary or it will indicate that there is a real place for the enterprise if the process concerned is sound in fact. Not until then need one undertake the final rigid examination of the process itself.

In case, then, that the process appears attractive upon its face, one of the first things to be considered is, of course, its relation to the state of the art. This can only be determined, and even then not always conclusively, by a thorough literature and patent search. By way of example, it will be recalled that the apparently impregnable patents of Willson for crystalline calcium carbide were finally found to have been anticipated by a patent in the seemingly remote art of incandescent lighting—namely, the Böhm patent for a filament of calcium carbide.

Where the product itself is new, the protection afforded by the patent covering it may greatly enhance the value of the opportunity created by the manufacturing process, since it prevents others from marketing the product, even though they should discover an alternative process for making it. By way of illustration one may cite celluloid, vulcanized rubber, and many synthetic dyes.

Provided the search has reasonably established the novelty of the process and indicated that adequate patent protection may be expected, one has still to consider its relative importance in the art: Is it so fundamentally new that it promises to ensure a broad monopoly, as was the case with the viscose process of Cross, Bevan, and Beadle, or is it supplementary to an existing process, as the Frank process for converting the already patented calcium carbide into calcium cyanamide? In the latter event the value of the process is obviously indeterminate until one has reached an understanding with the owners of the patent controlling the raw material.

Supplementary Process May Control Primary Process

A supplementary process may indeed sometimes have a large measure of control over an important primary process. In the early days of Tilghman's sulfite process for wood pulp the lead linings of the digesters were a source of endless trouble and delay, so that digester repairs alone were fifteen dollars per ton of product. Russell's method of lining the digesters with Portland cement and brick brought this down to a negligible amount and permitted a great expansion of the industry.

The Bessemer process, in its original form, would never have come into broad general use, because the steel produced was so contaminated with dissolved iron oxide as to be unsuitable for many purposes. Furthermore, the process could not be applied successfully to the treatment of iron rich in phosphorus. The importance and field of the process were,

however, soon vastly extended by two supplementary inventions. Robert Mushet eliminated the iron oxide by adding manganese, as spiegeleisen, at the end of the blow, while S. G. Thomas, by demonstrating that phosphorus could readily be removed in the presence of a slag rich in lime, made the process, as thus modified, available for the treatment of the high-phosphorus iron from the vast ore deposits of Lorraine, which thus became the basis of the German iron and steel industry.

The process of mercerizing cotton yarns and fabrics greatly increased their strength and their capacity for taking dyes. Unfortunately, it involved a 20 per cent shrinkage, and as a result its initial popularity soon waned. The process was practically forgotten until, years afterward, Thomas and Provost devised means of preventing this shrinkage and found to their surprise that they had thereby conferred upon the yarn a brilliant silky luster, which led to its widely extended use.

Secret Processes

Secret processes should rarely have a place even in a speculator's program, and never unless those who sponsor them permit thorough investigation by competent and hard-boiled experts. Like Jernegan's sea-water gold, the Hickman sugar process, the Lamoine diamond swindle, and many others, they are too often the device of charlatans. Moreover, the secrecy can seldom be long maintained, even in case of an honestly promoted and thoroughly sound process. Nevertheless, Sir Henry Bessemer, who was a prolific inventor, operated secretly for years the process for making bronze powder which brought him his initial fortune, and we ourselves similarly operated on the large scale for more than a decade a process of exceptionally high efficiency for the production of chlorate of potash. In each instance, however, the course was justified and possible only because of the extreme simplicity of the essential feature of the process, this being, in our own case, merely the suppression of reduction at the cathode by the addition of one per cent of calcium chloride to the bath of muriate of potash.

What Is a Chemical Project?

Since, strictly speaking, any industrial activity in which the ultimate nature and composition of the materials, rather than their mere form, is changed, is a chemical project, the making of iron and steel, Portland cement, leather, glass, paper, and many other things is actually a chemical manufacture, although in popular estimation not so regarded.

Although, when any of these industries is considered as a whole, the mechanical operations involved may so overshadow its strictly chemical aspect as to place the industry outside the scope of this paper, there nevertheless constantly appear specific processes directly related to the industry and so definitely chemical in character as to require consideration from that angle. Such, for example, are the Aston process for wrought iron and those for slag cement, chrome tanning, Pyrex glass, and sulfite wood pulp. Such developments are, however, rarely regarded as chemical either by their management or by investors, and there is, therefore, in such cases an increased danger that the strictly chemical character of these supplementary processes may be overlooked.

Evaluation Dependent on Stage of Development

In evaluating a new process nothing is more important than the stage of development in which it is presented. If still in the laboratory stage it is in effect a liability rather than an asset, for much time, effort, and money must be spent before a return from earnings can be expected. At best the

process is no more than an opportunity to develop presumably potential values, and for that development technical skill, a long purse, courage, and staying power are essential. The price of a process at this stage should seldom be other than a reasonable proportion of the equity and the underwriting of the estimated expense of carrying the development through the semi-works stage. All the parties at interest are speculating, not investing.

When the semi-works stage has been reached by several successive steps and operation has continued for several months, both the possibilities and the limitations of the process should be fairly well defined, and the speculative feature correspondingly reduced. The character and balance of equipment have been determined, conditions for control established, yields and costs approximately ascertained, and markets tested. Although still speculative, the process has now become a project which may be evaluated provisionally on the basis of the showing made. The controlling factors in this evaluation may now well be the estimated time and cost of further development, the cost of the commercial plant, the estimated annual earnings, and their capitalized value.

When, however, a process has been in operation in a commercial plant for a reasonable length of time, which may be a year or more, we have to deal with a going concern, the evaluation of which will be governed by the considerations involved in the appraisal of any manufacturing business, except as these may be modified or extended to meet the specialized requirements of the chemical industry.

Other Considerations Involved in Appraisal of Project

The relation of a chemical process to its raw material supply is often of even more vital consequence than at first sight appears. The raw material selected by Baeyer for his initial synthesis of indigo was toluene, but when the process was perfected it was found that toluene was not procurable in amount sufficient to make possible the displacement of natural indigo. Baeyer and his associates were thus forced to travel the long road again, starting from the cheaper and abundant naphthalene, but when they finally arrived Germany controlled the indigo market of the world.

If beryl were as common as bauxite, the beautiful metal beryllium would undoubtedly usurp much of the market for aluminum. Fortunately, the supply of the basic raw materials for chemical industry—salt, sulfur, the atmosphere, coal, oil, natural gas, lime, and cellulose—are available in amounts altogether adequate for any possible development.

Energy is a raw material in a very definite sense, and its form value is often important, as shown by the advantages of natural gas for firing boilers or for heating the tanks of glass works. In the electrochemical industries the cost of power may determine success or failure.

It is always perilous when a chemical company depends solely for its raw material upon another enterprise over which it exercises no control. I recall the case of the Standard Alcohol Company, which built a 5000-gallon plant to make grain alcohol from wood waste. It did this by a process which yielded 10.5 gallons of Cologne spirit per ton of waste. Elihu Thomson said he was not surprised, the alcohol obviously coming from the grain of the wood. Unfortunately the company, which had a choice of sites where the waste from many sawmills was available, chose one where it depended upon a single mill, the waste from which was just sufficient to permit the plant to operate at capacity. Unfortunately, when the plant was ready to begin operations the price of yellow pine lumber had so declined that the sawmill operated at only about one-quarter capacity, with the inevitable consequence that the alcohol company went into liquidation.

Another instance comes to mind in which the unfortunate selection of a site, coupled in this case with a flagrant disregard of ordinary precaution, resulted still more disastrously. The White Mountain Paper Company built at Portsmouth, N. H., what was to be the largest newsprint mill in the world. In the process they proposed to use sea water from the harbor. When the mill was built and the machinery installed, the president, during an interview with me, inquired casually if I thought the salt water would involve them in any difficulties. I told him he would never be able to make paper with it. He never was, and the idle plant stood for years a monument to ignorance of the first principles of evaluation of a chemical project.

The possibility that a chemical process may create a nuisance must always be kept in mind and has an important bearing on the selection of a location. There are processes which operate with a minimum of friction "far from the madding crowd." Damage suits, and injunctions which are sometimes permanent, play havoc with dividends.

In proportion to volume and value of output, chemical industries commonly require much less labor than most others. Moreover, such interest and sense of responsibility are developed in the workers that labor troubles are practically unknown. There was, indeed, a strike within fifteen minutes of my appointment as superintendent of the first plant entrusted to my care, but that was merely because my husky associates resented the suggestion that "a little child shall lead them." Even then we quickly reached so perfect an understanding that I was soon referred to as "the old man."

Chemical industry is, likewise, noticeably free from many of the operating risks common to other manufactures, as there is usually far less moving machinery in the chemical plant. It has, however, its own special hazards which are inherent in the nature of its materials and processes, but these are so well recognized and so carefully guarded against that even the manufacture of explosives is conducted with a remarkably high degree of safety.

There are other risks, in addition to those involved in operation, which should be carefully weighed in considering a chemical proposition. There is, for example, great danger of underestimating the time and capital required for reducing a laboratory process to commercial practice. One does not always go "from test tube to tank car in three years." Many have lost great opportunities in chemical industry simply through lack of staying power, and, as Doctor Baekeland said in his own Perkin Medal address, "remember that starting a chemical enterprise with insufficient capital is one of the most effective ways of ensuring failure."

Generous allowance must also be made for the rapid obsolescence of many types of chemical equipment. Furthermore, management must be of a quality competent to make the rapid adjustments necessitated by the frequency with which new processes and products appear. Doctor Haber attributes the success of German chemical industry to the fact that, from its commencement, the Germans realized the need for close coöperation of the chemist, the technician, and the selling department. It is easier and more profitable to adjust sales to the developments of one's own research department than to those resulting from the research of a competitor.

Major changes in the industry are apt to cast their shadow far ahead and thus to give more time to meet them than the style changes in some other industries allow. There is, nevertheless, always the possibility that the process in use may be displaced by a new one, as occurred when viscos rayon usurped the place of Chardonnart artificial silk. The encroachment of chlorine upon bleaching powder, the substitu-

tion of butanol for amyl alcohol, and of synthetic ammonia for Chile nitrate are examples of the similar replacement of established products.

A corresponding curtailment of market may be brought about by changes in other industries. Shingle stains are not needed for asbestos shingles; stainless steel competes with chromium plating; and the incandescent lamp replaced acetylene in automobile headlights.

Fortunately, the converse is even more often true. A great new market for chromium compounds was created by the shift to chrome tanning. Mercerized cotton increased the demand for caustic soda, and it was further increased by the viscose process, which also opened a great new outlet for carbon disulfide. A change in the method of finishing automobiles brought spectacular prosperity to a company loaded down with by-product butanol.

Adverse laws, tariff changes, the uncertainties of patent litigation, and the prospect of domestic and foreign competition must all be reckoned with. The Volstead Act imposed great burdens on the distillers of grain alcohol, but benefited methanol. The Pure Food Law restricts the use of saccharin. At the moment British chemical manufacturers are deeply and properly concerned over the repeal, effective January 15, of the British Dyestuffs Act.¹

All these considerations emphasize the great advantage of diversification of products as an assurance of stability, and add much weight to the importance of the capacity for tree-like expansion inherent in the chemical industries.

The relation of a proposed product to the established distribution system of the company is a matter of primary importance. The sale of a household disinfectant would involve altogether disproportionate expense to a company which had previously sold its customary products only to the textile industry. It is similarly important to ascertain whether the product is one for which a broad market already exists or one for which, however promising, the market must be created. Either possibility obviously calls for a careful market survey.

The final criterion of the value of any chemical enterprise is, of course, its earning power, but the full significance of the item of net earnings is not disclosed in its sum total on the balance sheet. It is especially important that this total be broken down into its major constituents and that the proportion contributed by each of them be considered not only as to its amount in dollars, but more particularly as to the probability of maintaining or increasing this proportion in the future. There is an obsolescence of products as there is of machines and, again, the company making a reasonably diversified line has the larger factor of safety.

There is in every new project, whether chemical or otherwise, a final element of uncertainty against which provision can rarely be made. We were once called upon to develop, from sulfite pulp, a paper binder-twine for use in harvesting machines. We found that the pulp as then made would not make a paper of sufficient strength. By spending some time at the mill we were at last enabled to produce a pulp which gave a paper of the required tensile test. The twine was made, but it was found necessary to waterproof it, so a method of doing that was worked out. Then it was discovered that, in spite of its strength, the twine broke in the knotter of the machine. The trouble proved to be due to the too sharp curvature of the usual knotter, so a new one was designed. Finally, our client got into production. The twine worked perfectly and every one was happy until the sheaves began to fall apart because the crickets ate the twine.

The story should, of course, end here, but there is another chapter. We added an entomologist to our staff and, aided by

¹ Since this was written the life of the act has been extended for one year.

his knowledge of the dietary aversions of crickets, we finally were enabled to treat the twine so that it went off their menu.

While giving due weight to all the foregoing, one must not forget that, however promising a chemical industry may seem to be, its conduct is, after all, only a form of human activity and its success or failure will finally be determined by the human element. The quality and character of the management, its business ability and experience, its attitude toward research, and the strength of its financial connections are primary and often decisive factors in the evaluation of a chemical project. This was summarized by one large investor in the phrase, "I put my money on men."

Chemical Industries and Present Industrial Situation

Now that we have given such consideration as the time allowed to the study of the factors involved in the evaluation of chemical projects, we may properly conclude our study by a brief reference to the relation of the chemical industries to our present industrial situation.

Prominent among the factors contributing to the exceptional prosperity which our country, until recently, enjoyed was the development of certain new industries, which furnished employment to millions of men, and to hundreds of millions of dollars. Some of these, like the automobile industry, have probably passed the peak of their demand for men and money alike. Industries age like human beings. They have the hazards and diseases of childhood, the capacity for development in vigorous youth, the stability and strength of maturity, and the conservatism and atrophy of age. The railroads are old, the automobile is approaching middle age, but our chemical industries are still in their energetic and elastic youth, with their great development still before them. They have had the vitality to withstand the present depression better than most others. While steel production has shrunk to 40 per cent of capacity, the chemical industries have brought out cellophane, new plastics, synthetic ammonia, methanol, and many other products to compensate for shrinkage in other lines. They have developed new catalysts, high-pressure processes and equipment, and have gone to new extremes of temperature both up and down the scale.

Since advances in chemistry react on every industry, while, conversely, every progressive trend in other industries makes new demands on chemistry, we may look with confidence to the chemical industries for contributions which should go far toward supplying the stimulus essential to the revival of our prosperity, and which the stationary or obsolescent industries can no longer furnish.

We may expect, for instance, a phenomenal development in the plastics industry, and in materials of construction adapted to the mass production of dwelling houses. New chemical agents are beginning to replace water in heating and power equipment, new products from water gas and from the waste gases of oil refineries are in sight, and even new foods are in prospect. Meanwhile sulfuric acid, chlorine, and soda remain as basic commodities as steel.

There is nothing mysterious about chemical industry. The appraisal of its projects involves consideration of some factors peculiar to itself, but proceeds upon the same sound lines as that of any others, and gives an equally dependable basis for opinion and decision. Therefore, quite aside from its cogent and well-established claim upon the community for its present conspicuous contributions to human welfare and national defense, chemical industry deserves, and will doubtless receive, the increasing interest and support of financiers and the investing public.

To a record of already great achievement it adds the vitality and promise of vigorous youth. Chemistry is a creative science, and the first chapter of its Book of Genesis is not yet written.

AMERICAN CONTEMPORARIES

Walter Louis Jennings

"THE proper study of mankind is man." Thus Alexander Pope illuminated the goal of all succeeding biographers. Those properly studious who are privileged to study Walter Louis Jennings will never forget their most interesting subject. Some of us who have been close to him for many years find here a rare gem of personality, revealing each year new facets, of original brightness and hue. Here is the cloistered scholar and gentleman of the world, combined.

As the late Edwin E. Slosson pointed out, the American Contemporaries series is chiefly valuable because of the personal intimacy of its expression. As biographer of Professor Jennings I should, therefore, report my first impressions.

Surrounded by shivering freshmen colleagues, following the purposeful crash of apparatus in the laboratory of general chemistry at Worcester Polytechnic Institute, I beheld the stern, striking visage of the white-haired director. He peered motionless through the glass panel of the door—all-seeing, unmoved or immovable. He spoke not—presently was gone. Not for a month did I behold him again, but I have never forgotten the first impressive moment when some one breathlessly remarked, "That's Doctor Jennings, head of the Department of Chemistry."

My subsequent contact was to run a wide gamut from classroom to laboratory, from the ballroom to tennis club—from the viewpoint of student to that of colleague. Yea, eventually I was to enjoy visits to the stately home where Doctor Jennings, assisted by his inimitable helpmate and three charming daughters, entertain with the elevating hospitality of New England, and the *savoir vivre* of the world. These same daughters—and yet so distinctive is the personality of each, there is no sameness—are Ruth, Frances, and Alice. There are no middle names and I presume their father, used to the nice simplicity of organic nomenclature, ruled them out. In this respect they do not take after their mother who, as Alice Emily Page, was born in Epsom, England.

As in the case of many an interesting family, it would be fascinating to be a biographer of these other members of the Jennings household. But now I shall shift the scenes rapidly to the stern and rockbound coast of Maine, and then proceed up the Penobscot River to locate Professor Jennings in the setting of Bangor, Maine, wherein he first began, November, 15, 1866, to see the light, and whence he migrated eventually to Harvard. An undergraduate, at Harvard, but taking a summer course in chemistry, Jennings was assigned the problem of preparing malic acid from berries of the mountain ash. In Hoboken, "After Dark" is thought to be a play, but in Cambridge in the late 80's it was a propitious setting in which Jennings could decimate the mountain ash trees in the Boston parkways, to get his first laboratory material. To young people there is characteristically a fascination in separating, and crystallizing, and classifying chemical products from the materials of nature. This natural fascination led Jennings to devote his life to the study of organic chemistry.

Receiving from Harvard, in 1889, the degree of A.B., he be-

came, successively, an assistant instructor in organic chemistry and quantitative analysis. The master of arts degree followed in 1890, and in 1892 the degree of Ph.D. The next two years brought Jennings to Europe. Having received the doctorate in the United States, and as winner of the Parker Fellowship, he was able to choose courses with some freedom when he began his "post-post-graduate" work in Germany. Accordingly he attended not only lectures on chemistry, but also those devoted to philosophy and philology. In Germany Jennings studied under Victor Meyer in Heidelberg, and under Emil Fischer in Berlin. If you will consult the *Berichte* of 1893, and 1894, you will find two interesting papers. No. 253 is entitled, "Emil Fischer und Walter L. Jennings: Ueber die Verbindungen der Zucker mit den mehrwerthigen Phenolen," while No. 425 has the caption: "Emil Fischer und Walter L. Jennings: Ueber die Constitution des Hydrocyanrosanilins und des Fuchsins." So favorably impressed was the great Emil Fischer with the work of the youthful Jennings, that he invited him to become an assistant in his private laboratory. This was a rare privilege. There were several locational milestones in the career of Fischer, but the high point of his career was in Berlin. It was at the beginning of his Berlin period that Jennings began his association. To a student of both men



Courtesy Plant Studio

Walter Louis Jennings

there can be no doubt that Jennings derived, and incorporated as part of his own nature, many attributes of the master. There was broad research vision, coupled with a high degree of manipulative skill, also seemingly inexhaustible energy and power of application. There was sympathetic recognition of all phases of a work, but when criticism was to be administered there was no attitude of apology. Clarity of criticism was achieved through no mincing of words.

Emil Fischer was profound and commanding. His laboratory manner was conducive to meticulous professional care in the handling of materials, and his assistants became imbued with the value of order and cleanliness as allies of analytical accuracy. Fischer was careful with advice, but unalterably definite in the pointing of errors or in the administration of reproof. He tolerated no evasion. One day Emil Fischer had gone to lunch and Jennings was working in the private laboratory. A flask of benzol caught fire and deposited flaky soot ubiquitously on the innumerable items of chemical glassware. Foreboding the return of the master, and frantic at this catastrophe in professionalism, Jennings clambered about and cleaned every piece of apparatus in the room. When Fischer returned all was in order and tranquility.

In Berlin, and in Heidelberg, it was not a case of all work and no play. Every man should have a hobby, and apparently the initials W. L. J. have been on tennis rackets, or prize loving cups, ever since student days of the champion at Harvard. In Germany he played tennis again; attended the famous concerts. In short, his life there was well rounded, although not battle-scarred, inasmuch as he was not a dueling member of a corps. In Heidelberg he met the lady who was to become Mrs.

Jennings. They met at one of the garden concerts in the courtyard of the old and famous castle. Here was a splendid setting to which the youth of the day migrated from all parts of the world. This mecca of literary lore and scientific emanation still was laden with the same free air that Goethe breathed. Castle courtyards were resonant to the presence of the greatest scholars and scientists of the golden age of Germany.

Completing his studies in Germany, Jennings was presently in London, and one day, as he ascended the steps of the Bodleian Library, whom should he meet coming down but Leonard P. Kinnicutt, famous for his studies in municipal sanitation, and then director of the Department of Chemistry at Worcester Tech.

Said Kinnicutt, "What are you doing?" Said Jennings, "I have just finished my work in Germany, and am going back to the United States to look for a job." Said Kinnicutt, "My professor of organic chemistry, George D. Moore, is just now resigning. How would you like to take his place?" "It sounds good!" said Jennings. Thus a bargain was struck which has endured to date since 1893.

Following the death of Doctor Kinnicutt, Professor Jennings succeeded him as director of the department. Although specialist in a different field of chemistry, Doctor Jennings, like his predecessor, had a taste for administration. We who have worked with him know that he excels in this capacity, at the same time not letting it interfere, in the slightest degree, with his thoroughness as teacher. He has builded the department to a commanding place as one of the four major departments at the institute. Many graduates occupying positions of usefulness and leadership in chemical industry owe their professional bearing and scientific method to days spent in the lecture rooms, and meticulous laboratories, under exacting but kindly leadership. The department now embraces, in addition to a complete curriculum of chemistry courses, a chemical engineering division which adds engineering poignancy to the earlier semesters of industrial chemistry.

That select circle in Worcester known as "The Bohemians" establishes for each member a beautiful, painted plaque in the nature of a coat of arms. The heraldic shield of our subject bears a tennis net taut against a background of cerulean blue. Pedaling across the top of the net, on a winged unicycle, is a stately professorial figure, with head in the form of an alembic. The tennis racket in hand provides a nice balance. The subject of this rare illustration is probably entitled to be ranked as the dean of American tennis tournament players. He has been playing hard tennis for forty-five years, ever since he was a freshman at Harvard. There is every reason to believe that again he will give several good men a hard battle in the tournament of 1931. In younger days he could be found at Center

Harbor, N. H., where then the best players gathered each summer; also at Longwood, and in the national championships at Newport. He has won many times, and is still winning. He is one of those very rare men who play their top game with a minimum of dashing around the court. Foot work is of the highest class. To Worcester folk Doctor Jennings' tennis is inseparable from his bicycle. There you can still observe a white-haired gentleman pedaling leisurely from his home to the tennis club, his racket before him, clamped to the bicycle handle.

Professor Jennings has, of course, all the usual affiliations. He is a fellow of the American Academy of Arts and Sciences and a member of innumerable learned societies. For many years he has been chairman, or member, of the Worcester Medical Milk Commission. He has been chairman of the Northeastern Section of the American Chemical Society; many times a councillor. His fraternal affiliations include the Bohemian, Cosmopolitan, Worcester Tennis, and Worcester Harvard clubs, also the Sigma Xi fraternity. During the war the Institute laboratories constituted one of the field stations in which research on government problems of chemical warfare was conducted. The most important contribution of Doctor Jennings was the preparation of cyanogen chloride by an improved method which he developed. In association with W. B. Scott, his report of this work appears in the *Journal of the American Chemical Society* in 1919. The statement, "Published by permission of the Director of Chemical Warfare Service," is but one clue to the intensive organic research which kept the "home fires" burning in Salisbury Laboratories, at any hour that you might choose to look.

It is the aim of the American Contemporaries series to sketch with fewest strokes, a series of human-interest pictures. Thus, even the younger men may see in more complete perspective a fellow-worker, whom their elders have been able to evaluate more gradually. Major characteristics indicate the mold and character; innumerable details reflect the personality, and give to the picture its distinctive name.

Above all, Doctor Jennings is a teacher. His best achievement is multiplied in the work of other men whom he has led. His students know that they will never meet one more sternly methodical, more penetrating, or more intolerant of evasion. One too will go far to meet a man who is more thoroughly the gentleman, more genuinely affable and entertaining. Even when a disciple of Professor Jennings attempts biography he must take care that the analysis is carried to complete qualitative and quantitative conclusion; also that the interpretation of results is correct. Yet here I pause, confident that, while corroborative analyses will be made, they will surely check with the present determination.

LEON V. QUIGLEY

BOOK REVIEWS

Bibliography of Organic Sulfur Compounds (1871-1929). By P. BORGSTROM, R. W. BOST, AND D. F. BROWN. 187 pages. American Petroleum Institute, 250 Park Ave., New York, 1930. Price, \$4.00.

This is a bibliography of organic sulfur compounds covering those "which may occur in petroleum products as well as their properties, uses, and methods of removal from petroleum products." It comprises 130 double-columned pages of references to the literature, and 30 double-columned pages of patent references. The literature references have been classified in 34 groups; some of these are rather short, some very long. In a few cases it is doubtful whether these group classifications are significant. For instance, it seems questionable to consider mercaptides separately from mercaptans, particularly since the former are covered by a few citations.

The basis for selection of articles has evidently been a broad one, and this is to be praised, since we have at present scant means of predicting what sulfur compounds may or may not occur in petroleum. While the work is strong from the academic side, it appears a trifle weak in covering the references to the more strictly technical and industrial studies. The section on the solvent action of liquid sulfur dioxide appears incomplete; there is no section on the doctor reaction, which has the beginnings of a respectable literature of its own; the papers of Wood, Lowy, and Faragher, and of Wendt and Diggs, which in 1924 first elucidated the chemistry of the doctor test, have apparently been omitted. The reviewer has noted in a brief search occasional other omissions of papers believed to be of marked interest to petroleum chemists. The impression is easily gained that the recent literature has been much better covered than that of earlier years; this is undoubtedly attributable to the change in the completeness of the abstract literature.

The classifying of papers in the different groups might occasionally be criticized. The group on mercaptans contains a fair amount of material which seems to belong in the general group. The cross references at the ends of the groups do not remedy this situation entirely. It is questionable whether space should have been devoted to laboratory directions for preparing compounds, as is done in some cases. The reader would almost certainly wish to look up an abstract or the original before undertaking a preparation.

The above criticisms are, after all, very minor ones; the reviewer feels that this bibliography will be of great value and that the compilers have performed an admirable service, not only for petroleum chemists, but for all organic chemists as well.—W. A. GRUSE

Industrial Microbiology. BY HENRY FIELD SMYTH AND WALTER LORD OBOLD. 1st edition. 313 pages. The Williams & Wilkins Company, Baltimore, Md., 1930.

The authors stress the need for guide to teachers and beginners in the investigation of microbiological processes applied to industry. For this purpose discussion of specific microorganisms and their application to a representative series of industrial problems has been brought together from the experience of the senior author's industrial practice and their joint graduate teaching. The reader is carefully warned that some of the applications of microbiology as described are protected by patents although their practices are already well known.

The material is arranged in 12 sections with chapters numbered 1-37. The section topics are as follows: I—General Introduction; II—The Production of Carboxylic Acids, Production of Alcohols and Ketones (alcohols, glycerine, and acetone); III—The Complex Nitrogenous Materials (glue, gelatine, leather, and tanning); IV—The Carbohydrate Materials (cellulose, wood, textile fibers, ensilage, xylose, and sucrose); V—The Fats and Oils; VI—Miscellaneous (fertilizers, garbage, gas production, sewage, etc.); VII—Microbial Thermogenesis; VIII—Microbial Food Preparation (vitamins, beverages, milk and cheese, meat, eggs, and refrigeration); IX—The Hydrocarbons (coal, petroleum, phenols, and rubber latex); X—Commercial Enzyme Production; XI—Biological Processes in Industry with Special Reference to the Application of Patent Laws; XII—Bacteriological Survey (tabulation of the names of organisms and the processes in which they are utilized).

The discussions of many of the topics are very brief, some of them giving the barest outline of present information and little guidance for further work. In the main, the purpose of guiding the student to the present literature and suggesting intelligent lines for further development is carried out. The bibliography of each topic is found at the end of the chapter and arranged in numerical order to text references. This is very convenient subject by subject, but failure to index these references by authors makes the references to particular workers inaccessible unless the subject matter is remembered.

To one familiar with only a few of the industrial projects which involve microorganisms, the wide range of topics included will open a surprising series of developments and possibilities. The book will therefore be useful to the teacher who wishes to cover more and more of the field, and serve as a reference book to present information and to the literature for the student who desires to go further in the fermentation field.—CHARLES THOM

A. S. T. M. Standards (Issued Triennially), 1930. Part I—Metals. 1000 pages. **Part II—Non-Metallic Materials.** 1214 pages. American Society for Testing Materials, Philadelphia, Pa., 1930. Parts I and II, each, cloth, \$7.50; half-leather, \$9.00; both parts, cloth, \$14.00; half-leather, \$17.00.

Of the 179 standards on metals published in Part I, 105 cover the ferrous metals, steel, cast iron, wrought iron, alloy steel, and ferro-alloys, and 67 relate to the nonferrous metals, nickel, copper, aluminum, etc., and many alloys, while 7 are of general interest.

The standards in Part I, assembled in a sequence determined by the specific materials or products to which they apply, cover steel rails and accessories; wheels and tires; structural and boiler steels; steel for welding; concrete reinforcement steel; bar steels; spring steel and springs; steel castings, chain, forgings, and axles; steel tubes and pipe; tool steel, steel for high-temperature service; zinc-coated wire and wire products; wrought-iron bars, castings, plates, and pipe; pig iron; cast iron and finished castings; malleable castings; and ferro-alloys.

The specifications in the nonferrous group cover ingot copper, zinc, lead, nickel, aluminum and aluminum alloys, copper wire and

cable, brasses and bronzes, solder metal, white metal-bearing alloys, copper and brass plates and tubes. Methods are also included for Brinell hardness tests, metallographic testing, preparation of micrographs for metals and alloys, and a recommended practice for radiographic testing of metal castings. Definitions of terms relating to wrought iron, to methods of testing, to metallography, and to specific gravity are also included. New standard specifications have been adopted this year for steel tie plates, iron and steel chain, gray-iron castings for valves, seamless copper tubing, and bronze and hard-drawn copper trolley wire, and several for galvanized wire and wire products and for zinc (hot-galvanized) coatings on structural steel shapes and plates. In addition to these specifications, there are new standard methods of sampling rolled and forged steel products for check analysis, test methods for galvanized wire and wire products, and a test for the change of resistance with temperature of electrical heating materials. Standard specifications for open-hearth steel rails, concrete reinforcement bars, steel pipe and boiler tubes, hot-rolled bar steels and cold-finished shafting, malleable castings and wrought iron bars, plates and pipe, that were revised during the year, have also been included.

The 251 standards in Part II cover the following miscellaneous groups of nonmetallic materials and products: cement; lime; gypsum; concrete and concrete aggregates; brick and refractories; pipe and drain tile; hollow building tile; paints; pigments; shellacs; varnishes; petroleum products and lubricants; bituminous and nonbituminous road materials; coal and coke; timber and timber preservatives; waterproofing and roofing materials; insulating materials and rubber products; textile materials; and thermometers for general use.

Included in this volume are new standards adopted this year comprising specifications for paving and building brick; sand-lime brick; wall, floor, and partition hollow clay tile; Keene's cement and gypsum plasters; gravel for bituminous concrete; several specifications for tar cements for road application; tolerances for cord tire fabrics and fabrics other than tire cord; methods of testing concrete aggregates; gypsum and gypsum products; analysis for color of paints; tests for sulfur in gasoline; melting point of petrolatum; test for autogenous ignition temperatures of petroleum products; mechanical analysis of coal; and test methods for electrical porcelain. The specifications for Portland cement, revised to include higher tensile strength requirements and the methods of testing cement changed by the inclusion of tolerances on weights and dimensions of apparatus, are also included. Of particular interest are the revised standard specifications for structural wood, joists and planks, beams and stringers, posts and timbers.—R. E. HESS

The United Kingdom. An Industrial, Commercial and Financial Handbook. BY HUGH BUTLER, American Trade Commissioner, and Officers of the Department of Commerce and States. 953 pages. Bureau of Foreign and Domestic Commerce, U. S. Department of Commerce, Washington, D. C., 1930. Price, \$1.75.

The chemical manufacturer, importer, and exporter should find this book of great interest and aid in the understanding of their competitors or markets. This publication is the first complete official analysis in one volume of the economic position of England, Scotland, Wales, and Northern Ireland.

According to the handbook, the United Kingdom is the second largest market for American chemicals, although it is also the third largest chemical producer. The chemical industry is well organized, in both the manufacturing and trading branches, through financial amalgamations and by means of associations, trade conventions, etc. Hundreds of separate manufacturing firms are included in the industry as a whole, but a large proportion of these firms have been amalgamated in a few large groups, the outstanding one of which is Imperial Chemical Industries, which controls the major part of the British production of alkalis, explosives, and heavy chemicals generally, has a leading share of the production of dyestuffs and nonferrous metals, and has many ramifications in other branches of the chemical and allied industries in Great Britain and throughout the world. Another large amalgamation is Lever Bros. (Ltd.), which controls most of the British production of soaps and glycerol and has a large interest in vegetable oils and oil products.

Practically all branches of the chemical industries cooperate closely through associations. The leading manufacturers' organization is the Association of British Chemical Manufacturers, affiliated with which are about a dozen smaller associations. Close relations are also maintained with other technical and commercial organizations. Price-fixing associations are common. Employees are well organized through trade unions and there are

in most branches corresponding employers federations to deal with questions of wages and employment.

Great Britain is a net exporter of chemical products, total exports in 1928 showing an increase of 24 per cent in the favorable balance of trade as compared with 1927 and 45 per cent as compared with 1913. British imports of chemical manufacturers in 1928 were about 15 per cent in value above those immediately before the war. Considerable amounts of imported chemicals are reexported.

The chapter on chemicals and allied products forms only a small portion of this tome but other chemical data are given in other chapters, especially that on Coal, Coke, and Petroleum.

The Microbiology of Starch and Sugars. By A. C. THAYSEN AND L. D. GALLOWAY. 336 pages. Oxford University Press, London, 1930. Price, \$8.50.

In the preface the authors state, "The volume has been written from the point of view of the research worker, and in addition to compiling existing knowledge it endeavors to point out paths which might be followed by workers who desire to extend their knowledge of the action of microorganisms on starch and sugar."

The book is divided into five parts dealing, respectively, with starch, glycogen, inulin, tetra-, tri-, and di-saccharides and glucosides, monoses, synthetic activities of microorganisms, the microbiology of cereals and cereal products, and the microbiology of the sugar industry. The parts are subdivided into appropriate chapters. Author and subject indexes are appended and literature citations are grouped at the end of each chapter. The bibliography is quite representative and fairly extensive.

The field laid out by the authors is wide and diversified and anyone acquainted with the subject realizes the tremendous amount of work involved in attempting to review the literature which has accumulated within the past quarter-century. The authors state that more than three thousand original papers were examined, and the thorough manner in which most of the subject matter is discussed testifies to their industry. The omissions noted were, for the most part, of minor importance.

This volume is quite timely, appearing as it does at a period when there is a widespread renewal of interest in fermentation processes from both the theoretical and practical viewpoints. It offers a summary of the evidence at hand concerning the mechanisms of various fermentations and points out the problems yet to be solved. It should prove to be one of the most valuable monographs available in English to the research worker entering the field of fermentation chemistry and a useful addition to the library of anyone interested in the activities of microorganisms.—O. E. MAY

The Engineer's Vest Pocket Book. By W. A. THOMAS. First edition. 151 pages. W. A. Thomas Co., 4554 Broadway, Chicago, Ill., 1930. Price, \$3.00.

This little book contains a wide variety of formulas, tables, and curves in compact form suitable for use as a finger-tip reference for the busy engineer. Data on the following divisions of engineering are included: mathematics, statics and dynamics, strength of materials, building construction, mechanical design, heat hydraulics, chemistry and physics, electrics, transportation, surveying, costs, and general information. A classified directory of the manufacturers, concerns, and individuals serving the engineering trade is appended.

Électrothermie appliquée. I—Les calculs électrothermiques—les pertes de chaleur dans les fours—le carbone en électrothermie—les électrodes en charbon et en graphite. By GEORGES FLUSIN. Published as a part of *Encyclopédie de chimie Industrielle*, edited by M. Matignon. 380 pages. J. B. Baillière et Fils, Paris, 1930. Price, bound, 85 fr.; paper, 70 fr.

This volume is a very peculiar arrangement of facts. The first chapter deals with the calculation and uses of heat values such as specific heat, heat of fusion, vaporization, transformation, formation, combination, reaction, etc. Chapter 2 takes up the formation of slags giving some phase diagrams and thermal values. Chapter 3 discusses the calculation of the charges for operation with or without slag formation; chapter 4, the input and output of an electric furnace expressed in energy terms; and chapter 5, heat losses in an electric furnace. In the second part of the volume, from page 135, there is a discussion of the forms of carbon both native and synthetic in four chapters covering 38 pages. Chapter 10 is given to a discussion of carbon electrodes, their

manufacture and uses, in 91 pages; then in chapter 11 is a discussion of graphite covering 100 pages.

It was rather astonishing to the reviewer to find a volume entitled "Applied Electrochemistry" giving a treatment of the elementary principles of thermochemistry, slags, and charge calculations, with the second part dealing entirely with the study of carbon as related to electric furnaces, not only as a tool but as a product. However, the reviewer believes from reading the advertising notes, and from the title of this volume that other volumes dealing with the remaining phases of electrochemistry and furnaces are to follow. Hence the peculiar combination of information included in the volume.

The work is very readable and the problems which are noted are well explained and discussed. Much information has been collected in the pages on carbon and graphite electrodes, and it has been well organized. It is a larger and more technical treatment of the subject than is given in Mantell's "Industrial Carbon." But one must remember that these two volumes are not meant for the same group of readers and so should not cover the same ground in the same manner.—C. J. BROCKMAN

Die Industrie des Kalziumkarbides—Monographien über angewandte Elektrochemie—Band LI. By RUDOLF TAUSSIG. 519 pages. 194 illustrations—22 plates. Wilhelm Knapp, Halle, 1930. Price, paper, 60 marks; bound, 64 marks.

In an industry which has developed as rapidly as carbide, the specialist has a wonderful field for presenting to the public an interesting picture, and Doctor Taussig certainly has made excellent use of such opportunity. His history of carbide production, while referring to the early American attempts and illustrating, by Patent Office drawings, certain of the peculiar early American furnaces, deals essentially with the early European developments.

The author has made wide search of technical literature on the theory of carbide production and the physical and chemical properties of the product, and has assembled in convenient and concise form practically all of the important literature.

That portion of the treatise devoted to the electric furnace is richly illustrated and admirably written, dealing only with the more modern and largest of the European carbide plants and their details. It is possible, through the photographs and dimensioned drawings, for the reader to familiarize himself thoroughly with the latest European practice in single-phase and multi-phase carbide furnaces. The latest development in carbide production abroad, the single-phase Miguet furnace, is treated at considerable length and with numerous excellent illustrations of the largest installation in Europe and some records of performance.

Manufacturers of auxiliary equipment, electrodes, regulators, and insulating material have been drawn upon freely for complete data on their products, many of which are arranged in tabular form for easy comparison.

An extensive chapter on the preparation of raw materials describes European equipment and goes into considerable detail on the behavior of the several materials available for carbide manufacture. The dust problem is touched upon, but some of the apparatus described has not been entirely successful in certain European installations, an experience which seems to have been omitted when discussing the equipment.

A very complete chapter on the chemical control of the carbide plant, both as to raw materials and finished products, describes not only the apparatus of the laboratory but the standard methods of analysis. From the technical standpoint the author devotes attention to the utilization of carbide and of acetylene.

The author has gone extensively into the commercial and economical side of the industry, an unusual procedure in a work of this nature. The development of the industry itself internally as to efficiencies and outputs, and externally as to marketing and earning capacity, is touched upon. The decreasing power consumption per unit of product and the more efficient utilization of raw materials and electrodes over the years are strikingly brought out in a number of tables.

The final chapter introduces the difficulties which the carbide industry experienced in its early days from overproduction and excessive price cutting, and the various attempts to build up a carbide syndicate in Europe which could exercise some control over the industry. The carbide developments of the various countries, with statistics of production, import, and export, have been assembled in concise form. Unfortunately very little space is given to American and Canadian developments in comparison with their importance, and Doctor Taussig has not taken the pains to check the accuracy of this American information.

The volume closes with a detailed history of the European carbide syndicates, the specifications of the German Acetylene Union for carbide, a bibliography of the German patents, and a

reference list of carbide literature. The pleasant impression of this interesting work, with its beautiful illustrations and drawings, is somewhat offset at the end of the book by almost a full page of typographical corrections to the text.

Nothing that has yet appeared on the carbide industry approaches to any degree the completeness of Doctor Taussig's work which has brought to us the practice of a surprisingly late date. Not only is the book recommended to the specialist in carbide, but its treatment of the complicated problems involved in the construction of transformers, connections, and electrodes for carrying very heavy currents should be of interest to everyone in the electric furnace field.—W. S. LANDIS

Enzyklopädie der technischen Chemie. By FRITZ ULLMANN. 2nd revised edition. Band VI—Gold bis Kühler. 844 pages. Urban & Schwarzenberg, Berlin, 1930. Price, paper, 45 marks; bound, 54 marks.

Volume VI of this valuable work is quite up to the standard of the first five volumes, all of which have been briefly reviewed in previous issues [IND. ENG. CHEM., 21, 393 (1929); 21, 89 (1929); 22, 200(1930); 22, 1024 (1930)]. The present volume includes quite valuable and complete treatises in German by well-known authors on such important subjects as wood and its products, indigo and indigoids, iodine and its compounds, coffee and cocoa, potassium and the potash industry, refrigeration, war gases, catalysis, rubber (by E. A. Hauser), cobalt and cobalt colors and compounds, carbon in its various forms, coke ovens, reducer gas, crystallization, and condensing apparatus. An index to this volume is again inserted separately, together with a table of contents showing the author of each subject treated. The work is a monumental one, well collated and well written, and in the reviewer's opinion should be on the shelves of all important reference libraries.—CHARLES L. PARSONS

Zement. Technische Fortschrittsberichte, Fortschritte der chemische Technologie in Einzeldarstellungen—Band XXV. By I. F. WECHE, translated by B. RASSOW. 96 pages. Theodor Steinkopff, Germany, 1930. Price, paper, 4.80 marks; bound, 6 marks.

This is one of a series of technical reports reviewing the progress and more recent developments in the field of applied chemistry. The purpose of this particular volume is to outline the evolution of cement and the development of the technology of its manufacture since the beginning of the twentieth century.

Following a short historical introduction, the general subject Portland cement is taken up. Under this subject are discussed the raw materials, preparation and calculation of the raw mixture, technology of manufacture, clinker cooling and constitution, admixtures, properties, testing and specifications, and methods of study of raw materials and cements. The greater portion of the book is occupied with the technology of manufacture of Portland cement and is illustrated with flow sheets, and diagrams and photographs of machines, kilns, and instruments necessary in the manufacture of cement. The remainder of the book deals with super cements, slag, alumina, and other special cements which are on the market today. The closing section contains a few statistics on production and costs.

All sections of the book, except possibly the one treating on the technology of manufacture, are too brief to do justice to the subjects discussed. Practically all references are to German developments, and most of the non-German references are to developments made prior to the war, so that in this respect the book is out of date. Very little attention is paid to the progress of the industry in other countries, so that at best one can only hope to obtain an idea of German methods and German theories.—L. T. BROWN MILLER

Jahresbericht VIII der chemisch-technischen Reichsanstalt. viii + 236 pages. Verlag Chemie, G. m. b. H., Berlin, 1930. Price, paper, 18 marks.

Biologists manifest great interest in the geographical distribution of plants and animals, most of which are restricted in their range by the major barriers—terrestrial organisms by the seas and marine forms by the continents. Few are the species of land creatures that have even an approximately world-wide distribution. One that has a range limited entirely to civilized countries is *Homo director*, a being characterized unmistakably by his confirmed habit of writing annual reports. These, to paraphrase Ovid, are "not all alike, nor yet unlike, but as annual

reports should be." They differ in details, but their general plan is the same whoever writes them.

The interest lies in the details, but no one reader of the present day can claim to be so multiscient that he fully appreciates all of the details of such an annual report as this "Jahresbericht." At most he will be able to realize that it deals with investigations on a variety of subjects, yet the variety is not so great as "chemisch-technisch" might lead him to expect, for 151 pages, or about five-eighths of the book, are given up to explosives, the combustibility of magnesium alloys, and closely related subjects. These are scattered throughout the book from the first page to the 226th. The 45-page chapter on metal chemistry and metal protection describes the institute's work on corrosion, methods of testing paints, metallographic investigations, and a few other items. This leaves but 34 pages for the discussion of cellulose and nitrocellulose, leather, printing ink for playing cards, miscellaneous testing, and participation in the preparation of specifications. On the whole the report is interesting, but from its nature is not readily susceptible of satisfactory condensation.—C. E. WATERS

Chemiker-Kalendar, 1931. Ein Hilfsbuch für Chemiker, Physiker, Mineralogen, Industrielle, Pharmazeuten, Hüttenmänner, u.s.w. Founded by RUDOLF BIEDERMANN, continued by W. A. ROTH, edited by I. KOPPEL. In three parts. I—Taschenbuch. II—Dichten, Löslichkeiten, Analyse. III—Theoretischer Teil. Julius Springer, Berlin, 1931. Price, 20 marks.

This well-known reference book is in its fifty-second year. The arrangement is much like that of former years: a small pocket book (Part I) containing a combined calendar and diary, a few pages of cross-section paper, and 103 pages of tables useful to the analytical chemist; and Parts II and III combined in one volume of 1322 pages, which, through the use of thinner paper, is not unduly bulky.

Part I has one new table for the reduction of gas volumes to normal. Part II has new sections on analytical chemistry; ceramics; the manufacture and analysis of glass; fats, waxes, gums, and bitumens; dyeing and textile finishing; rubber, gutta-percha, and balata. Part III (theoretical) has new sections on parachor; viscosity; catalysis in organic chemical technology; band and Raman spectra; the chemical industry of Italy; the chemical industry of Germany in comparison with that of the world.

In Part II articles on various subjects, such as air, foundations, mortar and cement, explosives, ethereal oils and perfumes, and paper, cellulose, and artificial silk, which appeared in earlier editions of this work, are not repeated, reference merely being made to the earlier edition in which the article appears.—F. C. ZEISBERG

Neuere Torfchemie. By G. STADNIKOFF. 167 pages. Theodor Steinkopff, Dresden and Leipzig, 1930. Price, 12 marks.

This book, though small, presents practically all of value that is known about peat today. Its contents are indicated by the following chapter headings: 1—Properties of the Moisture in Peat; 2—The Dehydration of Peat; 3—Properties of the Dry Residues; 4—The Bitumens in Peat; 5—The Humic Acids in Peat; 6—Peat Tar.

While Chapters 3 to 6 present concisely the subject matter to be expected under their headings, brought up to date with the discrimination of an experienced student in this field, yet it is more particularly Chapters 1 and 2, or the first half of the book, that appear to the reviewer to be specially valuable, because they present one of the greatest and most recent industrial triumphs of colloid chemistry—the solution of the problem of the economic dehydration of peat. In other words, the first seventy pages comprise a clear, comprehensive, modest recital of a great technical triumph destined to play a prominent part in the life of northern Europe.—E. P. SCHOCH

Glas—Seine Herstellung und Verwendung. By F. H. ZSCHACKE. Technische Fortschrittsberichte, Band XXIV. xiv + 220 pages, 23 figures. 15.5 × 22 cm. Theodor Steinkopff, Dresden and Leipzig, 1930. Price, paper, 72 marks; bound, 73.50 marks.

As stated in the introduction by F. Eckert, this is a comprehensive and uncritical summary of the literature appearing during and since the World War, dealing with both the scientific and the technical aspects of the manufacture and properties of glass.—GEORGE W. MOREY

MARKET REPORT—JANUARY, 1931

THESE PRICES, UNLESS OTHERWISE SPECIFIED, ARE THOSE PREVAILING IN THE NEW YORK MARKET, JANUARY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals							
Acetaldehyde, drums, 1c-1, wks.	18½	Glacial, c/l, bbls.	100 lbs.	9.23	Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Acetaldol, 50-gal. drums.27	Glacial, U. S. P., c/l, carboys	100 lbs.	9.73	Iron-free, bags, wks.	100 lbs.	1.90
Acetylene tetrachloride, <i>see</i> Tetrachloroethane		Acetylsalicylic, bbls.	lb.	.85	Aminoazobenzene, 100-lb. kegs.	lb.	1.15
Amyl furoate, 1-lb. tins.	5.00	Anthranilic, 99-100%, drums.	lb.	.85	Ammonia, anhydrous, cyl., wks.	lb.	.15½
Aroclors.40	Benzoic, tech., bbls.	lb.	.40	50,000-lb. tanks, wks.	lb.	.05625
Butyl carbitol, <i>see</i> Diethylene glycol monobutyl ether		Boric, bbls.	lb.	.06½	Ammonia, aqua, 26%, tanks, wks.	lb.	.05½
Cellosolve, <i>see</i> Ethylene glycol monobutyl ether		Butyric, 100% basis, cbys.	lb.	.80	Ammonium acetate, kegs.	lb.	.33
Furoate, tech., 50-gal. drums.50	Chloroacetic, mono-, bbls., wks. lb. Di-, cbys.	lb.	1.00	Bifluoride, bbls.	lb.	.21
Carbitol, <i>see</i> Diethylene glycol monoethyl ether		Tri-, bbls.	lb.	2.50	Bromide, 50-lb. boxes.	lb.	.43
Cellosolve, <i>see</i> Ethylene glycol monoethyl ether		Chlorosulfonic, drums, wks.	lb.	.04½	Carbonate, tech., casks.	lb.	.10½
Acetate, <i>see</i> Ethylene glycol monoethyl ether acetate		Chromic, 99%, drums.	lb.	15½	Chloride, gray, bbls.	100 lbs.	5.40
Crotonaldehyde, 50-gal. drums.32	Cinnamic, bottles.	lb.	3.25	Lump, casks.	lb.	.10½
Dichloroethyl ether, 50-gal. drums lb.	.06	Citric, U. S. P., kegs, bbls.	lb.	.40	Iodide, 25-lb. jars.	lb.	5.20
Diethylene glycol, drums.14	Cresylic, pale, drums.	gal.	.58	Nitrate, tech., cryst., bbls.	lb.	.08½
Monobutyl ether, drums.24	Formic, 90%, cbys., N. Y.	lb.	10½	Oxalate, kegs.	lb.	.22
Monoethyl ether, drums.15	Gallic, U. S. P., bbls.	lb.	.74	Persulfate, cases.	lb.	.26
Diethylene oxide, 50-gal. drums.50	Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40	Phosphate, dibasic, tech., bbls. lb.	lb.	11½
Dioxan, <i>see</i> Diethylene oxide		H, bbls., wks.	lb.	.65	Sulfate, bulk, wks.	100 lbs.	1.75
Diphenyl.30	Hydroiodic, 10%, U. S. P., 5-lb. bot.	lb.	.67	Thiocyanate, tech., kegs.	lb.	.36
Ethyl acetoacetate, 50-gal. drums.65	Hydrobromic, 48%, cbys., wks. lb.	lb.	.45	Amyl acetate, tech., drums.	lb.	.22
Carbonate, 90%, 50-gal. drums.	1.85	Hydrochloric, 20%, tanks, wks.	100 lbs.	1.35	Aniline oil, drums.	lb.	.15
Chlorocarbonate, carboys.30	Hydrofluoric, 30%, bbls., wks. lb.	lb.	.06	Anthracene, 80-85%, casks, wks. lb.	lb.	.60
Ether, absolute, 50-gal. drums.50	60%, bbls., wks.	lb.	.13	Anthraquinone, subl., bbls.	lb.	.60
Furoate, 1-lb. tins.	5.00	Hydrofluosilicic, 35%, bbls., wks.	lb.	.11	Antimony, metal.	lb.	.07½
Ethylene chlorhydrin, 40%, 10-gal. cbys.75	Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.85	Antimony chloride, drums.	lb.	.13
Dichloride, 50-gal. drums.05	Lactic, 22%, dark, bbls.	lb.	.04	Oxide, bbls.	lb.	.09½
Glycol, 50-gal. drums.25	48%, light, bbls., wks.	lb.	.11	Salt, dom., bbls.	lb.	.22
Monobutyl ether, drums, wks.24	Mixed, tanks, wks.	N unit	.07	Sulfide, crimson, bbls.	lb.	.25
Monoethyl ether, drums, wks.17	Molybdic, 85%, kegs.	lb.	1.25	Golden, bbls.	lb.	.16
Monoethyl ether acetate, drums, wks.19½	Naphthionic, tech., bbls.	lb.	nom.	Vermilion, bbls.	lb.	.38
Monomethyl ether, drums.21	Nitric, C. P., cbys.	lb.	.11	Tartrolactate, bbls.	lb.	.45
Oxide, cyl.	2.00	Nitric, 36%, c/l, cbys., wks.	100 lbs.	5.00	Argols, red powder, bbls.	lb.	.07½
Furfuramide (tech.), 100-lb. drums. lb.	.30	Oxalic, bbls., wks.	lb.	.11	Arsenic, metal, kegs.	lb.	.30
Furfuryl acetate, 1-lb. tins.	5.00	Phosphoric, 50%, U. S. P.	lb.	.14	Red, kegs, cases.	lb.	.09½
Alcohol, tech., 100-lb. drums.50	Picramic, bbls.	lb.	.65	White, c/l, kegs.	lb.	.04
Furoic acid (tech.), 100-lb. drums. lb.	.50	Picric, bbls., c/l.	lb.	.30	Asbestine, bulk, c/l.	ton	15.00
Isopropyl ether, drums.10	Pyrogallic.	lb.	1.50	Barium carbonate, bbls., bags, wks.	ton	58.00
Lead dithiofuroate, 100-lb. drums. lb.	1.00	Salicylic, tech., bbls.	lb.	.33	Chloride, bbls., wks.	ton	63.00
Magnesium peroxide, 100-lb. cs.	1.15	Stearic, d. p., bbls., c/l.	lb.	13½	Dioxide, drs., wks.	lb.	.12
Methyl acetate, drums.	1.20	Sulfanilic, 250-lb. bbls.	lb.	.15	Hydroxide, bbls.	lb.	.04½
Cellosolve, <i>see</i> Ethylene glycol monomethyl ether		Sulfuric, 66%, c/l, cbys., wks.	100 lbs.	1.60	Nitrate, casks.	lb.	.07½
Furoate, tech., 50-gal. drums.50	66% tanks, wks.	ton	15.00	Barium thiocyanate, 400-lb. bbls. lb.	lb.	.27
Paraldehyde, 110-55 gal. drums.20½	60% tanks, wks.	ton	10.50	Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Phosphorus oxychloride, 175 cyl.20	Oleum, 20%, tanks, wks.	ton	18.50	Benzaldehyde, tech., drums.	lb.	.60
Propyl furoate, 1-lb. tins.	5.00	40%, tanks, wks.	ton	42.00	F. F. C., cbys.	lb.	1.40
Strontium peroxide, 100-lb. drums. lb.	1.25	Sulfurous, U. S. P., 6%, cbys.	lb.	.05	U. S. P., cbys.	lb.	1.15
Sulfuryl chloride, 600-lb. drums, crude.10	Tannic, tech., bbls.	lb.	.23	Benzene, pure, tanks, mills.	gal.	.25
Distilled.35	Tartaric, U. S. P., cryst., bbls.	lb.	31½	Benzidine base, bbls.	lb.	.65
Tetrachloroethane, 50-gal. drums. lb.	.09	Tungstic, kegs.	lb.	1.40	Benzoyl chloride, cbys.	lb.	1.00
Trichloroethylene, 50-gal. drums. lb.	.10	Valeric, C. P., 10-lb. bot.	lb.	2.50	Benzyl acetate, F. F. C., bottles.	lb.	.75
Triethanolamine, 50-gal. drums.40	Alcohol, U. S. P., 190 proof, bbls.	gal.	2.62	Alcohol, 5-liter bot.	lb.	1.20
Vinyl chloride, 16-lb. cyl.	1.00	Amyl, Imp. drums.	gal.	1.75	Chloride, tech., drums.	lb.	.30
Zinc dithiofuroate, 100-lb. drums. lb.	1.00	Butyl, drums, c/l, wks.	lb.	15½	Beta-naphthol, bbls.	lb.	.22
Perborate, 100-lb. drums.	1.25	Cologne spirit, bbls.	gal.	2.69	Beta-naphthylamine, bbls.	lb.	.58
Peroxide, 100-lb. drums.	1.25	Denatured, No. 5, comp. denat., c/l, drums.	gal.	.39	Bismuth, metal, cases.	lb.	1.25
		No. 1, comp. denat., drums. gal.	gal.	.41	Bismuth, nitrate, 25-lb. jars.	lb.	1.25
		Isoamyl, drums.	gal.	4.00	Oxychloride, boxes.	lb.	2.95
		Isobutyl, ref., drums.	lb.	1.00	Subnitrate, U. S. P., 25-lb. jars. lb.	lb.	1.35
		Isopropyl, ref., drums.	gal.	.60	Blanc fixe, dry, bbls.	ton	70.00
		Propyl, ref., drums.	lb.	1.00	Bleaching powder, drums, wks.	100 lbs.	2.00
		Wood, <i>see</i> Methanol			Bone ash, kegs.	lb.	.06
		Alpha-naphthol, bbls.	lb.	.73	Bone black, bbls.	lb.	.08½
		Alpha-naphthylamine, bbls.	lb.	.32	Borax, bags.	lb.	.02½
		Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30	Bordeaux mixture, bbls.	lb.	11½
		Chrome, casks, wks.	100 lbs.	5.00	British gum, com., c/l.	100 lbs.	4.37
		Potash, lump, bbls., wks.	100 lbs.	3.35	Bromine, bot.	lb.	.45
		Soda, bbls., wks.	100 lbs.	3.45	Bromobenzene, drums.	lb.	.50
		Aluminum, metal, N. Y.	lb.	233	Bromoform, jars.	lb.	1.80
		Aluminum chloride, anhyd., commercial, wks., drums extra, c/l. lb.	lb.	.05	Butylacetate, drums, c/l.	lb.	.17
		Aluminum stearate, 100-lb. bbl.	lb.	.19	Cadmium bromide, 50-lb. jars.	lb.	1.40
					Cadmium metal, cases.	lb.	.70
					Cadmium sulfide, boxes.	lb.	.90
					Caffeine, U. S. P., 5-lb. cans.	lb.	2.40
					Calcium acetate, bags.	100 lbs.	2.00
					Arsenate, bbls.	lb.	.07
					Carbide, drums.	lb.	.05½
					Chloride, drums, wks.	ton	20.00
					Cyanide, 100-lb. drums.	lb.	.30
					Lactate, U. S. P., bbls.	lb.	.37

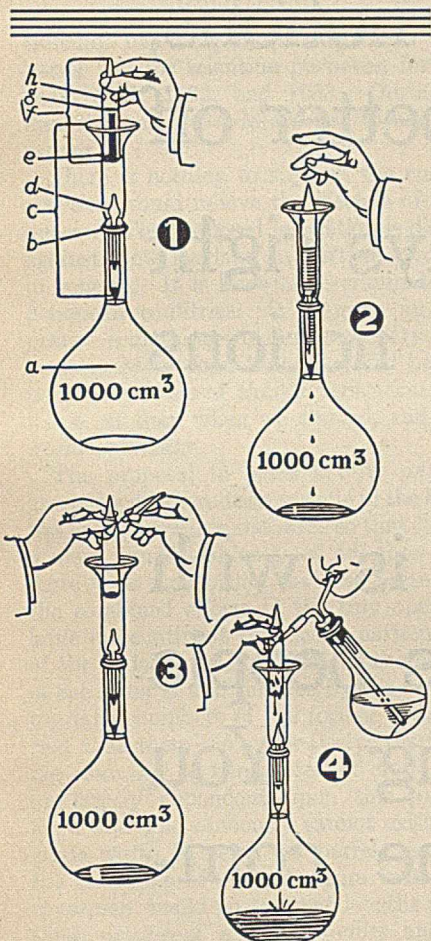
Chemicals Previously Quoted

Acetanilide, U. S. P. pow., bbls.	lb.	.24
Acetic anhydride, 92-95%, cbys.	lb.	.21
Acetone, C. P., drums, wks.	lb.	.10
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l, bbls.	100 lbs.	2.60
56%, c/l, bbls.	100 lbs.	4.85

Nitrate, bbls..... ton	40.00	Kieselguhr, bags..... ton	60.00	Platinum, metal..... oz.	36.00
Phosphate, monobas., bbls.... lb.	.08	Lead, metal..... 100 lbs.	4.75	Potash, caustic, drums..... lb.	.06½
Tribas., bbls..... lb.	.11	Lead acetate, bbls., white..... lb.	.12	Potassium acetate, kegs..... lb.	.28
Calcium carbonate, tech., bgs,100 lbs.	1.00	Arsenate, bbls..... lb.	.13	Bicarbonate, casks..... lb.	.09½
U. S. P., precip., 175-lb. bbl..... lb.	.06½	Oxide, litharge, bbls..... lb.	.08½	Bichromate, casks..... lb.	.09
Camphor, Jap., cases..... lb.	.55	Peroxide, drums..... lb.	.20	Binoxalate, bbls..... lb.	.14
Camphor, monobrom., cs..... lb.	1.85	Red, bbls..... lb.	.103	Bromate, cs..... lb.	.35
Caramel, bbls..... gal.	.63	Sulfate, bbls..... lb.	.06½	Carbonate, 80-85%, calc., casks lb.	.05½
Carbazole, bbls..... lb.	.75	White, basic carb., bbls..... lb.	.07½	Chlorate, kegs..... lb.	.08
Carbon, activated, drums..... lb.	.08	Lime, hydrated, bbls..... 100 lbs.	.85	Chloride..... ton	34.55
Carbon bisulfide, drums..... lb.	.05½	Lime, live, chemical, bbls., wks. 100 lbs.	1.05	Cyanide, cases..... lb.	.55
Carbon black, cases..... lb.	.12	Limestone, ground, bags, wks.... ton	4.50	Meta-bisulfite, bbls..... lb.	.11
Carbon dioxide, liq. cyl..... lb.	.06	Lithium carbonate, 100-lb. kgs.... lb.	1.35	Permanganate, drums..... lb.	.16
Carbon tetrachloride, drums..... lb.	.06½	Lithopone, bbls..... lb.	.04½	Prussiate, red, casks..... lb.	.38
Casein, stand. gr., bbls..... lb.	.09½	Magnesite, crude..... ton	36.00	Yellow, casks..... lb.	.18½
Cellulose acetate, bbls..... lb.	.80	Calcined, 500-lb. bbls., wks.... ton	50.00	Titanium oxalate, bbls..... lb.	.21
Cerium oxalate, kegs..... lb.	.32	Magnesium, metal sticks, wks.... lb.	.85	Pyridine, drums..... gal.	1.50
Charcoal, willow, powd., bbls.... lb.	.06	Magnesium carbonate, bags..... lb.	.06	Quinine bisulfate, 100 oz..... oz.	.40
China clay, bulk..... ton	8.00	Chloride, drums..... ton	36.00	Sulfate, 100-oz. cans..... oz.	.40
Chloral hydrate, drums..... lb.	.70	Fluosilicate, cryst., bbls..... lb.	.10	Resorcinol, tech., kegs..... lb.	.90
Chloramine, U. S. P., 5-lb. bot.... lb.	1.50	Oxide, U. S. P., light, bbls..... lb.	.42	Rochelle salt, bbls., U. S. P..... lb.	.19
Chlorine, liq., c/l, cyl..... lb.	.04	Manganese chloride, casks..... lb.	.07½	R salt, bbls..... lb.	.42
Chlorobenzene, mono-, drums..... lb.	.10	Dioxide, 80%, bbls..... ton	80.00	Saccharin, cans..... lb.	1.70
Chloroform, tech., drums..... lb.	.15	Sulfate, casks..... lb.	.07	Salt cake, bulk..... ton	18.00
Chromium acetate, 20° soln., bbls lb.	.05	Mercury bichloride, cryst., 25 lbs. lb.	1.63	Salt peter, gran., bbls..... lb.	.06½
Coal tar, bbls., wks..... gal.	.10	Mercury, flasks, 75 lbs..... flask	106.00	Silica, ref., bags..... ton	22.00
Cobalt, metal, kegs..... lb.	2.50	Meta-nitroaniline, bbls..... lb.	.67	Silver nitrate, 16-oz. bot..... oz.	.24½
Cobalt oxide, bbls..... lb.	2.10	Meta-phenylenediamine, bbls..... lb.	.80	Soda ash, 58%, light, bags, con- tract, wks..... 100 lbs.	1.15
Cod-liver oil, bbls..... bbl.	30.00	Meta-toluylenediamine, bbls..... lb.	.67	Soda, caustic, 76%, solid, drums, contract, wks..... 100 lbs.	2.15
Collodion, drums..... lb.	.15	Methanol, pure, synthetic, drums, wks..... gal.	.42	Sodium acetate, bbls..... lb.	.04½
Copperas, c/l, bulk..... ton	13.00	Tanks, wks..... gal.	.40	Benzoate, bbls..... lb.	.42
Copper, metal, elec..... 100 lbs.	10.00	Methyl acetone, drums..... gal.	.57	Bicarbonate, bbls..... 100 lbs.	2.00
Copper carbonate, bbls..... lb.	.08½	Salicylate, cases..... lb.	.42	Bichromate, casks..... lb.	.07
Chloride, bbls..... lb.	.22	Methyl chloride, cylinders..... lb.	.45	Bisulfite, bbls..... lb.	.04
Cyanide, drums..... lb.	.41	Michler's ketone, bbls..... lb.	3.00	Bromide, bbls., U. S. P..... lb.	.37
Oxide, red, bbls..... lb.	.15½	Naphtha, solvent, tanks..... gal.	.35	Chlorate, kegs..... lb.	.05½
Sulfate, c/l, bbls..... 100 lbs.	4.00	Naphthalene, flake, bbls..... lb.	.04½	Chloride, bags..... ton	12.00
Cotton, soluble, bbls..... lb.	.40	Nickel, metal..... lb.	.35	Cyanide, cases..... lb.	.15½
Cream tartar, bbls..... lb.	.24½	Nickel salt, single, bbls..... lb.	.10½	Fluoride, bbls..... lb.	.08
Cyanamide, bulk, N. Y. Nitrogen unit	1.39	Double, bbls..... lb.	.10½	Metallic, drums, 12¼-lb. bricks lb.	.19½
Diaminophenol, kegs..... lb.	3.80	Niter cake, bulk..... ton	12.00 lb.	52
Dianisidine, bbls..... lb.	2.35	Nitrobenzene, drums..... lb.	.09	Naphthionate, bbls..... lb.	.07
Dibutylphthalate, drums, wks.... lb.	.24½	Oil, castor, No. 1..... lb.	.11½ 100 lbs.	2.05
Diethylaniline, drums..... lb.	.55	China wood, bbls..... lb.	.08	Nitrite, bbls..... lb.	.07½
Diethylene glycol, drums..... lb.	.14	Coconut, Ceylon, tanks..... lb.	.04½	Perborate, bbls..... lb.	.18
Diethyl phthalate, drums..... lb.	.23	Cod, N. F., tanks..... gal.	.44	Peroxide, cases..... lb.	.21
Diethyl sulfate, tech., drums..... lb.	.30	Corn, crude, tanks, mills..... lb.	.07½	Phosphate, trisodium..... 100 lbs.	3.40
Dimethylaniline, drums..... lb.	.26	Cottonseed, crude, tanks..... lb.	.05½	Picramate, kegs..... lb.	.69
Dimethylsulfate, drums..... lb.	.45	Lard, edible, bbls..... lb.	.13	Prussiate, bbls..... lb.	.11½
Dinitrobenzene, drums..... lb.	.15½	Linseed, bbls..... lb.	.094	Silicate, drums, tanks, 40° 100 lbs.	.75
Dinitrochlorobenzene, bbls..... lb.	.13	Menhaden, crude, tanks..... gal.	.22	Silicofluoride, bbls..... lb.	.04
Dinitronaphthalene, bbls..... lb.	.34	Neat's-foot, pure, bbls..... lb.	.11½	Stannate, drums..... lb.	.21
Dinitrophenol, bbls..... lb.	.29	Oleo, No. 1, bbls..... lb.	.08½	Sulfate, anhyd., bbls..... lb.	.02
Diphenylamine, bbls..... lb.	.37	Olive oil, denat., bbls..... gal.	.70	Sulfide, cryst., bbls..... lb.	.02½
Diphenylguanidine, bbls..... lb.	.30	Foods, bbls..... lb.	.06½	Solid, 60 %..... lb.	.03½
Epsom salt, tech., bbls., c/l, N. Y. 100 lbs.	1.70	Palm, Lagos, casks..... lb.	.05½	Sulfocyanide, bbls..... lb.	.28
Ether, nitrous, bot..... lb.	.80	Peanut, crude, bbls..... lb.	.10	Thiosulfate, reg., cryst., bbls. lb.	.02½
Ether, U. S. P., drums..... lb.	.13	Perilla, bbls..... lb.	.07	Tungstate, kegs..... lb.	.81
Ethyl acetate, drums, c/l..... lb.	.098	Rapeseed, bbls., English..... gal.	.74	Strontium carbonate, tech., bbls. lb.	.07½
Bromide, drums..... lb.	.50	Red, bbls..... lb.	.08½	Nitrate, bbls..... lb.	.09
Chloride, drums..... lb.	.22	Soy bean, crude, bbls..... lb.	.07	Strychnine alkaloid, 100 oz., powder..... oz.	.56
Methyl ketone, drums..... lb.	.30	Sperm, 38°, bbls..... gal.	.84	Sulfate, powder..... oz.	.46
Ethylbenzylamine, 300-lb. drums lb.	.88	Whale, bbls., natural, winter gal.	.72	Sulfur, bulk, mines, wks..... ton	18.00
Ethylene dichloride..... lb.	.05	Ortho-aminophenol, kegs..... lb.	2.15	Sulfur chloride, red, drums..... lb.	.05
Chlorohydrin, anhyd., drums. lb.	.75	Ortho-anisidine, drums..... lb.	2.50	Yellow, drums..... lb.	.03½
Glycol, c/l, wks..... lb.	.25	Ortho-dichlorobenzene, drums..... lb.	.08	Sulfur dioxide, commercial, cyl.... lb.	.07
Feldspar, bulk..... ton	15.00	Ortho-nitrochlorobenzene, drums lb.	.28	Sulfuryl chloride, drums..... lb.	.10
Ferric chloride, tech., bbls..... lb.	.05	Ortho-nitrophenol, bbls..... lb.	.85	Thiocarbamilid, bbls..... lb.	26½
Ferrous chloride, cryst., bbls.... lb.	.06	Ortho-nitrotoluene, drums..... lb.	.16	Tin, Amer., stand..... lb.	.18½
Ferrous sulfide, bbls..... 100 lbs.	2.50	Ortho-toluidine, bbls..... lb.	.27	Tin tetrachloride, bbls..... lb.	.14½
Fluorspar, 98%, bags..... ton	41.00	Palladium, metal..... oz.	22.00	Oxide, bbls..... lb.	.25½
Formaldehyde, bbls..... lb.	.06	Para-aminophenol, kegs..... lb.	.84	Titanium dioxide, bbls., wks.... ton	21
Formaniline, drums..... lb.	.37½	Para-dichlorobenzene..... lb.	.17	Toluene, tanks..... gal.	.29
Fuller's earth, bags, c/l, mines. ton	15.00	Para-formaldehyde, cases..... lb.	.38	Tribromophenol, cases..... lb.	1.10
Furfural, drums, tech., contract, works..... lb.	.10	Paraldehyde, tech., drums..... lb.	.20½	Triphenylguanidine, drums..... lb.	.58
Glauber's salt, bbls..... 100 lbs.	1.00	Para-nitroaniline, drums..... lb.	.48	Triphenyl phosphate, bbls..... lb.	.60
Glucose, 70°, bags, dry..... 100 lbs.	3.14	Para-nitrochlorobenzene, drums lb.	.25	Tungsten..... Wo unit	15.50
Glycerine, C. P., drums..... lb.	.14	Para-nitrophenol, bbls..... lb.	.45	Urea, pure, cases..... lb.	.15
G salt, bbls..... lb.	.42	Para-nitrophenol, bbls..... lb.	.92	Whiting, bags..... 100 lbs.	1.00
Hexamethylenetetramine, tech., drums..... lb.	.46	Para-nitrotoluene, bbls..... lb.	.29	Xylene, 10°, tanks, wks..... gal.	.28
Hydrogen peroxide, 25 vol., bbls. lb.	.05½	Para-phenylenediamine, bbls..... lb.	1.15	Xylidine, drums..... lb.	.36
Hydroquinone, kegs..... lb.	1.20	Para-toluidine, bbls..... lb.	.44	Zinc, metal, N. Y..... 100 lbs.	4.35
Indigo, 20%, paste, bbls..... lb.	.12	Paris Green, 250-lb. kegs..... lb.	.25	Zinc ammonium chloride, bbls. lb.	.05½
Iodine, crude, 200-lb. kgs..... lb.	4.20	Phenol, drums..... lb.	.14½	Chloride, granulated, drums. lb.	.06½
Iodine, resub., jars..... lb.	4.65	Phenolphthalein, drums..... lb.	1.10	Oxide, Amer., bbls..... lb.	.06½
Iodoform, bot..... lb.	6.00	Phenylethyl alcohol, 1-lb. bot.... lb.	7.00	Stearate, bbls..... lb.	.20
Iridium, metal..... oz.	280.00	Phosphorus, red, cases..... lb.	.42	Zinc dust, bbls., c/l..... lb.	.06
		Phosphorus trichloride, cyl..... lb.	.35		
		Phthalic anhydride, bbls..... lb.	.15		

Accurate Volumetric Solutions

without those tiresome preliminaries



- a Measuring Flask
b Rubber Ring
c Breaking Funnel
d Point for Piercing
e Lower Cavity (after breaking, contents run through this)
f Tube with Fixanal substance
g Contents of Tube (solid or liquid)
h Upper Cavity of Tube (for washing out)

DIRECTIONS

- (1) Place funnel in volumetric flask
- (2) Slide one breaking thorn into funnel
- (3) Slide capsule into funnel. Thorn punctures capsule and contents fall into volumetric flask
- (4) Pierce side of capsule at indented point, using second thorn. Then—fill volumetric flask to 1000cc mark with distilled water.

WHO wants preliminaries, when the main bout can be staged at once? And who wants to spend 2 to 5 hours preparing his own volumetric solution, when he can have it in just 5 minutes?

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