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Industry, the Educator

IN HIS discussion before the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY, R. E. Rose made a point generally overlooked and worthy of much emphasis. Too many consider industries to be organizations whose sole thought is to get as much as possible and give the minimum in exchange. Industries are admittedly neither philanthropic nor eleemosynary institutions, but they do act as great educational forces and afford thousands who have never entered colleges, and still other thousands unable to complete their high school education, an opportunity to learn by trial and error, to equip themselves for advancement, and to enjoy a useful and successful maturity. During this educational period—and, for that matter, there is no end to education in industry—the mistakes are paid for by the employer. Many employees go through long periods of unproductiveness, and frequently, even after a considerable investment in an employee, the employer loses him through unavoidable causes. Industry even cares for the physical well-being of the employee, frequently provides healthful recreation, and stands between him and his material wants.

These observations apply to the chemist who enters industry in whatever capacity, much as they do to employees of other classifications. If the foundation of his work has been carefully laid, if, in addition to his science, he has acquired some acquaintance with psychology, with economics, and has mastered the art of getting on well with his fellows—all the way from the common laborer to the president of the corporation—then he not only finds his place with less difficulty, but makes the most of the educational opportunities offered by his employment, continues his education with greater ease and profit, and makes progress that encourages him to still greater efforts.

Experience serves to emphasize the weak spots in one's training, but fortunately today there are many opportunities for making up such deficiencies, not the least of which are the meetings of the AMERICAN CHEMICAL SOCIETY and its publications. Industry is helpful in this direction also. In some plants the senior men occasionally meet groups and discuss problems in a manner that amounts to advanced instruction. It is not unique to find men given leave or actually sent elsewhere for intensive study in a particular specialty. Such a practice with carefully chosen men is not only commendable, but is one measure of the foresight of an industry.

Will You Be There?

WHEN the International Conference on Bituminous Coal was about to open its sessions in Pittsburgh last year, the general manager of one of the great local coal companies issued orders to his staff that they were not to absent themselves from their customary places in order to attend this Conference, for he was convinced that they would earn more for the concern by sticking to their jobs. Several hundred men felt so keenly the value offered by the Conference that they came many miles to attend. The man in Pittsburgh who underrated the opportunity at his door either had a staff who, on other occasions, had demonstrated their inability to observe and absorb, or else he will some day find himself surpassed by those who make the most of each opportunity for advancement.

We habitually urge attendance at local section, regional, and semiannual meetings of the AMERICAN CHEMICAL SOCIETY as well as those of other scientific groups. There is no substitute. The best of the papers are published. Sometimes it is possible to include the discussion, but the papers, as is well known, do not form the most valuable part of a meeting. The gatherings in the lobbies and corridors are often more important than the sessions in the halls.

The Chemical Exposition is another meeting place, different in character and therefore valuable. At our meetings we stress what the science is doing, what it hopes to do, and try to look around the corner. At the Exposition, tangible results of the application of the science are offered for examination, comparison, and inquiry.

Do not be deceived. You cannot afford to lose contact with your colleagues. You may think you can do better for yourself, your employer, or your science by habitually staying at your desk or in your plant. The immediate return may sometimes seem to prove this. But, by and by, if you insist upon staying in your niche, you become encysted and the procession of progress will stream by before you know it and without noticing you.

Our Foreign Trade

WHILE the chemical industries of other lands continue to address their attention to combines, cartels, and international agreements, some of which are strongly opposed by the domestic shareholders of the companies concerned, the United States foreign trade has enjoyed a general increase. Commerce Reports of the Department of Commerce is the authority for the statement that the United States exports of chemicals and allied products attained the high figure of $97,188,000 during the first six months of 1927—15 per cent more than the first six months of 1926. The imports of $103,936,000, although higher than in some of the preceding years, were 11 per cent below those of the corresponding period a year ago. The imports, as in other periods, were largely made up of crude and partially manufactured products not indigenous to this country and used as raw materials in the American chemical industry. In consequence, they are always large. The difference between our exports of finished products and the imports, so large a portion of which were raw materials, is therefore smaller than previously. The improvement in exports was general, increases being recorded especially in industrial chemicals, pigments, paints, and crude coal-tar products. Fertilizers, medicinals, and toilet preparations were at their previous volume.

Since chemical manufacture outside the specialty groups is peculiarly well adapted to quantity production, export trade is of greatest importance in providing outlets for domestic surpluses. Our home market will always be our best market, but if manufacturers are to attain those low costs of production which give them a favorable place, both at home and abroad, quantities must be manufactured, and a satisfactory export trade is quite often the difference between low cost quantity production and smaller outputs at considerably higher prices. In all instances, therefore, the condition of our export trade is a matter of real moment, and our manufacturers are to be congratulated upon its healthy growth.

Junk

NOTWITHSTANDING the financial success of many junk dealers, it is only recently that the more successful in metals have been designated "secondary metal" men. The change in title is one indication of our growing appreciation of the importance of recovering and preparing for reuse many of the metals which are becoming more scarce, and some of which would be in the famine stage but for such reworking.

Metals from secondary sources in 1926 had a value of $274,540,900—nearly $31,000,000 more than in 1925—and this does not cover all metals of the group. Copper, brass, lead, and antimony showed the greatest increases, the smelters that treat mainly ore recovering 112,559 pounds of copper from scrap. Secondary smelters increased the recovery of lead 15,000 tons over 1925, much of this increase being traced to battery plates from motor cars. The largest increase in the recovery of zinc was from scrap alloys, while secondary tin increased 2400 tons, owing to the large quantities of old cans and tin-plate clippings processed. The old cans treated increased more than 10,700 long tons, most of them being handled by a new plant at Los Angeles.

The growth of the secondary metal business is one indication of conservation, though increase in the turnover of metals would naturally follow the phenomenal industrial growth of the last few years. Even the ability to rework many of the metals and their alloys does not excuse us from choosing the metals best suited for a particular purpose, nor does it justify the continued, though but occasional, use of some important metals in a form which makes their recovery impossible.

Delaware, We Apologize

ON OUR editorial page last month, we expressed gratitude to the Virginia Section for its contribution to the Endowment Fund. We erroneously stated that the second to contribute from a balance after a national meeting was the South Jersey Section. Our memory simply played us a trick. Reference to records shows that it was not the South Jersey but the Delaware Section which is entitled to this honor. The first to call our attention to this mistake was not a member of the Delaware Section. We are glad to make suitable correction in this prominent place.

The Frasch Bequest

IT SEEMS a long time ago that we were able to announce that Mrs. Elizabeth Blee Frasch, widow of Herman Frasch, had left a considerable sum of money, the income from which was to be used in chemical research related to agriculture, the trustees to profit by such advice as the AMERICAN CHEMICAL SOCIETY might give. Since then efforts have been made by relatives to set aside the will, asserting that the terms of the gift were too indefinite to be upheld by the court as a charitable bequest. The case has now been argued in two courts and in each instance the will has been upheld.

In contesting the bequest it was urged that the income might be used for private research which would deprive the gift of its charitable purposes, but the court pointed out that

> Research is the method used by modern universities and scientific foundations to increase the sum of human knowledge. Research conducted for such purpose and by such institutions is clearly "educational" and "benevolent" within the meaning of the statute. Not every charitable, educational or benevolent use is enumerated in the Statute of Elizabeth, although that statute was intended to limit the trusts for charitable uses, which might be enforced by a court of equity. Conceptions of public charity, benevolence and education change with passing generations.

It is doubtful whether an appeal will be taken by the plaintiff but, if so, the opinions already given will, we believe, be upheld, and in due course the SOCIETY may be called upon to give its best advice to the trustees of the fund. The soundness and wisdom of such counsel will go a long way toward demonstrating the capacity of the AMERICAN CHEMICAL SOCIETY to administer and to assist in administering substantial sums in the interest of scientific progress.

The Look Ahead

THE lay and technical press has given much space to the action of the Standard Oil Company in acquiring the American rights to the Bergius process for the production of motor fuels from coal. Details of this process were given in our News Edition last autumn, and need not be repeated here. The thing that interests us most is the long look ahead taken at a time when there is a flood of petroleum.

Comments on the predictions relative to the supply of petroleum have been made pointing out that, as the time for the fulfilment of prophecies has come around, in each case more petroleum is being produced than ever before. We all recognize that petroleum is not an inexhaustible natural resource, but our actions belie our thoughts, and we go along as if we had no thought of the morrow. But here is a great corporation, famous the world over, prosperous beyond the dreams of avarice, and yet taking steps designed to insure keeping in the oil business when liquid fuel from coal rather than from petroleum will command the markets of the world. How different from the attitude of another American industry which has sought to justify itself for lack of foresight with the argument that the synthetic processes are so totally different from those employed in their established plants that they could not be expected to undertake them!

So much for the future, but what of the present? Much has been justly said of wasteful America, and while some maintain that our lack of knowledge of tomorrow's needs justifies us in making the most of such raw materials as satisfy us today, nevertheless a temporary abundance never justifies waste. The excessive production of crude oil in the present year can scarcely fail to bring us impoverishment in this natural resource years sooner than otherwise would have been the case. Here and there a prophet has been crying in the wilderness, boards have considered solemn reports, better methods of coöperative drilling have been advocated, but little has been done. Just why producers cannot appreciate the wisdom of acting in concert to make the supplies underground last as long as possible and meet the demands for gasoline by the more strict and universal applications of our scientific knowledge is difficult to understand.

There have been warnings that the only way to prevent government interference and to postpone the day of federal control is for the industry to control itself, and yet such self-control takes place with geological slowness. It does not require very great foresight to anticipate the steps that may be taken if oil producers and refiners fail to put into practice the knowledge that true conservation means the most efficient use of natural resources. That means applying science to the full.

Our Crying Need

IT IS difficult for those who depend upon *Chemical Abstracts* as the key to the world's chemistry to appreciate the problems which confront the SOCIETY with respect to that preëminent publication, without causing some to reach conclusions that would be unjustified. Baldly stated, *Chemical Abstracts* remains the best journal in its field, but unless further finances can be found for its development and maintenance it cannot hold that enviable position for long.

From time to time there have been small differences of opinion concerning the activities of our SOCIETY, but we have never heard anything but praise and constructive criticism of *Chemical Abstracts*. There are no two ways about it. The SOCIETY is proud of that publication, and any move to do otherwise than strengthen it would bring the wrath of thousands down upon the heads of the offenders. While we chemists and our allies have multiplied our efforts, bringing to conclusion thousands of investigations which merit publication, the money with which to prepare and publish the abstracts of such papers printed throughout the world has scarcely increased in arithmetical proportion, whereas the task confronting the editors and abstractors has gone along in a geometrical ratio.

If you will take the trouble to compare the abstracts of today with those of several years ago, you will realize the large number of clever devices that have been evolved and put into practice to the end that more information might constantly be packed into the too brief paragraphs. The limit of economy has been reached in this direction. You will also note that to conserve space a change has been made in the style of printing, which fortunately is unobjectionable because one does not read page after page of abstracts at one sitting. If you complain to the editor that certain German and French patent information is not included, or if you think the abstract not sufficiently informative, or if you go to him with suggestions for "analytical abstracts," or any one of a number of other useful ideas, you will find him most receptive and will come away convinced that but one thing stands between our present effort and perfection. That is money. The policy has always been to make abstracts complete. The ideal is so to record the world's literature that, having exhausted the information in *Chemical Abstracts*, one may be sure he has covered the literature in his field. This is a commendable policy, but we realize that in view of the limited funds, tomorrow or the day after a decision must be reached as to whether this can be continued.

We would not have you jump to the conclusion that the SOCIETY has been niggardly in its treatment of *Chemical Abstracts*, for such is far from the truth. We continue to spend much more upon this activity than any other publication, as an examination of the Treasurer's report clearly shows. The sum is undoubtedly much greater than that spent for any other abstract journal in the world, and it is greatly to the credit of chemists that it has all been possible through their own efforts, for aid has come only in a few special cases as, for example, in the printing of the Decennial Indexes.

The editor of *Chemical Abstracts* estimates that with the present growth of the world's chemical literature, there should be a steady annual increase of five per cent in *Chemical Abstracts*, but a mere five per cent increase in the present budget, even if our Directors were able to vote it, would not suffice. In true American fashion we want bigger and better abstracts. We know how to do the job, but we must have help in financing it.

Having had a little experience in approaching industry for financial support of worthy enterprises, our sympathy lies wholly with the corporations. They are beset by thousands of solicitors for funds, in most cases for worthy purposes. They are called upon to subscribe generously, not only for local and domestic enterprises but for projects in other lands, where America is looked upon as an inexhaustible source of money. And many are the theories evolved to justify appeals for funds today in other lands for things we would not attempt at home. But, like other pleaders for a special cause, we believe ours merits special consideration because it offers an opportunity, not for donations nor for subscriptions, but for investments easily justified to stockholders and leading to actual profits through economies.

Whatever its line of activity, how great a sum would an individual firm have to spend to secure for itself the surveys which *Chemical Abstracts* offers? One needs but run through the list of publications abstracted, selecting those that would have to be examined, to find that the subscription prices alone would amount to three figures. Now add the time of translators and abstractors and the cost of distributing the resulting information to the works, and we begin to see what *Chemical Abstracts* means to industry, educational institutions, and independent investigators. Through united efforts and the enormous amount of underpaid and gratuitous work given to *Chemical Abstracts*, this service is made available to members of the SOCIETY and others at a ridiculously low rate. Foundations established for advancement of public welfare and science are equally indebted with corporations.

Many look with greater favor upon annual payments for the maintenance of such service than endowment for the general use of the SOCIETY, and there are no legal obstacles in the way of such annual payments. Not less than fifty thousand dollars per year should be secured in this fashion. It is a pitifully small sum when the returns are considered, or perhaps you would prefer to say is a modest investment, the possible returns upon which are incalculable.

The need is really urgent. What are you going to do about it?

Analysis within the Law

AS A result of discussions published in the *Nucleus*, inquiries have reached us concerning the legal status of the analyst who is asked to turn his attention to a sample of alcohol brought to him in the course of his daily practice. Although many laboratories derive a large proportion of their business from this class of work, it seems strange that only a few have wondered what their legal status might be. We have made inquiry and are authoritatively informed that the legal status of the analyst is the same as that of his client: If the client legally possesses the material offered for analysis, the analyst is within the law in performing the work; on the other hand, if the owner has no permit or does not legally possess the material containing alcohol, the analyst is outside the law, not only in performing the work but in having the material in his possession. Although the analyst is without power to demand the permit, it is in his own interest to ascertain whether he is within the law.

Elimination and Recovery of Phenols from Coke-Plant Ammonia Liquors[1]

By Robert M. Crawford

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In previous articles[2] the writer has described a successful method for eliminating phenols from ammonia still wastes by the continuous, countercurrent extraction of the raw liquor with benzene—or, more properly, motor fuel—in a process wherein the phenols removed from the liquor are recovered as a salable by-product in the form of crude tar acids. The purpose of this article is to describe a further substantial improvement in the process wherein a less costly and more efficient solvent, readily available at any coke plant, can be utilized and additional salable crude tar acids can be incidentally recovered.

Motor fuel is so easily available at any coke plant having light-oil and benzene equipment, that its use as a solvent for extracting the ammonia liquor is logical. Owing, however, to the relatively high vapor pressure of such a solvent at the temperature of the operation and also to its solubility in the extracted liquor, the item of "solvent loss" constitutes one of the major costs of the operation. The "solvent loss" is determined by inventory and is the quantity of new solvent added to the operation from time to time. It is really an apparent solvent loss and is greater than the actual solvent loss, which cannot be accurately determined because that portion of solvent leaving the system in solution in the extracted ammonia liquor passes through the ammonia stills with the liquor, is vaporized, and passes into the main gas stream where its vapors augment the normal light-oil content of the gas, and is recovered along with the normal light oil in the benzene scrubbers. Therefore, this recovery of solvent is charged as a consumption, although it is an apparent, and not an actual consumption of solvent.

Phenol Extraction Efficiency of Coal-Tar Light Oils

A motor fuel solvent is also unsatisfactory for other reasons and in the endeavor to seek means for improving the operation an investigation was made of the use of neutral coal-tar light oils for this purpose.

Representative crude ammonia liquor was procured from a coke plant and light oils were obtained by distilling representative coke-plant tars. These light oils contained tar acids in varying amount, and in order to provide neutral light oils for the tests, they were separately extracted with 10 per cent caustic soda solution until the tar-acid content was below 1 per cent. A typical light oil as used for the tests had the following general properties: specific gravity at 30° C., 0.953; limpid point, 40° C., tar acids, 0.6 per cent. Distillation data for this oil are as follows:

° C.	% *by vol.*	° C.	% *by vol.*
Below 170	18	Below 235	73
Below 190	41	Below 300	83
Below 210	61	Residue and loss	17

Measured quantities of the ammonia liquor were extracted with measured quantities of motor fuel and the neutral light-oil solvents, and the distribution coefficient (partition ratio) of the phenols was determined.

In every case the light-oil solvents exhibited much higher phenol extraction efficiency and lower solubility in the extracted liquor than a motor-fuel solvent; with a solvent-to-liquor ratio of 1:1, which is common in practice, the phenol coefficient with motor fuel was 73 per cent, whereas with the light-oil solvents it averaged 93 per cent; and whereas the solubility of motor fuel in the extracted liquor was 5 per cent, the light-oil solvents were soluble only to the extent of about 1 per cent.

With the light-oil solvents, no difficulty was experienced by the formation of emulsions so long as clean light oils were distilled from the tars. Even with repeated use on fresh ammonia liquor—removing the phenols from the oil with caustic soda before each extraction—no emulsions were encountered and separations were clean. The reddish color in the ammonia liquor, which appears to be due to dispersed free carbon, or tarry matter, in solution, was substantially removed by the solvents. This feature is important, because a motor-fuel solvent does not dissolve free carbon, or tarry matter, so readily, and in practice, if the cycling motor fuel is not removed periodically for cleaning, emulsions form which appear to be due to dispersed free carbon segregated in the motor fuel, and separations are incomplete. With the light-oil solvents the free carbon seems to be taken into solution readily and not in the dispersed condition.

Production and Use of Solvent

The most logical source of a light-oil solvent for the purpose is from the tar normally produced at the coke plant itself. To obtain the solvent, the raw tar would be passed continuously through a simple steam-heated, multi-pass dehydrator for distilling off a light-oil fraction having a specific gravity of about 0.95 at 30° C. Dehydration of the tar is effected in this distillation, and a simple decanter would separate the water and oil condensate; the water, or, more properly, weak ammonia liquor, sent to the liquor storage, and the light oil pumped to the phenol extraction plant. The light oil thus collected contains tar acids which must be removed before the oil is suitable for a solvent. This is easily accomplished by introducing the oil into the phenol extraction system at the first caustic extractor along with the normal cycling solvent, where the phenols are removed to augment the normal phenol recovery from the extraction of the ammonia liquor. The acid-free, or neutral, light oil leaving the caustic extractors then enters the cycling system as the solvent for extracting the liquor.

Since new solvent is being added to the extraction system continuously from the tar dehydrator, a quantity of cycling extraction solvent must be removed. A suitable quantity would, therefore, be bled from the extraction system and mixed continuously with the distilled tar leaving the tar still, and thus prevent depletion of the normal coke-plant tar yield, except for water and acids removed from, and mechanical losses of, the light oil. It is obvious that the tar produced by such a system would be substantially dehydrated and would be preferred by the tar distiller to ordinary grades of raw tar.

The accompanying flow sheet illustrates this process.

The feature of a continuous supply of fresh solvent to, and the continuous removal of used solvent from, the ammonia-liquor extraction plant is an important advantage because the solvent can be replenished automatically and

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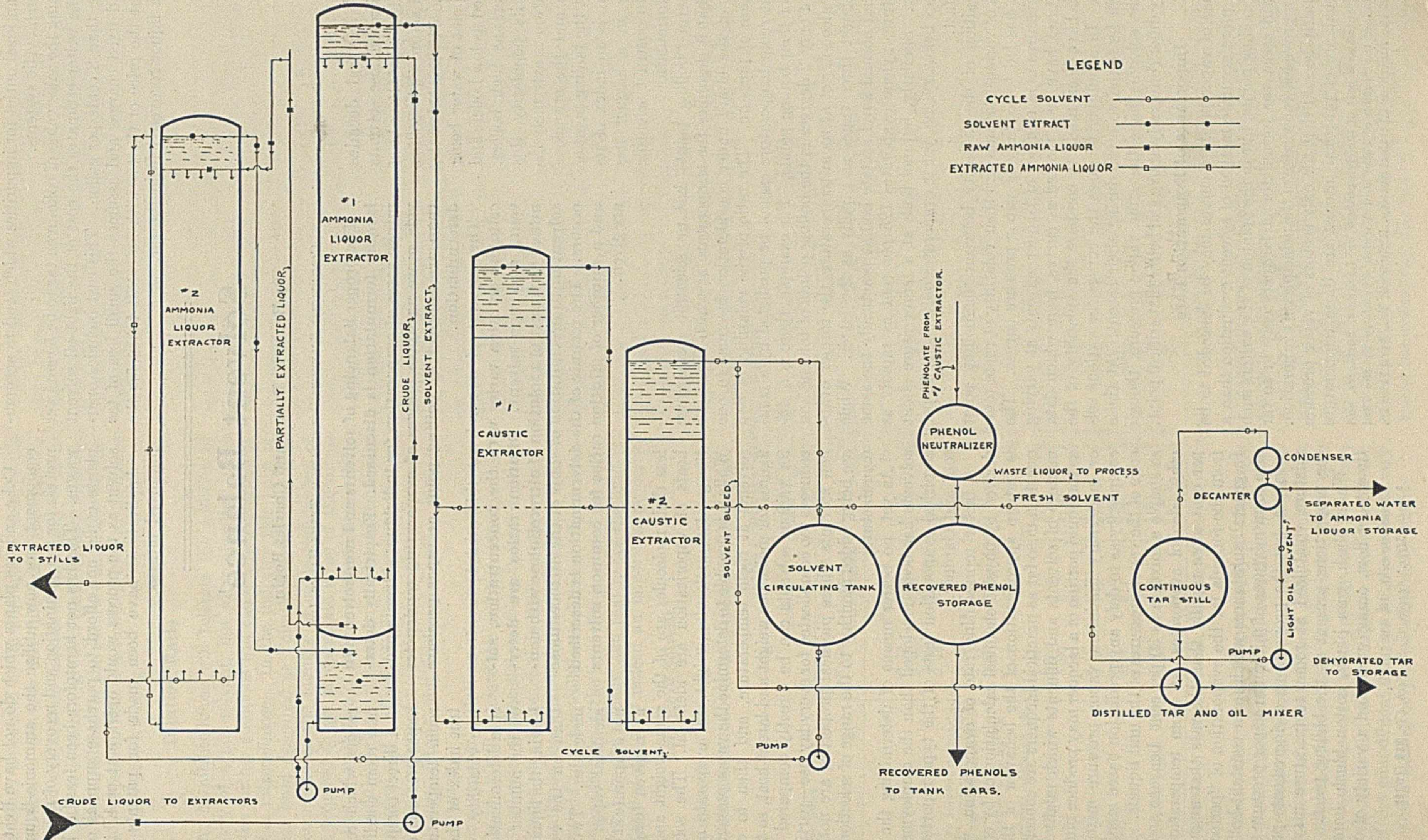
[1] Received May 24, 1927.

[2] This Journal, 18, 313 (1926); 19, 168 (1927); *Blast Furnace Steel Plant*, 14 (1926).



Continuous Countercurrent Phenol Extraction System for Ammonia Liquor there is an ideal outlet for impurities which tend to accumulate in such cyclic systems.

Assuming the sales value of coke-oven tar to be 5 cents per gallon, the writer estimates the cost of the light-oil solvent to be less than 8 cents per gallon. This cost includes operating and fixed charges and assumes the small loss of tar volume at the price of the tar with no credit taken for the ammonia liquor recovered from the tar.

Coke and gas plants which do not have light-oil recovery equipment can now utilize the ammonia-liquor extraction process for the elimination and recovery of phenols from still wastes. This has not heretofore been feasible because such plants could not afford to purchase supplies of motor-fuel solvent as the process would operate at prohibitive costs.

Applications have been made for patents covering the improved process.

Solvent Balance[1]

By Bruce K. Brown and Charles Bogin

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The proper balancing of solvents and non-solvents in lacquer formulation is discussed. Empirically determined rates of evaporation for individual solvents provide more accurate indices of evaporating tendencies than are afforded by boiling point or vapor pressure determination.

The amount of non-solvent tolerated by a nitrocellulose solution varies with the concentration, solvent, and non-solvent. Dilution ratios are determined by titrating a solution of nitrocellulose with non-solvent until precipitation of some of the nitrocellulose occurs. The technic of the determination is described and a number of dilution ratios for common solvents are given.

For several decades nitrocellulose solvents and diluents have been classified according to boiling point, those boiling below the boiling point of water being designated as low boilers and the others as high boilers. Despite its popularity, this classification is extremely inaccurate and the erroneous idea that the boiling point of a solvent is an index of its behavior in a lacquer has tended to obstruct scientific lacquer formulation.

The term "boiling point" has no scientific significance except that it describes the temperature at which the vapor pressure of the liquid under consideration is equal to one atmosphere of pressure. The ratio of the volatility of two liquids at room temperature cannot be predicted by a comparison of their boiling points. For example, there is a difference of only 2 degrees in the boiling points of toluene and isobutyl alcohol, yet at room temperature the former evaporates almost three times as rapidly as the latter. While xylene and normal amyl acetate boil at practically the same temperature, xylene evaporates 125 per cent as rapidly as the ester. Similarly, butanol boils at a temperature about 22 degrees below xylene, yet it evaporates only about 80 per cent as fast.

Recognition of the disparity between the boiling point relations of various solvents and their volatility at room temperature has led to a study of vapor pressure curves. The vapor pressures of a number of lacquer solvents at varying temperatures have been plotted as curves, from which data attempts have been made to compare the volatility of the solvents. In a number of cases the curves for various solvents will be found to cross during their ascent. At these points the solvents have the same vapor pressure, though they may differ conversely above and below that critical point.

Importance of Evaporation Rate

The use of vapor pressure curves may be conceded to be a vastly more accurate method of solvent evaluation than a study of boiling points, but in the opinion of the writers such curves will assist the formulator of lacquers only in so far as they improve his knowledge of the principles of evaporation. It may fairly be said that the only sectors of vapor pressure curves that are of practical interest are those temperature ranges which represent normal room conditions.

A direct comparison of the vapor pressures of solvents at room temperature is not a true index of their comparative volatility. Vapor pressure determinations are based on the number of molecules leaving the liquid state rather than on the weight of the molecules. Two solvents of identical vapor pressure will not evaporate at the same rate at a given temperature, unless their molecules are of the same weight and their latent heats of vaporization are identical. The solvent having the greatest molecular weight will evaporate most rapidly. While it is possible to determine the vapor pressures of lacquer solvents at room temperature, and then to correct these figures for molecular weight and latent heat, so that the data for various solvents can be directly compared, such a procedure is too complicated for everyday use—particularly since new solvents whose physical properties are not well known are being added monthly to the range of selection for lacquer manufacture.

As yet, no better means of determining the volatility of solvents has been developed than the employment of purely empirical evaporation tests of the type reported by Davidson[2] and Gardner.[3]

A factor representing rate of evaporation, whether it is derived by physico-chemical calculation or by empirical test, is but an approximation of the behavior of the solvent in question in so far as practical lacquers are concerned. Every mixture of solvents and diluents which might be employed as the liquid portion of a lacquer may produce binary, ternary, or quaternary minimum vapor pressure mixtures of such complexity as to defy any prediction based merely on knowledge of the vapor pressures of the unit liquids. For example, so simple a mixture as 30 per cent benzene and 70 per cent ethyl alcohol evaporates (at room temperature) about 25 per cent more rapidly than the rate that might be derived from the formula for the evaporation of "perfect mixtures." In general, substances which form constant-boiling mixtures also form mixtures of minimum vapor pressure at room temperature, but the proportions of ingredients present in the mixture volatilized at room temperature may differ from the proportions present at the boiling point.

Water blush, gum blush, cotton blush, improper drying time, poor flow, orange peel, and a variety of other lacquer

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[1] Presented as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] This Journal, **18**, 669 (1926).

[3] *Paint Mfrs.' Assocn. U. S., Tech. Cir.* **218** (1924).

imperfections may be caused by an improper balance of the evaporation rates of solvents and diluents. The achievement of a proper evaporation balance is manifestly of great importance, and it is to be regretted that adequate scientific data are not yet available for the accurate and rapid adjustment of the evaporation rate of a complete lacquer by means of predetermined proportioning.

Dilution Ratio

A solution of nitrocellulose will tolerate the addition of some quantity of a non-solvent, but after a critical point is reached the further additions will cause a precipitation or gelling of the nitrocellulose. In the industry this limit of tolerance has been described as "dilution ratio," and it is ordinarily expressed as the number of cubic centimeters of non-solvent required to gel or coagulate some of the nitrocellulose in 1 cc. of a solution of definite concentration. Like many other useful indexes in the lacquer art, the dilution ratio is wholly empirical and is affected by the following variables: nature of solvent, nature of non-solvent, grade of nitrocellulose, temperature of tests, and final concentration of nitrocellulose in solution.

In the same manner, solutions of some gums in hydrocarbons or alcohols will tolerate the addition of only a certain quantity of ester (nitrocellulose solvent), and a critical limit of tolerance may be reached in such instances also.

It may readily be seen that the amount of diluent that it is possible to add to a nitrocellulose solution to form a lacquer may depend largely on the limit of tolerance of the nitrocellulose solvent for the diluent, and that hence the limit of tolerance (dilution ratio) is indeed an important property.

Balance of Solvent

While the amounts of diluents that can be added to lacquers in manufacture without causing incompatibility or gelling may be readily determined from a study of the limits of tolerance of the ingredients, it will be remembered that the liquid ingredients of lacquer evaporate at varying rates and that the *balance* of solvent, diluent, gum, and nitrocellulose may be disturbed during the drying period. If one type of ingredient evaporates much more rapidly than the other, the limit of tolerance of the nitrocellulose solutions for the diluents or of the gum-diluent solution for the solvents may be exceeded and a gelling or precipitation may occur.

Table I—Dilution Ratios[a] of Common Solvents

Solvent	Toluene		Toluene—50:50 Mixture Solvent and Butanol		Butanol		Xylene		V. M. P. Naphtha	
	Ratio	Final Concn. Nitrocellulose	Ratio	Final Concn. Nitrocellulose	Ratio	Final Concn. Nitrocellulose	Ratio	Final Concn. Nitrocellulose	Ratio	Final Concn. Nitrocellulose
		Per cent		*Per cent*		*Per cent*		*Per cent*		*Per cent*
Ethyl acetate	3.73	7.0	3.20	9.0	8.40	8.5	3.30	8.8	1.25	7.8
Isopropyl acetate	3.27	7.0	2.70	8.1	8.85	7.6	3.27	8.0	1.25	7.8
sec-Butyl acetate	2.60	8.3	2.20	9.0	8.20	8.7	2.60	8.3	1.20	8.0
n-Butyl acetate	2.93	8.1	2.40	9.0	8.16	7.3	2.73	8.6	1.75	8.0
"Medium-boiling solvent acetate" (A. D. Little)	2.93	7.6	2.15	7.3	6.75	8.1	2.26	7.6	1.00	8.7
Amyl acetate from fusel oil	2.53	7.9	2.25	7.0	7.28	7.0	2.40	8.2	1.50	7.0
n-Amyl acetate	2.20	8.6	2.00	8.8	7.28	7.0	2.20	8.7	1.40	7.3
Acetate of ethyl ether of ethylene glycol	2.60	8.2	2.50	8.0	7.20	8.7	2.46	8.5	1.12	8.1
"High-boiling solvent acetate" (A. D. Little)	1.93	6.8	1.80	6.5	5.40	8.6	1.70	7.0	0.80	7.8
n-Butyl propionate (water-white)	2.30	8.0	2.00	8.5	7.50	7.8	2.26	8.2	1.30	7.6
Ethyl lactate	5.80	8.2	4.30	7.6	10.20	8.9	4.80	8.3	0.68	8.3
Acetone	4.90	8.1	5.30	7.5	7.00	7.2	4.00	7.2	0.68	8.3
Diacetone alcohol	3.53	9.0	4.00	7.2	8.13	7.5	2.86	8.0	0.53	7.6
Mesityl oxide	4.80	7.2	3.90	7.6	9.20	7.8	4.30	7.0	0.95	9.0
Dibutyl phthalate	2.77	7.2	2.70	8.2	8.00	8.9	2.93	7.7	1.70	8.5
Tricresyl phosphate	3.95	8.1	3.44	5.7	4.91	7.7	5.00	6.7	0.67	7.0
Dibutyl tartrate	8.00	8.9	5.94	6.5	15.00	8.0	7.70	7.0	1.40	7.3
"Diatol"	1.20	8.1	1.33	7.6	6.10	7.0	1.12	8.7	0.57	7.5
Ethyl ether of ethylene glycol	5.30	8.0	3.10	7.3	7.50	8.0	4.70	8.4	1.05	8.6
Diethyl carbonate	0.76	10.0	1.50	8.0	6.20	7.0	0.70	8.2	0.27	9.2

[a] Expressed as number of cubic centimeters of non-solvent that may be added to 1 cc. of nitrocellulose solution without causing coagulation or precipitation.

While the proper balance of solvents and diluents to produce lacquers of desirable evaporation rates is incapable of definite prediction, the balance of solvent and non-solvent requisite to a complete compatibility of the ingredients, both in the liquid lacquer and during the drying period, is more easily ascertained.

Determination of Dilution Ratio

The method of determining the dilution ratio (limit of tolerance) of a solvent consists simply in titrating a nitrocellulose solution until so much non-solvent has been added that the nitrocellulose becomes gelled or precipitated. This determination is adaptable to back-titration, and if an excess of non-solvent has been added the mixture may be "brought back" by merely adding a little more of the nitrocellulose solvent and retitrating until a sharp end point is reached.

The amount of non-solvent tolerable by a nitrocellulose solution varies with the concentration of the solution, and in the past various experimenters have fallen into the error of comparing dilution ratios determined for solutions of varying concentration. For example, Davidson[2] performed tests on nitrocellulose solutions of initial concentration of 10 per cent. While the figures thus obtained are scientifically accurate, since solvents vary widely in their tolerance for non-solvents, the final mixtures of solvent and non-solvent vary just as widely in their volume and in the consequent concentration of nitrocellulose therein. Furthermore, since all dilution ratios vary with the concentration of nitrocellulose, and since the purpose of determining the dilution ratio is to learn the amount of non-solvent that will be tolerated in a completed lacquer, the only dilution ratios of real value are those that are determined from mixtures which approximate the concentration of true lacquers at the time the end points of the tests are reached. An ordinary nitrocellulose lacquer contains from 8 to 12 per cent of nitrocellulose.

Table I presents the dilution ratios of a number of common nitrocellulose solvents as determined with "$^1/_2$-second cotton" at room temperature. In each case the concentration of nitrocellulose in the final mixture of solvent and non-solvent is approximately 8 per cent. This uniformity makes the ratios of different solvents directly comparable. It was accomplished by means of preliminary determinations of the dilution ratios employing a nitrocellulose solution of known initial concentration, the data being used in adjusting the initial concentration of nitrocellulose in the solvent, so that after all of the non-solvent tolerable had been added the concentration of nitrocellulose in the resultant mixture would approximate 8 per cent.

In the past it has been generally assumed that the dilution ratio of a solvent for the typical non-solvent—toluene—affords a fair index for solvent evaluation. But the dilution ratio of a solvent, like its evaporating quality, may be affected by the presence of other liquids in the completed lacquer. Table I clearly indicates this, and shows the utter unreliability of dilution ratios based on toluene alone.

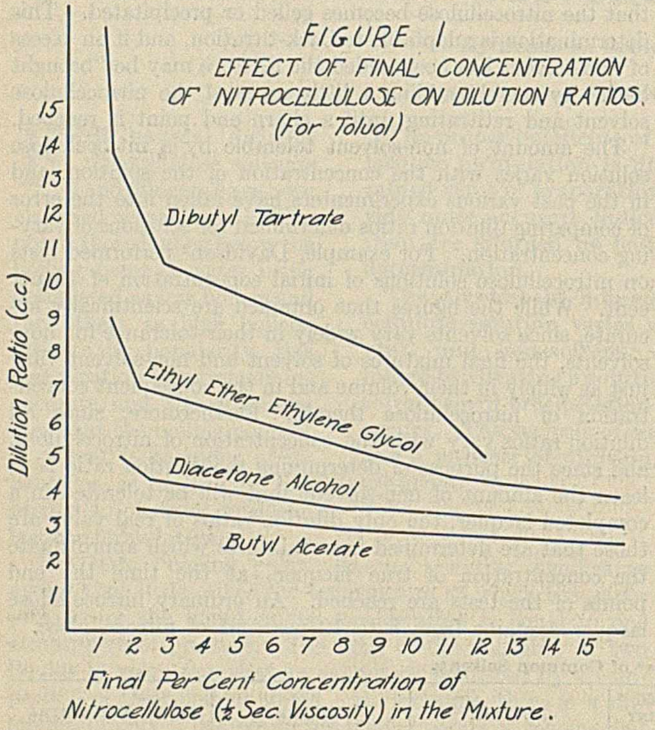

FIGURE 1
EFFECT OF FINAL CONCENTRATION OF NITROCELLULOSE ON DILUTION RATIOS.
(For Toluol)

For toluene the average dilution ratio of the simple ester solvents is about 2.9 (Table I) whereas hydroxyl-bearing solvents such as ethyl lactate, ethyl ether of ethylene glycol, and diacetone alcohol, show a markedly superior tolerance, ranging from 3.5 to 5.0.

A second series of determinations gives the dilution ratio, for toluene, of a 50:50 mixture of solvent and butanol. The final mixture approximates the average lacquer more closely than does the mixture obtained with toluene alone, since alcohol diluents, as well as hydrocarbons, are employed in commercial lacquers. The addition of butanol reduced the dilution ratios of the simple ester solvents, such as the acetates, only slightly, whereas the hydroxyl-bearing solvents, particularly ethyl ether of ethylene glycol, were profoundly affected.

The dilution ratios of the pure solvents for butanol are notably high since most solvents bear considerable admixture with butanol. In general, the ratios for xylene are slightly lower than those for toluene.

The figures for V. M. P. naphtha are interesting for several reasons. While the unavailability of closely boiling fractions of petroleum hydrocarbons has hindered the use of these materials in the past, this difficulty has now been overcome and fractions of almost any reasonable boiling range are available. Petroleum hydrocarbons are less expensive than coal-tar diluents at the present time, and in the brush lacquer field they are especially valuable, since lacquers containing these materials in place of benzene and its homologs have a much retarded solvent action on previously applied coats of lacquer. Whereas the hydroxyl-bearing solvents show marked superiority in dilution ratios for toluene over the simple esters, in the case of naphtha the condition is completely reversed, and the simple esters tolerate from 50 to 100 per cent more naphtha than do such materials as ethyl lactate, ethyl ether of ethylene glycol, and diacetone alcohol.

Data on the dilution ratios for naphtha of mixtures of solvents and butanol are not yet available, but it is hoped that they may soon be published. The effect of the presence of gums in the nitrocellulose solutions employed in the study of dilution ratios also merits attention.

Effect of Final Concentration of Nitrocellulose on Dilution Ratios

In presenting these dilution ratios it was remarked that unless the final concentration of the nitrocellulose in the mixture approximates the quantity present in a commercial lacquer the figures are of little value. This point is illustrated in Figures 1 and 2. In Figure 1 the dilution ratios for toluene of dibutyl tartrate, ethyl ether of ethylene glycol, diacetone alcohol, and normal butyl acetate, determined for final concentrations of nitrocellulose, are reported. (Dibutyl tartrate is a plasticizer; it is included in the data because its dilution ratios are uniformly higher than those of any solvent known to the authors.) At a point corresponding to 2 per cent nitrocellulose in the final mixture the dilution ratios for ethyl ether of ethylene glycol, diacetone alcohol, and butyl acetate are, respectively, 7.0, 4.5, and 3.5—a maximum difference amounting to 100 per cent. At 8 per cent concentration the figures for the same solvents are 5.2, 3.5, and 2.9—a gross difference of about 76 per cent. At 12 per cent concentration the corresponding figures are approximately 4.2, 3.2, and 2.7—a maximum difference of about 55 per cent. It is thus seen that differences of dilution ratio are unduly magnified at low final concentrations of nitrocellulose.

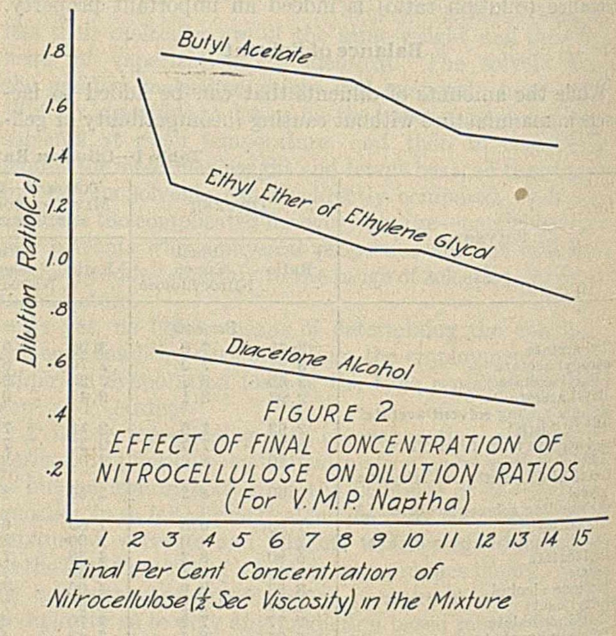

FIGURE 2
EFFECT OF FINAL CONCENTRATION OF NITROCELLULOSE ON DILUTION RATIOS
(For V.M.P. Naptha)

The curves for V. M. P. naphtha (Figure 2) show that the dilution ratios of the solvents depend on the final concentration of nitrocellulose in the mixture. None of the solvents reported are as tolerant of petroleum hydrocarbons as they are of toluene. The same general rule applies—an increase in final concentration causes a reduction in dilution ratio. In the case of naphtha ratios, however, the simple ester solvents, such as butyl acetate, will stand the most dilution with non-solvent.

These curves also illustrate the fallacy of comparing dilution ratios obtained for different solvents where a uniform initial concentration of nitrocellulose—say, 10 per cent—is employed, and the final concentration is disregarded. In such cases the natural difference of dilution ratios is exaggerated. For example, with a solvent having a high dilution ratio the final concentration of the nitrocellulose, after all the non-solvent has been added, will be less than the final concentration of nitrocellulose obtained in testing a solvent having a lower dilution ratio, to which less non-solvent may be added. The curves clearly indicate that at low final concentrations of nitrocellulose the dilution ratios of the solvents may be expected to be larger than at the higher concentrations, which are more comparable with actual lacquers.

In the preparation of a satisfactory lacquer the use of diluent ratios must be tempered by the evaporation balance of the liquid mixture. Diluent ratios represent merely the limit of tolerance of solvent for non-solvent in the complete lacquer, and are no indication of tolerance during the drying period. If solvent and non-solvent present are adjusted in evaporation rates so that neither is completely evaporated before the lacquer film sets during drying, the diluent ratio will not be exceeded and a satisfactory film should result. This is not always the case. For example, the data presented show that a mixture comprising 1 part of ethyl acetate and 3 parts of xylene will retain 8 per cent of nitrocellulose in homogeneous colloidal solution. But if such a mixture is employed as a lacquer a badly blushed film of poor adherence and low tensile strength will result, since all of the solvent will evaporate before the film dries and the remaining xylene will coagulate (blush) the nitrocellulose.

Acknowledgment

C. W. Simms, of this laboratory, performed many of the laboratory tests on which this paper is based and the authors' thanks are due him.

Lacquer Surfacers[1]

By F. M. Beegle and C. M. Simmons

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In developing a suitable lacquer surfacer for use in automobile production, it was thought desirable to grind the pigments on a burr stone mill, such as all paint factories possess, thereby obviating the necessity of purchasing special equipment. Various combinations of chemical plasticizers, oils, and gum were therefore tried in order to secure a liquid that would wet sufficient pigment to give satisfactory filling and feed through the mill. A mixture of castor oil, linseed oil, and dibutyl tartrate gave a very good grinding mixture when Titanox, Keystone filler, talc, and iron oxide formed the bulk of the pigment.

Gums

In accordance with good varnish reasoning it was believed that the less gum used the tougher and more waterproof would be the product. Consequently, a batch of surfacer was made with the ingredients mentioned above, without any gum. This surfacer was very elastic and held out the finishing lacquer in a very satisfactory manner, but on spraying an automobile body with it and sending to the rubbing deck after sufficient drying, it rubbed very tough, and in spots where the water lay for a time it blistered from the primer.

Considerable work was then done to find the cause of the blistering, retaining the idea that no gum should be used. Grinds were made with the same pigment combinations and oils, but substituting Lindol, dibutyl phthalate, and diamyl phthalate for the dibutyl tartrate. All combinations were better than the one using dibutyl tartrate, because this plasticizer seemed to allow the water to pass quickly through the film.

From this point considerable stress was placed on a water test and all batches were sprayed on, force-dried 1 hour at 66° C. (150° F.), sanded to a smooth surface, and stood in a pail of tap water overnight. The formula for any surfacer showing a tendency to blister was discarded.

The varnish theory had to be discarded because it was found necessary to include gum in the formulas in order to get adhesion and a material to stand a satisfactory water test. The tendency to blister was found to decrease as the gum increased up to an optimum point. Fortunately, the gum content giving optimum waterproofness was about the same as the gum content giving satisfactory rubbing properties. The addition of the gum solution to the oils and chemical plasticizer gave a very satisfactory grinding liquid.

After the proper ratio of oil, chemical plasticizer, gum, total amount of pigments, and cotton was established to give proper adhesion, waterproofness, sufficient filling and sanding, work was started to determine the gum or combination of gums to be used to secure the best results. Shellac, dammar, ester gum, and kauri gum solutions were used.

On all tests that could be completed in a week or 10 days it was decided that the gums gave the best results in the order named above. However, very good results could be obtained by using a combination of dammar and ester gum.

It was found that a very valuable test could be made on lacquer surfacers by applying two coats on top of a good, long oil-baked primer, force-drying 1 hour at 66° C. (150° F.), rubbing to a surface, then coating with two double coats of lacquer. After the film had dried about an hour, the panels were hung in an electric oven and baked overnight at 121° C. (250° F.). This treatment caused many lacquer surfacers to crack open and pull the finishing lacquer with them, giving the appearance of sun-baked mud.

Optimum Cotton Solution

Surfacers were made using the formula with the best oil, chemical plasticizer, pigments, and gum combinations with $^1/_2$-second cotton solution in one case, and with 7-second cotton solutions in other cases, after reducing the latter to the viscosity of the $^1/_2$-second solution by use of various catalysts. The same number of grams of cotton per liter of solvents was used in all cases.

The surfacer made from $^1/_2$-second cotton was the best of the series, irrespective of the catalyst used with the 7-second cotton, even though the catalyst were only heat and pressure. A weather test on the roof bore out the conclusions of the quick tests in this case.

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[1] Received April 23, 1927.

Pigments

The next step was to vary the pigment combinations. Into 850 grams of plasticizers and gum solutions the following pigments were ground:

A— 850 grams Titanox, 850 Keystone filler, and 170 talc
B—1190 grams white lead, 1190 Keystone filler, and 170 talc
C—1075 grams zinc oxide, 1075 Keystone filler, and 170 talc
D—1190 grams Titanox, 1190 white lead, and 170 talc
E—1075 grams Titanox, 1075 zinc oxide, and 170 talc
F—1190 grams lithopone, 1190 Keystone filler, and 170 talc
G—1190 grams silica, 1190 Keystone filler, and 170 talc

These bases were then thinned with $^1/_2$-second cotton solution, some additional gum solution, and reducer.

Two panels, previously primed with oil primer and baked, were sprayed with two coats of each surfacer. The films were force-dried in an electric oven at 66° C. (150° F.) for 45 minutes. Both panels were sanded to a good surface. One stood in water overnight, while the other was sprayed with two double coats of lacquer and baked 48 hours in an oven at 121° C. (250° F.).

The next morning the panels which were stood in water were cut with a knife, both above and below the water line, to ascertain their relative elasticity and adherence to the primer. All the surfacers were found to stand a good water and knife test.

The combination of Titanox and white lead and the combination of lithopone with Keystone filler all sanded well, while the silica with Keystone filler sanded very hard, and the zinc oxide with Keystone and Titanox with white lead sanded hard.

The surfacer containing zinc oxide and Keystone cut the best, both above and below water, but it stood the bending test poorly. On cutting after baking, the films gave a ribbon in the following order: A, F, B, C, E, D, and G. The bending test after baking gave the following order of results: D, A, F, B, E, C, and G.

Panels coated with those surfacers made with the seven pigment combinations were sprayed over half the surface with two coats of blue finishing lacquer and exposed on the roof for about 6 months. At the end of this time the surfacer made with white lead and Keystone showed the best, both with and without finishing lacquer over it. The combination of lithopone and Keystone was a close second. The combination of Titanox and white lead was the poorest, while the other combinations varied between these two extremes.

Conclusions

1—A good lacquer surfacer can be manufactured on a burr stone mill.

2—A combination of oil, chemical plasticizer, and gum solution makes a good grinding medium.

3—A satisfactory lacquer for production work must stand a good water test.

4—Gum is essential for waterproofness, adhesion, and satisfactory rubbing properties.

5—Gums are satisfactory in the following order: shellac, dammar, ester gum, and kauri. However, a combination of dammar and ester gum may be used with satisfactory results.

6—Half-second cotton gives better results than cotton of higher viscosity reduced to $^1/_2$-second viscosity.

7—Of all pigment combinations used, white lead and Keystone filler showed the best results after 6 months' outdoor exposure, both with and without finishing lacquer sprayed over the surfacer.

Uniform Varnish Films for Exposure Tests[1]

By H. A. Gardner and G. G. Sward

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When panels of any type are brush-coated with varnish, it is considered necessary to apply at least two and preferably three coats in order to get a continuous film and one of sufficient thickness to give fairly good durability over a period of three months' exposure in the summer. It has been found, however, that various operators working with the same varnish may apply films of marked variation in thickness. Naturally, when exposed the durability of such panels would vary. It was thought that much more uniform results could be obtained if the various operators would use some uniform method of preparing films. The writers, for their own work, have standardized upon one-coat films which are spun upon revolving disks. The apparatus consists of a 12-inch (30-cm.) circular spinning table, set within a drain pan 18 inches (46 cm.) in diameter and 8 inches (20 cm.) high to catch the varnish thrown off by centrifugal force. The power is furnished by a 0.1 horsepower motor. The speed of the apparatus is controlled by varying the size of the pulleys.

Walker and Thompson[2] have prepared films of paint and varnish by spinning on glass disks. They found that plastic materials, such as paint, gave films that were much thicker at the center than at the edge of a 25-cm. disk. On the other hand, viscous materials, such as varnish, gave films varying but a few microns over the entire disk. For a study of many properties of the paint they decided that a speed of 300 r. p. m. maintained for 3 minutes produced the best results. No extensive study of varnish films was made.

Pulsifer[3] found that the thickness of a normal brush coat of a varnish could be expressed as $F = {}^1/_2\,(10V + N)$, where F equals the thickness in microns, V equals the absolute viscosity in poises at 25° C., and N equals the percentage of non-volatile matter in the varnish. For example, a varnish possessing a viscosity of 1.4 poises and a non-volatile percentage of 50 should give a film 32 microns thick.

None of the above investigators attempted to control the thickness of the film by altering the conditions of preparation to suit the material under consideration.

Preparation of Films

In view of the influence of the film thickness upon the results of most tests on varnish films, it was thought desirable to study the spinning method to learn if films of predetermined thickness could be prepared. The method was essentially the same as that of Walker and Thompson,[2] but using, in-

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[1] Received April 6, 1927. Presented under the title "Methods of Producing Uniform Films for Exposure Tests" as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Proc. Am. Soc. Testing Materials*, **22**, Pt. II, 464 (1922).

[3] *Drugs, Oils, Paints*, **39**, 354 (1924).

stead of glass disks, metal panels 6 by 12 inches (15 by 30 cm.) Two reasons exist for the change. The metal panels are cheaper and varnish films prepared by this method may be used for exposure tests. The varnishes were first flowed over the entire panel, which was then placed on the spinning device and spun for the desired time and at the desired speed. If any uncoated portions were shown after flowing, they were immediately coated by the varnish as soon as the panel was spun.

Five varnishes ranging in viscosity from 0.95 to 2.2 poises and from 40 to 70 per cent non-volatile content were prepared. (Table I) Numbers 1, 3, and 5 comprise a series in which the viscosity is constant, and the per cent non-volatile is variable. Numbers 2, 3, and 4 comprise a series in which the viscosity is variable and the per cent non-volatile is constant.

Table I—Properties of Varnishes

Varnish	Per Cent Non-Volatile	Viscosity Gardner-Holdt Scale	Poises
1	40	F	1.4
2	50	C-D	0.95
3	50	F	1.4
4	50	I	2.2
5	70	F	1.4

With these varnishes the following variables were studied—speed of spinning, duration of spinning, viscosity of the varnish, and per cent non-volatile of the varnish. Three speeds were available—215, 290, and 375 r. p. m. Three time intervals were selected—30, 60, and 120 seconds. All panels were prepared at 25° C.

Measurement of Film Thickness

After preparation and thorough drying of the films, the thicknesses were measured with an Ames dial. The instrument may be read with a precision of ±1 micron. Measurements were made at distances of 3, 8, and 13 cm. from the center of the panel, at least two measurements being made at each distance. The variation in thickness at any specific distance from the center seldom exceeded 1 micron, and the variation over the entire panel was usually not more than 3 microns.

Table II—Variation of Film Thickness with Speed of Spinning
(Spun for 60 seconds)

Varnish	Speed	Film Thickness at Indicated Distances from Center 3 cm.	8 cm.	13 cm.	Mean
	R. p. m.	μ	μ	μ	μ
1	215	26	25	26	26
	290	22	21	21	21
	375	18	19	20	19
2	215	31	31	33	32
	290	25	26	26	26
	375	22	23	21	22
3	215	37	35	38	37
	290	29	29	29	29
	375	26	25	24	25
4	215	61	60	59	60
	290	44	43	43	44
	375	40	39	38	39
5	215	44	44	45	44
	290	34	36	36	35
	375	31	30	29	30

Table III—Variation in Film Thickness with Time of Spinning
(Speed, 290 r. p. m.)

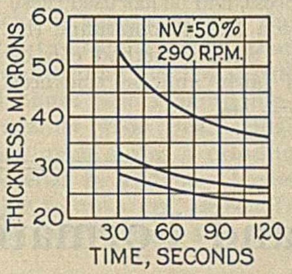
Varnish	Time	Thickness of Film at Indicated Distances from Center 3 cm.	8 cm.	13 cm.	Mean
	Seconds	μ	μ	μ	μ
2	30	27	29	31	29
	60	25	26	26	26
	120	23	23	22	23
3	30	33	33	33	33
	60	29	29	29	29
	120	25	27	25	26
4	30	54	53	53	53
	60	44	43	43	43
	120	35	36	36	36

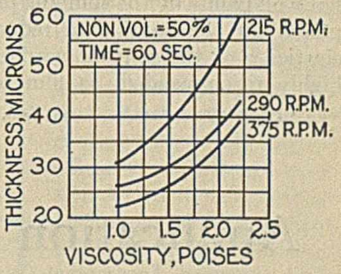
Table IV—Variation in Film Thickness with Viscosity
(Non-volatile of each, 50 per cent)

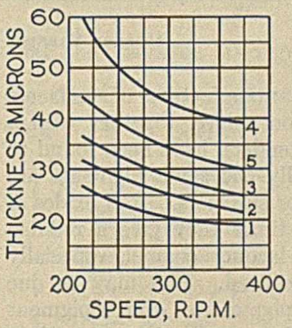
Varnish	Viscosity	Speed	Thickness at Indicated Distance from Center 3 cm.	8 cm.	13 cm.	Mean
	Poises	*R. p. m.*	μ	μ	μ	μ
2	0.95	215	31	31	33	32
3	1.4	215	38	35	38	37
4	2.2	215	61	60	59	60
2	0.95	290	25	26	26	26
3	1.4	290	29	29	29	29
4	2.2	290	44	43	43	43
2	0.95	375	22	23	21	22
3	1.4	375	26	25	25	25
4	2.2	375	40	39	38	39

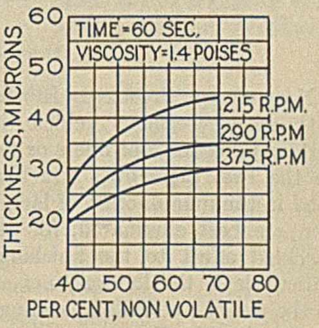
Table V—Variation of Film Thickness with Non-Volatile Percentage
(Viscosity of each, 1.4 poises)

Varnish	Non-Volatile	Speed	Thickness at Indicated Distance from Center 3 cm.	8 cm.	13 cm.	Mean
	Per cent	*R. p. m.*	μ	μ	μ	μ
1	40	215	26	25	26	26
3	50	215	37	35	38	37
5	70	215	44	44	45	44
1	40	290	22	21	21	21
3	50	290	29	29	29	29
5	70	290	34	36	36	35
1	40	375	18	19	20	19
3	50	375	26	25	24	25
5	70	375	31	30	29	30









The data obtained are presented in Tables II, III, IV, and V and graphically in the accompanying curves. An examination of the curves reveals that none of the functions, not even the viscosity or the percentage non-volatile, is a straight line.

Calculation of Film Thickness

If the thickness is calculated according to Pulsifer's formula $\left(F = \frac{10V+N}{2}\right)$, which is probably satisfactory for brushed films, the results do not correspond in any regular manner with the writers' observed values for spun films. In other words, there is no speed or time of spinning which yields a film comparable with a brush coat for varnishes varying widely in their properties.

After some calculation, the best formula developed for calculating the thickness of spun films was

$$F = 0.4N + V^4 + 3$$

where F = film thickness, microns
N = per cent non-volatile
V = viscosity, poises

This formula gives values which do not deviate much from those observed at 290 r. p. m. for 60 seconds. For speeds of 215 and 375 r. p. m., multiply the values for 290 r. p. m. by the factors 1.3 and 0.8, respectively. For times of spinning of 30 and 120 seconds, respectively, multiply the values obtained at 60 seconds by the factors 1.1 and 0.9, respectively. The observed and calculated values are shown in Table VI.

Films for Tensile Strength and Elongation Tests

In preparing films for the determination of tensile strength and elongation, tin-plate panels amalgamated with mercury are used. Upon such panels the coatings are poured, allowed to dry, and then stripped previous to cutting up into test pieces. The writers have now adopted the spinning device for the preparation of films of fairly uniform thickness upon such panels. After spinning to the desired thickness, the coating is allowed to dry and then is stripped. Very smooth films of the desired thickness are obtained.

Other Tests by This Method

Hickson[4] refers to the preparation of panels coated with flat wall paints by the spinning process, and he has used these panels for the kauri gum reduction test to determine the elasticity of the applied product. Such a method can be highly recommended, as films of fairly uniform thickness are readily obtained. Similarly, linseed oil extension tests upon varnishes can be made by coating panels by this same process. It is believed that differences in results obtained by different operators with the kauri gum reduction test on varnishes are often due to differences in film thickness. Some may be thick and some may be thin. The use of the spinning method should greatly reduce such variations.

Table VI—Observed and Calculated Film Thicknesses

$F = 0.4N + V^4 + 3$ at 290 r. p. m. and 60 seconds
Factors: For 215 r. p. m. 1.3, 375 r. p. m. 0.8; for 30 seconds 1.1, 120 seconds 0.9

VARNISH	VIS-COSITY	NON-VOLATILE	SPEED	TIME	FILM THICKNESS Obsd.	FILM THICKNESS Calcd.	FILM THICKNESS Diff.
	Poises	*Per cent*	*R. p. m.*	*Sec.*	μ	μ	μ
1	1.4	40	215	60	26	30	+4
			290	60	21	23	+2
			375	60	19	18	−1
2	0.95	50	215	60	32	31	−1
			290	30	29	26	−3
			290	60	26	24	−2
			290	120	23	22	−1
			375	60	22	19	−3
3	1.4	50	215	60	37	35	−2
			290	30	33	30	−3
			290	60	29	27	−2
			290	120	26	24	−2
			375	60	25	22	−3
4	2.2	50	215	60	60	60	0
			290	30	53	51	−2
			290	60	43	46	+3
			290	120	36	41	+5
			375	60	39	37	−2
5	1.4	70	215	60	44	46	+2
			290	60	35	35	0
			375	60	30	28	−2
					Maximum deviation		+5
					Mean deviation		±2

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[4] *Paint Mfrs.' Assocn. U. S., Tech. Circ.* 305.

Application and Formation of Lacquer Surfacers[1]

By F. W. Hopkins

Murphy Varnish Co., Newark, N. J.

Nature of Pigment—In the manufacture of surfacers with an oleoresinous vehicle, iron oxides, together with a certain percentage of fillers or extenders, have been found to be the best pigments. Practically the same pigments are used in the manufacture of lacquer surfacers. Red oxides of iron are best eliminated, for at times they give a reddish speckled effect to the finishing lacquer enamel, especially noticeable if the lighter tints are used. This may be due to the use of a so-called bleeding pigment, or even a pigment of the non-bleeding type after fine sanding if precautions have not been taken to clean carefully. Some of the dust is stirred up by the air from the spray gun and settles in the undried lacquer enamel.

Pigments high in magnesium silicate content should not be used, as they impart to the lacquer surfacer a very smooth, greasy character. A lacquer enamel applied over such a surface is liable to peel off, especially when a masking tape has been used over a freshly lacquered enameled surface.

Percentage of Pigment—In the manufacture of a lacquer surfacer it is necessary to maintain a definite percentage of pigment, so that when the surfacer is reduced it will have good filling and building qualities. The customary reduction is approximately equal parts thinner and surfacer, or 100 per cent.

Reduction in Thinning—If the surfacer is overly pigmented, and reduced as usual, it may crack after application, producing a so-called crackled-finish effect over the primer. A lacquer surfacer reduced to excess will not fill sufficiently, and thus thinner will be sprayed and wasted, instead of pigment and binder. In this case, on rubbing the surfacer, it would be very easy to rub through into the primer.

Unless the pigments are stirred thoroughly into the vehicle, a condition exists which may be identical either to excess pigmentation or excess reduction, depending upon whether the surfacer is from the bottom or top of the can. Most of the complaints on lacquer surfacer would never have occurred had the operator mixed the material thoroughly.

Spray Nozzle and Gun Manipulation—The spray nozzle used in the application of the surfacer should be of medium size so that too much material will not be sprayed in one coat. In manipulating the spray gun the operator should be careful to hold the gun about 8 to 10 inches from the surface which is being finished. If held any nearer the surface too much pigment may be deposited within a given area, and a crackled effect will probably result. Too great a distance will produce little more than spray dust.

If a lacquer surfacer is not properly reduced or is overpigmented, or applied improperly, it may appear to produce a satisfactory surface, but after rubbing and the application of a lacquer enamel the surface will crack open.

Ideal Surfacer—An ideal surfacer is, therefore, one which builds quickly, dries rapidly without indications of orange peel, and sands easily to a hard, non-porous surface of such character that lacquer enamels may be applied with perfect adhesion. Such a surfacer must be free from any pigments which bleed or discolor the lacquer enamel.

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[1] Presented under the title "Lacquer Surfacers" as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

Protecting Wood with Aluminum Paint[1]

By Junius D. Edwards and Robert I. Wray

Aluminum Company of America, New Kensington, Pa.

Data are presented in confirmation of the conclusions of Dunlap and Browne that paint coatings continue to protect wood adequately against weathering only so long as they maintain a reasonable degree of moisture-excluding efficiency, as measured by the Dunlap method. The data indicate further that coatings having a moisture-excluding efficiency still higher than the traditional house paints afford materially greater protection against wood weathering. Aluminum paints or coatings made up of a priming coat of aluminum paint covered by ordinary house paints are highly impermeable to moisture, especially effective in preventing wood weathering, and very durable.

IT IS natural to think of aluminum paint, with its metallic aluminum pigment, as a protective medium for metals. Its use for protecting wood also has much merit. Two of the outstanding characteristics of an aluminum paint film are its durability and high moisture-proofing power. The checking and cracking of wood as the result of rapid changes in its moisture content are minimized by a moisture-proof coating, such as aluminum paint, and the durable character of the paint assures maintenance of the protection.

Dunlap and Browne, of the Forest Products Laboratory, have been so impressed with the importance of moisture-proofing efficiency as a factor in determining the effective value of a paint coating on wood that they have proposed it as a quantitative measure of wood protection. They state:[2]

> The method to be discussed is based upon the understanding that paint is used to protect wood against weathering. The process of weathering, as considered here, has nothing to do with the action of fungi or other living organisms upon wood, but is attributed principally to the disintegrating effect of internal stresses set up in the wood as a result of the fluctuating moisture content of those portions exposed directly to the weather. Other factors, such as mechanical abrasion and photochemical conversion of cellulose to oxycellulose, doubtless play parts in the weathering process, but swelling and shrinking in response to changing atmospheric conditions are believed to take the leading part.
>
> Paint coatings protect wood against weathering by damping out extreme fluctuations in moisture content through their retarding action on the passage of moisture into or out of the wood. It is not necessary for the coating to prevent the transfusion of moisture completely; it need only retard the movement. It is impossible as yet to say precisely what degree of moisture-retarding efficiency is required for the coating to furnish adequate protection from weathering; this will probably depend upon various extrinsic factors such as the species of wood and the climatic conditions. But, as will be seen, it is not necessary to fix the point exactly in order to apply the technic suggested herein to the comparison of the protective values of different paints when applied to wood.

The present writers have obtained additional data that support these views. Certain of these data, showing the effect of aluminum bronze powder in increasing the moisture-proofing efficiency of oils and varnishes, have already been presented.[3] In making these measurements, the method described by Dunlap[4] has been employed and his paper should be consulted for details. It is sufficient to say that the efficiency of a coating is determined by the relative amounts of moisture absorbed by bare and coated birch panels when exposed to a 95 to 100 per cent saturated atmosphere for 14 days.

Moisture-Proofing Tests

Table I gives comparative data on the moisture-proofing efficiency of three coats of aluminum paint and three coats of different types of white paints, as well as combinations of the white paints as top coats with aluminum paint, zinc dust paint, and red lead as primers. The moisture-proofing efficiency obviously depends to an important extent upon the thickness of the coating. In painting small test panels it was difficult to regulate the amount of paint applied with the desired precision. In the present case two sets of panels were painted at two different times and tested. In general, where the moisture-proofing efficiency of the duplicates was not in close agreement, the one with the thicker paint coating showed the highest efficiency, although occasionally there were discrepancies not to be explained in this way. Although agreement between duplicates is not always so close as desired, it is believed that the averages are significant.

Table I—Moisture-Proofing Efficiency of Various Paints

Panel No.	Coating	1st Series	2nd Series	Average
		Per cent	*Per cent*	*Per cent*
1	3 coats aluminum paint	89	90	90
2	1 coat aluminum paint, 2 coats white paint No. 1	79	90	85
3	1 coat aluminum paint, 2 coats white paint No. 2	89	81	85
4	1 coat aluminum paint, 2 coats white paint No. 3	90	82	86
5	1 coat zinc dust paint, 2 coats white paint No. 1	80	79	80
6	1 coat zinc dust paint, 2 coats white paint No. 3	79	82	80
7	1 coat red lead, 2 coats white paint No. 1	69	76	72
8	1 coat red lead, 2 coats white paint No. 3	76	75	76
9	3 coats white paint No. 1	79	72	76
10	3 coats white paint No. 3	79	83	81
11	Birch panel without coating	0	0	0
12	Birch panel without coating	0	0	0

Formulas of Paints Used

(Percentages by weight)

Aluminum paint:		
Standard varnish aluminum powder		21
Kettle-bodied linseed oil	60	79
Mineral spirits and drier	40	
Zinc dust paint:		
Zinc oxide	20	79
Zinc dust	80	
Boiled linseed oil	82	21
Mineral spirits and drier	18	
Red lead paint:		
Dry red lead (95 per cent Pb_3O_4)		79
Raw and boiled linseed oil	94	21
Turpentine	6	

White paint No. 1—white lead, zinc oxide inert paint—"55-35-10" formula.
White paint No. 2—titanium oxide, zinc oxide paint.
White paint No. 3—lithopone, zinc oxide, inert—"40-40-20" formula.

The white paints were commercial paints purchased on the open market.

No data are yet available on the effect of exposure on the moisture-proofing power of the coatings on the test panels

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[1] Received April 1, 1927. Presented as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Unpublished paper read before the Section of Paint and Varnish Chemistry of the American Chemical Society at Madison, Wis., May, 1926.

[3] This Journal, **17**, 639 (1925).

[4] *Ibid.*, **18**, 1230 (1926).

of Table I. However, a few measurements on aluminum painted and varnished panels of the same character, which had been exposed for one year, are given in Table II.

Table II—Moisture-Proofing Efficiency of Various Coatings for Wood after One Year Outdoors at New Kensington, Pa.

(Southern exposure, vertical suspension)

COATING APPLIED (3 COATS)	BEFORE EXPOSURE Pine[a]	BEFORE EXPOSURE Birch	AFTER 1 YEAR'S EXPOSURE Pine[a]	AFTER 1 YEAR'S EXPOSURE Birch
	Per cent	*Per cent*	*Per cent*	*Per cent*
Aluminum paint made with spar varnish No. 1:				
Applied by dipping	87	93	91	89
Applied by brushing	85	92	77	90
Spar varnish No. 1 (dipped)	43	63	46	42
Spar varnish No. 2 (dipped)	62	76	59	75

[a] Western yellow pine.

For comparison with the data of Table I, the moisture-proofing efficiency of paint coatings on western yellow pine was measured after 18 months' exposure. Samples were cut from large exposure panels and the back and cut ends coated with aluminum foil, in order to measure the moisture-proofing efficiency of the coating on the exposed face only. A similar technic has been suggested by Dunlap and Browne. (Table III)

Table III—Moisture-Proofing Efficiency of Aluminum and White Paints after 18 Months Outdoors at New Kensington, Pa.

(Southern exposure, 45-degree position)

PANEL No.	COATING[a]	
		Per cent
1	Aluminum paint made with kettle-bodied linseed oil	70
2	Same as on No. 1	71
3	Same as on No. 1	71
4	Same as on No. 1	57
5	Aluminum paint made with long oil varnish	83
6	Same as on No. 5	81
7	White lead-zinc oxide paint ("55-35-10" formula)	11
8	Same as on No. 7	8
9	Same as on No. 7	24
10	Same as on No. 7	16
11	Bare	0
12	Entirely coated with aluminum foil	100

[a] Two coats on western yellow pine.

Tables II and III show that the observed moisture-proofing power of any particular paint is lower on western yellow pine than on birch. The paint film itself doubtless has the same permeability on each wood, but the absorptive characteristics of the two woods differ. In the case of the first tests given in Table II, the bare (blank) western yellow pine panel absorbed 4.24 grams of water and the birch panel, 9.18 grams. The aluminum-painted panels absorbed about the same amounts of water—namely, 0.54 and 0.63 gram, respectively. However, the calculated efficiencies are appreciably different.

$$\frac{4.24 - 0.54}{4.24} = 87 \text{ per cent and } \frac{9.18 - 0.63}{9.18} = 93 \text{ per cent}$$

Exposure Tests

For comparison with these moisture-proofing tests, exposure tests are given covering periods up to 3 years. H. A. Gardner[5] has described a series of seventy test panels arranged to test the efficiency of aluminum paint as a protection for wood, and also its value as a primer under white paints. These tests were made on five different kinds of wood and with a variety of paints. Mr. Gardner sent a duplicate set of panels to the writers, who exposed them in the "industrial atmosphere" of New Kensington. After 2 years' exposure only a few of the panels were in good enough condition to be continued longer in the test. Table IV describes the condition of part of these panels after 2 and 3 years' exposure.

Table IV—Paint Tests on Various Types of Wooden Panels

(Exposed January 11, 1924, at New Kensington, Pa.; southern exposure, 45-degree position)

PANEL No.	WOOD AND PAINT NOS.[a]	CONDITION AFTER 2 YEARS
1	W-6-6-6	Moderate fine wood checking on upper half of panel; paint flaking above wood checks
2	W-1-6-6	Wood sound; moderate paint checking
3	F-6-6-6	Slight checking of wood on upper half; moderate paint checking; rosin exudations
4	F-1-6-6	Wood sound; moderate paint checking; rosin exudations
5	C-6-6-6	Many fine wood checks over entire panel; paint flaking above wood checks
6	C-1-6-6	Wood sound; moderate paint checking
7	Y-6-6-6	Wood checking very badly; paint scaling badly over entire panel
8	Y-1-6-6	Medium checking of wood; moderate paint checking
9	R-6-6-6	Wood sound; moderate paint checking
10	R-1-6-6	Wood sound; moderate paint checking
11	W-3-3-3	Wood checked badly; paint nearly all chalked off
12	W-1-3-3	Many fine wood checks; top coats completely chalked off
13	F-3-3-3	Considerable checking of wood; paint badly chalked; rosin exudations
14	F-1-3-3	Slight checking of wood; top coats practically chalked off
15	C-3-3-3	Fine surface checking of wood; paint nearly all chalked off
16	C-1-3-3	A few fine surface checks in wood; top coats of paint chalked off
17	Y-3-3-3	Wood badly checked; paint scaling and badly chalked
18	Y-1-3-3	Wood badly checked; top coats all chalked off; primer flaking
19	R-3-3-3	Slight checking of wood (edge grained); considerable chalking of paint
20	R-1-3-3	Medium checking of wood (flat grained); paint flaking and chalking
21	W-2-2-2	Wood badly checked; paint flaking badly
22	W-1-2-2	Moderate number of fine wood checks; slight flaking of paint
23	F-2-2-2	Wood badly checked; paint flaking badly
24	F-1-2-2	Slight wood checking; moderate paint checking
25	C-2-2-2	Moderate wood checking; paint flaking badly
26	C-1-2-2	Slight wood checking; moderate paint checking
27	Y-2-2-2	Wood very badly checked; paint nearly all scaled off
28	Y-1-2-2	Wood badly checked; paint flaking badly on summer wood
29	R-2-2-2	Wood (flat grain) very badly checked; paint flaking and checking
30	R-1-2-2	Wood (edge grain) sound; moderate checking of paint
51	W-4-4-4	Wood sound; paint sound
52	F-4-4-4	Wood sound; paint sound; rosin exudation
53	C-4-4-4	Wood sound; paint sound
54	Y-4-4-4	Wood sound; paint sound
55	R-4-4-4	Wood sound; paint sound
		CONDITION AFTER 3 YEARS
9	R-6-6-6	Wood sound; considerable paint checking
10	R-1-6-6	Wood sound; considerable paint checking
26	C-1-2-2	Considerable wood checking; slight flaking of paint; considerable chalking
30	R-1-2-2	Wood sound; paint shows moderate checking; top coats entirely chalked off
51	W-4-4-4	Wood sound; paint sound
52	F-4-4-4	Wood sound; paint sound; some rosin exudation
53	C-4-4-4	Wood checking in one small area over summer wood; paint cracked at this point, otherwise sound condition
54	Y-4-4-4	One fine wood check about an inch long near top of panel, otherwise sound; paint coating sound condition
55	R-4-4-4	Wood sound; paint sound

[a] *Key to Numbers and Letters*

W—white pine; F—douglas fir; C—cypress; Y—yellow pine; R—redwood.

Paint No. 1—Aluminum paint with spar varnish (diluted 2:1).
Paint No. 2—White lead-zinc oxide paint (50:50).
Paint No. 3—Titanox-zinc oxide paint (3:2).
Paint No. 4—Aluminum paint with heavy-bodied linseed oil (diluted 3:2—turpentine).
Paint No. 6—Basic carbonate white lead paint.

Example: Panel W-1-6-6 is a white pine panel with a priming coat of aluminum paint No. 1 and two top coats of white lead paint No. 6.

In summarizing the results of these tests one point stood out above everything else. The five panels (51 to 55) which received three coats of aluminum paint made with heavy-bodied linseed oil showed no signs of wood weathering after 2 years' exposure, and the paint films themselves were in sound condition without any sign of checking or chalking. Even after 3 years' exposure their condition was excellent. The performance of the aluminum paint on the yellow pine was particularly noteworthy. No other paint combination gave adequate protection to the yellow pine. After 3 years' exposure the protection of the yellow pine was almost perfect, there being but one very fine wood check on the panel, with the paint still in good condition.

The panels having an aluminum primer with two top coats of white were, in general, better protected than similar panels having three coats of white.

There were fifteen pairs of panels with and without the aluminum primer, and in twelve cases the aluminum primer

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[5] *Paint Mfrs.' Assocn. U. S., Tech. Circ.* **231** (April, 1925).

was distinctly helpful in protecting the wood. In two cases there was no choice, and in one (19 and 20) the panel with the aluminum primer was distinctly worse, although the difference in the grain of wood could readily explain this.

In these exposure tests the paint coatings having the highest initial moisture-proofing efficiency proved the most durable and gave the best protection; these were the aluminum paint coatings. The next in order of moisture-proofing efficiency, as well as durability, were the combinations of a prime coat of aluminum paint with top coats of white. That aluminum paint may have high moisture-proofing efficiency after 18 months' severe exposure is shown by other tests (Table III), where there were observed values of 70 to 80 per cent. The white paint exposed at the same time was badly deteriorated and the checking of the wood indicated failure in its moisture-proofing power, which according to the writers' measurements was only about 10 to 20 per cent.

Heat-bodied (kettle-bodied) linseed oil, diluted with about 40 per cent mineral spirits or turpentine and with added drier, makes the most generally satisfactory vehicle for aluminum paint for protecting wood. Varnishes should only be used when they are exceptionally long in oil—say, an 80-gallon varnish, or better.

Conclusion

These tests show that moisture-proofing efficiency and wood protection go hand in hand. It is important also that relatively high impermeability be maintained if the protection is to continue. Checking and cracking of the wood resulting from failure of the moisture-proofing power of the paint film must accelerate the mechanical disintegration of the overlying paint film. Disintegration of the paint film further accelerates wood weathering, and so a vicious cycle is established. In a very practical sense, therefore, protected wood helps preserve the paint.

Dilution Ratios of Nitrocellulose Solvents[1]

By J. G. Davidson and E. W. Reid

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A continuation of previous work[2] discussing, in addition to the usual aromatic hydrocarbon diluents, a number of experiments carried out with various types of gasoline.

THE dilution ratio of a nitrocellulose solvent is a measure of its solvent power and is obtained by dividing the volume of diluent that must be added to cause incipient precipitation of the nitrocellulose by the volume of solvent in which the nitrocellulose is dissolved, or

$$\frac{Vd}{Vn} = \text{D. R.}$$

where Vd = volume of diluent
Vn = volume of solvent

It therefore corresponds to the solvent-power numbers of Mardles,[3] who defines them as "the volume of the liquid (diluent) in cc. required to begin precipitation from 1 cc. of a 5/100 concentration sol."

Determination of Dilution Ratios

The dilution ratio (D. R.) will vary with the following factors: (1) solvent, (2) diluent, (3) temperature, (4) type of nitrocellulose, and (5) concentration of nitrocellulose. For the purpose of this paper variables (3) and (4) have been eliminated by using the same type of nitrocellulose and by working with all solutions at a temperature of approximately 20° C. The influence of variable (5) is described briefly at the end of the paper, but with this exception all solutions from which data were derived contained the same concentration of nitrocellulose. The procedure was approximately the same as reported before,[2] although the concentration of nitrocellulose was somewhat greater for these experiments. It consisted simply in dissolving 2.5 grams of dry $^1/_2$-second nitrocellulose in 7.5 grams of solvent. After solution was complete the diluent was carefully added with vigorous stirring until precipitation of nitrocellulose was just evident.

Some investigators maintain that results determined in this manner are subject to error because the solutions become supersaturated and there is considerable lag in the appearance of the precipitate even though the true dilution ratio has been exceeded. In order to obtain a true measure of the solvent power it is proposed to start with nitrocellulose and a diluent to which mixture solvent is gradually added with stirring until the nitrocellulose just dissolves. Another advocated method involves the production of various mixtures of solvent and diluent. The solvent power of each mixture is determined and the composition of the mixture which is just able to dissolve the nitrocellulose is noted. The ratio of the diluent to true solvent in this mixture may also be called the dilution ratio.

The authors have experimented with all three methods and find no great difference in the results. Certainly the relative rating of the various solvents by each method is the same.

Results

Table I shows that the ethers of the glycols have in general better dilution ratios than the butyl esters with respect to benzene, toluene, and xylene. Figure 1 expresses the same information in a graphic manner. The numbers in the tables and at the bottom of the charts correspond with the numbers shown opposite the list of compounds below:

NUMBER FOR TABLE I		NUMBER FOR CHARTS
1	Methyl ether of ethylene glycol	1
2	Methyl ether of propylene glycol	1
3	Ethyl ether of ethylene glycol	2
4	Ethyl ether of propylene glycol	2
5	Propyl ether of ethylene glycol	3
6	Propyl ether of propylene glycol	3
7	Isopropyl ether of ethylene glycol	4
8	Butyl ether of ethylene glycol	5
9	Butyl ether of propylene glycol	5
10	Isobutyl ether of ethylene glycol	6
11	Isobutyl ether of propylene glycol	6
12	Isoamyl ether of ethylene glycol	7
13	Isoamyl ether of propylene glycol	7
14	Ethylene glycol monoethyl ether acetate	8
15	Butyl acetate	9
16	Secondary butyl acetate	10
17	Butyl propionate, commercial	11

On the charts, the dotted lines represent the ethers of propylene glycol and the numbers refer to the same alkyl

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[1] Presented by J. G. Davidson under the title "Diluents and Dilution Ratios" as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] THIS JOURNAL, **18**, 669 (1926).

[3] *J. Soc. Chem. Ind.*, **42**, 129T (1923).

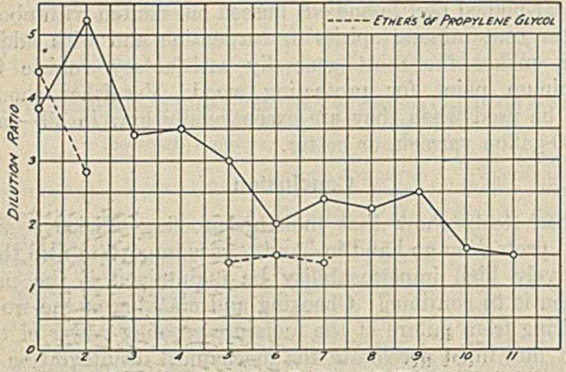

Figure 1—Dilution Ratio with Toluene

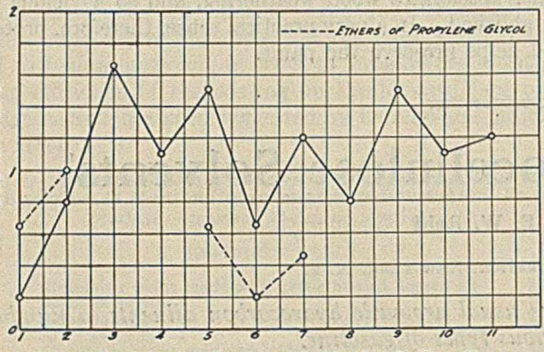

Figure 2—Dilution Ratio with 80–120° C. Gasoline

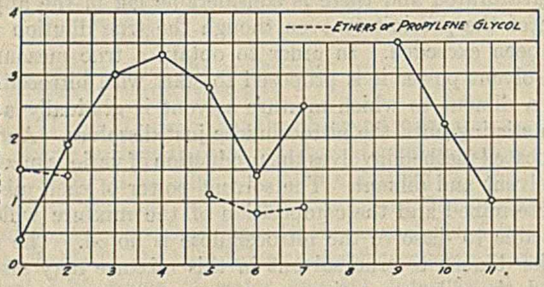

Figure 3—Dilution Ratio with Turpentine

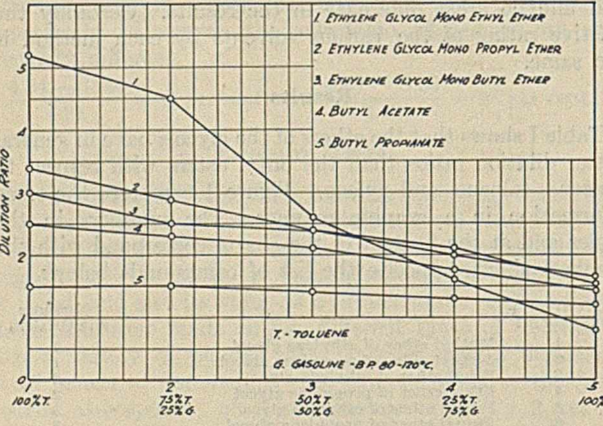

Figure 4—Decrease in Dilution Ratio as Gasoline Is Added

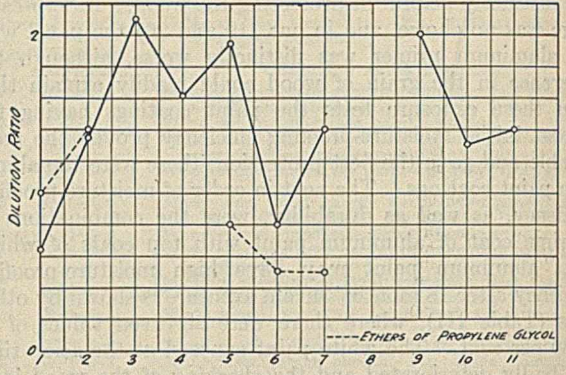

Figure 5—Dilution Ratio with Vapor-Phase Cracked Gasoline (50–221° C.)

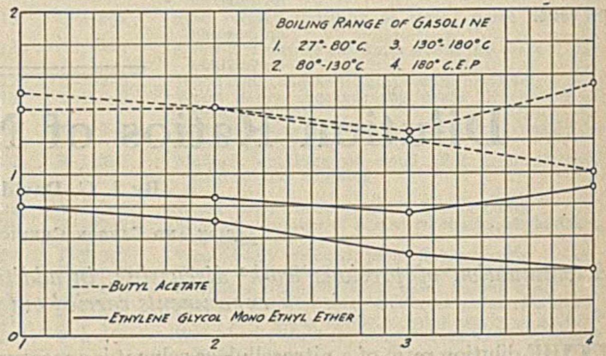

Figure 6—Variation of Dilution Ratio with Boiling Range of Gasoline—25 Per Cent Nitrocellulose Solution

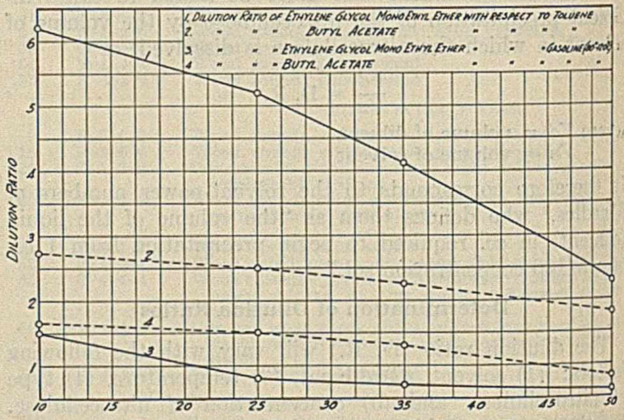

Figure 7—Effect of Nitrocellulose Concentration on the Dilution Ratio

group as in the case of ethylene glycol. For example, point 5 on the dotted line represents the dilution ratio for the monobutyl ether of propylene glycol.

Variation in Solvents

McBain[4] and his co-workers maintain that the value of a solvent can be determined by the apparent viscosity of the solution produced by dissolving cellulose nitrate in the solvent. He defines the apparent viscosity as "the logarithm of the viscosity of the (cotton) solution divided by that of the solvent calculated per gram of nitrocotton in 100 grams of solvent." The present writers have not yet investigated the solvent power of the glycol ethers by this method, but certain observations have convinced them that neither this generalization nor the following, to which both Mardles and McBain subscribe—"Within any homogeneous series the lower the molecular weight the greater the solvent power"—will fit all cases set forth in this paper. Table I bears out in general the assumption that the higher members of any homologous series are poorer solvents than the members of lower molecular weight. For example, when the dilution ratio with respect to toluene is taken as a criterion, ethylene glycol monobutyl ether is a poorer solvent than ethylene glycol monoethyl ether, and in turn propylene

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[4] *J. Phys. Chem.*, **30**, 312 (1926).

Table I—Dilution Ratios of Nitrocotton Solutions

Diluent	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
AROMATICS																	
Benzene	4.3	3.7	4.8	2.7	3.0		3.2	2.6	1.2	1.5	1.2	2.2	2.4		2.6	1.5	1.3
Toluene	3.8	4.4	5.2	2.8	3.4		3.5	3.0	1.4	2.0	1.5	2.4	1.4	2.2	2.5	1.6	1.5
Xylene	2.4	3.5	4.0	2.8	3.6		2.8	2.8	1.5	2.0	1.3		1.4		2.4	1.5	1.4
Turpentine	0.4	1.5	1.9	1.4	3.0		3.3	2.8	1.1	1.4	0.8	2.5	0.9		3.5	2.2	1.0
GASOLINES																	
(1) Straight-run Pennsylvania	0.2	0.4	0.6	0.8				1.2	0.4						1.3		
(2) Straight-run midcontinent	0.2	0.5	0.6	0.8			1.4	0.5							1.3		
(3) A. No. 1 gulf	0.2	0.5	0.6	0.8	1.5	0.6	0.9	1.4	0.5	0.7	0.3	0.9	0.4		1.4	1.0	1.2
(4) Coastal naphtha	0.2	0.5	0.6	0.9	1.4	0.7	1.0	1.4	0.5		0.4	1.1	0.4		1.5	0.9	1.2
(5) Vapor-phase cracked	0.6	1.0	1.3	1.4	2.1	1.0	1.6	1.9	0.8	0.9	0.5	1.4	0.5		2.0	1.3	1.4
(6) Venezuela naphtha	0.2	0.5	0.5	0.8	1.2	0.7	0.9	1.4	0.5		0.3	1.1	0.4		1.5	0.9	1.2
(7) California naphtha	0.2	0.4	0.5	0.7				1.3	0.6						1.3		
(8) 500 type pressure still distillate (435° F., 224° C.)	0.2	0.5	0.7	0.9	1.3	0.9	1.0	1.6	0.6	0.8	0.4	1.2	0.5		1.5	1.0	1.2
(9) 300 type pressure still distillate heavy (435° F., 224° C.)	0.1	0.5	0.5	0.7	1.0	0.8	0.8	1.1	0.6		0.3	1.2	0.4		1.3	0.9	1.0
(10) Straight-run (80-120° C.)	0.2	0.6	0.8	1.0	1.6	0.7	1.1	1.5	0.6	0.6	0.3	1.2	0.4	0.8	1.5	1.1	1.2
25% Toluene 75% Gasoline (10)	0.4	0.9	1.6	1.3	2.0	1.1	1.5	2.2	0.9	1.1	0.5	1.7	0.6		1.7	1.4	1.3
50% Toluene 50% Gasoline (10)	0.9	1.8	2.6	1.9	2.4	1.3	2.3	2.4	1.0	1.3	0.7	1.8	0.8		2.1	1.5	1.4
75% Toluene 25% Gasoline (10)	2.7	3.5	4.5	2.7	2.9	1.8	2.5	2.4	1.4	1.6	0.9	1.9	0.9		2.3	1.7	1.5

glycol monobutyl ether is a poorer solvent than ethylene glycol monobutyl ether. A superficial observation of the relative viscosities of the test solutions leads to the same conclusions.

With turpentine or gasoline as the diluent the results are much more erratic. The glycol ethers then vary greatly among themselves, but even under these conditions the normal propyl and butyl ethers of ethylene glycol have dilution ratios that are equal to or better than the ratios for the butyl esters (Figures 2 and 3).

Certainly—at least as far as the dilution ratios with gasoline are concerned—the normal propyl and butyl ethers are better solvents than the ethers of lower molecular weight, and in the case of the methyl and ethyl compounds the ethers of propylene glycol are better solvents than the ethers of ethylene glycol. These results are opposed to the assumption that in a homologous series the compounds of higher molecular weight are the poorer solvents. It should also be noted (Figure 2) that the secondary ethers are poorer solvents than the normal ethers.

The dilution ratios with the gasolines are almost invariably smaller than with the aromatic hydrocarbons. For the glycol ethers the differences are more pronounced than for the butyl esters. Figure 4 shows the decrease in dilution ratios, starting with 100 per cent toluene as a diluent and proceeding to 100 per cent gasoline.

Since the dilution ratio may be taken as a measure of solvent power, all other factors being discarded, the value of a diluent is proportional to the dilution ratio in which it plays a part. Thus in the case of the monoethyl ether of ethylene glycol, which has a dilution ratio of 5.2 for toluene and 0.8 for gasoline, the toluene is worth about six times the price of gasoline as a diluent. When butyl acetate is the solvent chosen, toluene is worth only about twice as much as gasoline, for the respective dilution ratios are then only 2.5 and 1.5.

This is important in the production of thinners for automobile base lacquers. If the thinner used is not a true solvent for nitrocellulose, drowning of the base lacquer with the thinner will result in the precipitation of small aggregates of nitrocotton that will not quickly go into solution again and are liable to interfere with the action of the spray gun or mar the lacquered surface on which they are deposited.

Variation in Gasolines

Attention should also be drawn to the great variation in the dilution ratios of a given solvent with different types of gasoline. Thus, the dilution ratio of the monoethyl ether of ethylene glycol is 1.3 with respect to a vapor-phase cracked gasoline, while it is only 0.6 for a straight-run Pennsylvania gasoline of the same approximate boiling range (Table I). The obvious explanation seems to be in the high content of aromatic hydrocarbons in the vapor-phase cracked gasoline (Tables II and III). Many of the cracked gasolines have very pronounced odors which militate against their use in lacquers, and even though straight-run gasolines are inferior from the standpoint of dilution ratios, they will no doubt continue to be used owing to their lack of obnoxious odor.

Table II—Distillation Ranges of Gasolines

Gasoline	1	2	3	4	5	6	7	8	9	10
Barometer, mm.	749	749	743.9	743.9	743.9	746.8	746.8	746.8	745.7	745.7
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Initial boiling point	48	45	52	71	50	58	63	58	85	78
% off										
10	80	74	87	102	83	95	135	94.3	160	83
20	91.5	88	101	110	96	109	149	115	189	84
30	101	100	115.5	118.5	109	119	159	144	206.5	86
40	109.5	112	127	128.5	122	128	167	163	220	87.5
50	119	125	137.5	142	135	137	174	179	232.5	90
60	129.5	138.5	148	155.5	150	147	181	190.5	240.5	91.5
70	141.5	152	159	166.5	166	157	189.5	200	250	94
80	158	165.5	171.5	179	182	169	198	208	261	97
90	186.5	183.5	190	194	198	185	209	218	276.5	102
95	218	201	205	206.5	216.5	199	219	228	280	107
98	221	213	218	218	221	211	229	237		121.5

Table III—Comparison of Dilution Ratios of Straight-Run and Cracked Gasoline Fractions

BOILING RANGE OF FRACTION ° C.	DILUTION RATIOS 75% Ethylene glycol monoethyl ether 25% Nitrocotton	 75% Butyl acetate 25% Nitrocotton
	STRAIGHT-RUN GASOLINE	
27 to 80	0.8	1.4
80 to 130	0.7	1.4
130 to 180	0.5	1.2
180 to E. P.	0.4	0.9
	CRACKED GASOLINE	
27 to 80	0.9	1.5
80 to 130	0.8	1.4
130 to 180	0.7	1.3
180 to E. P.	0.9	1.5

In general, it will not be possible to use gasolines with heavy ends, as they will not only slow down the rate of drying in a lacquer film but, as gasoline is not a solvent for nitrocellulose, they will unbalance the solvent mixture toward the end of the drying period, with consequent precipitation of the nitrocellulose. Gasoline 10 (Table II) is a low-boiling fraction of straight-run gasoline having a boiling range between 80° and 120° C., which seems to approximate the type of gasoline usable in lacquer work. This gasoline gave most of the solvents a better dilution ratio than was obtained with a gasoline of higher boiling range. Tests were therefore conducted with various fractions of gasoline, and in general the lower boiling fractions were found to work out better from the standpoint of dilution ratios (Figure 6).

Effect of Concentration of Nitrocellulose

The figures in Figure 7 are of interest in connection with the influence of the nitrocellulose concentrations upon the dilution ratio. The dilution ratio of a concentrated solution of nitrocellulose is much lower than that of a dilute solution, confirming the observations of Mardles, who reached the same conclusion with respect to cellulose nitrate dissolved in acetone.

Conclusions

1—The dilution ratio is a reasonably accurate measure of solvent power.

2—Other conditions remaining the same, the dilution ratios of nitrocellulose solvents are greater with respect to the aromatic hydrocarbons than to gasolines.

3—The glycol ethers have better dilution ratios with respect to the aromatic hydrocarbons than the butyl esters. With respect to gasoline the ratios are approximately equal.

4—Cracked gasolines are better diluents than straight-run gasolines of the same boiling range.

5—The lower boiling fractions of a given gasoline are better diluents than the higher boiling fractions.

6—The dilution ratio decreases as the concentration of nitrocellulose is increased.

The Effect of Thinners upon the Consistency of Nitrocellulose Solutions[1]

By P. E. Marling and J. M. Purdy

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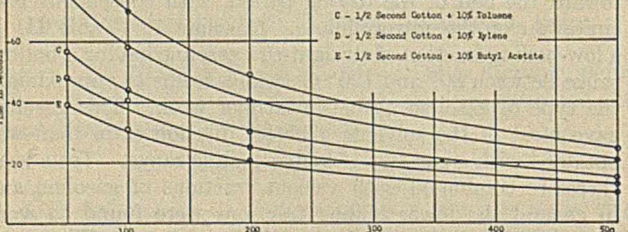
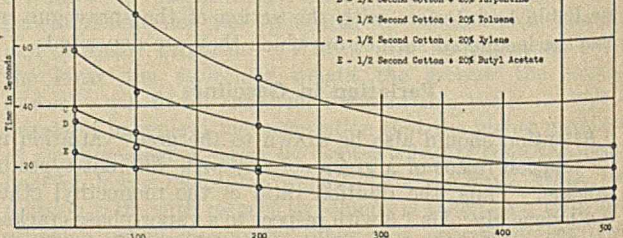
The purpose of these experiments was to determine the effect of the addition of different thinners and various amounts of the same thinner upon the consistency of nitrocellulose solutions. These nitrocellulose solutions contained 25 per cent nitrocellulose and 75 per cent solvent. The solvent was 50 per cent ethyl alcohol and butyl acetate, and 50 per cent toluene, by volume. The addition of the thinners was based on the volume of the original solution. Thus, 60 cc. of thinner were added to 600 cc. of the original solution, for a 10 per cent addition of thinner. Increasing amounts of thinner were used until the nitrocellulose precipitated out of solution and would not go back into solution upon stirring. In the case of butyl acetate thinner, which is a solvent for the nitrocellulose and therefore does not precipitate the nitrocellulose, the percentage was carried to 50.

The consistency was measured with a mobilometer as described by Gardner[2] and Parks. The weight of the plunger of the mobilometer was 151 grams and the measurements were made using additional weights (50, 100, 200, and 500 grams) which were placed on top of the plunger. The experiments were made in a constant temperature room at 25° C.

Tables I, II, and III show the effect of adding different percentages of turpentine, toluene, xylene, and butyl acetate to 1/2-, 4-, and 10-second nitrocellulose solutions, respectively.





Figures 1 to 4 show in a graphic manner the effect of adding the same percentage of turpentine, toluene, xylene, and butyl acetate to 1/2-second nitrocellulose solution. The turpentine could only be carried to 35 per cent; therefore this thinner is not shown in Figure 4. These curves are representative of the results obtained with 4- and 10-second nitrocellulose solutions when thinned in the same proportion as the 1/2-second nitrocellulose solution.

Summary

(1) The consistency of 1/2-, 4-, and 10-second nitrocellulose solutions is reduced by increasing the amounts of thinner. No exceptions to this general rule were observed.

(2) Butyl acetate, which is a solvent for the nitrocellulose and was used as a blank to compare the results of the turpentine, toluene, and xylene, has the greatest effect in reducing the consistency of the solutions.

(3) Turpentine has the least effect in reducing the consistency and not more than 35 per cent could be added to any of the original nitrocellulose solutions.

(4) Toluene and xylene are very similar in their effect on reducing the consistency of the nitrocellulose solutions. Percentages from 5 to 40 of xylene with 1/2-second nitrocellulose solution reduced the consistency more than the same percentages of toluene. The opposite effect was observed with 4-second nitrocellulose solution as 5, 20, 30, 40, and 45 per cent of toluene reduced the consistency more than the same percentages of xylene. The 10 per cent addition of thinner was an exception to this observation in the 4-second nitrocellulose solution. The consistency of the 10-second nitrocellulose solution was reduced more with xylene than

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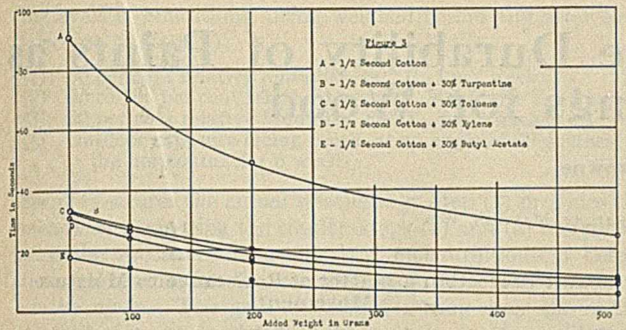
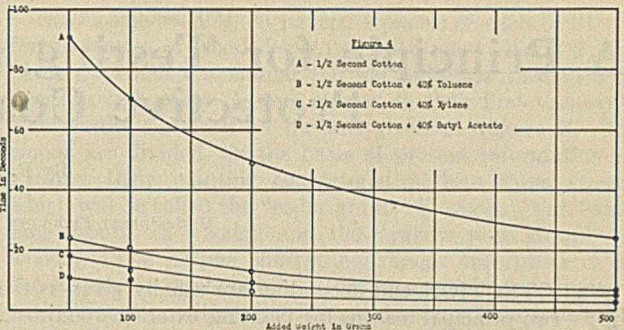
[1] Presented as a part of the Symposium on Lacquers, Surfacers, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Paint Mfrs.' Assocn. U. S., Tech. Circ.* **265**; see also This Journal, **19**, 724 (1927).





with toluene. Values were obtained as high as 40 per cent toluene and 30 per cent xylene with the 10-second nitrocellulose solution.

Table I—1/2-Second Nitrocellulose

Added Weight *Grams*	Nitrocellulose Solution *Seconds*	Turpentine *Seconds*	Toluene *Seconds*	Xylene *Seconds*	Butyl Acetate *Seconds*
		5%	5%	5%	5%
50	91	83	71	65	59
100	70	64	56	49	47.5
200	49	45	36.5	35	32
500	24	22	19	17	17
		10%	10%	10%	10%
50		76	57	48	39
100		58.5	44	41	31
200		40.5	30	25	21.5
500		20.3	15	13	10.5
		20%	20%	20%	20%
50		58.7	39	35	25
100		44.5	30	26.5	19.5
200		33.7	18.7	18	13.5
500		17	10	10	7
		30%	30%	30%	30%
50		33.2	31	31	18.5
100		27	26.7	24	14.2
200		20	17	16	9.5
500		10	8.7	8	5
			40%	40%	40%
50			24	18	11.5
100			20.7	13	10
200			13	9	6
500			6	5	3
		35%	45%	45%	50%
50		28.2	23.5	12.7	7
100		26	16.5	10	6
200		15	10	7	4
500		8	6	4	3

Table II—4-Second Nitrocellulose

Added Weight *Grams*	Nitrocellulose Solution *Seconds*	Turpentine *Seconds*	Toluene *Seconds*	Xylene *Seconds*	Butyl Acetate *Seconds*
		5%	5%	5%	5%
50	412	359	317	325	287
100	317	293	260	225	204
200	213	203	202	160	139
500	94	93	90	65	60
		10%	10%	10%	10%
50		290	279	216	215
100		225	211	189	166
200		151	136	124	112
500		69.5	60.5	56	50.5
		20%	20%	20%	20%
50		242	176	192	125
100		186	140	151	95
200		124	88	97	59
500		54	46.5	44	27
		30%	30%	30%	30%
50		191	102	141	91
100		155	88	99.5	63
200		100	54	65	42
500		44.5	24.5	31.7	18
			40%	40%	40%
50			91	121	50
100			61	81	34.5
200			43	56.5	23.5
500			18	24	10
		35%	45%	45%	50%
50		136	76	112.5	27
100		103.5	55	76	22
200		70	31	53.5	13.5
500		33	15	22.5	7

Table III—10-Second Nitrocellulose

Added Weight *Grams*	Nitrocellulose Solution *Seconds*	Turpentine *Seconds*	Toluene *Seconds*	Xylene *Seconds*	Butyl Acetate *Seconds*
		5%	5%	5%	5%
50	932	657	710	684	570
100	707	559	575	546	414
200	472	396	372	324	291
500	201	169	168	156	127
		10%	10%	10%	10%
50		578	547	496.5	455
100		415	404	349.5	348
200		295	296	224	231
500		140	130	110	103
		20%	20%	20%	20%
50		422	373	372	227
100		334	295	276	160
200		204	189	197	109
500		104	85	83	52
		30%	30%	30%	30%
50		321	243	224	144
100		274	192	170.5	115
200		170	130	118.5	77
500		70	68	51	32
		35%	40%	40%	50%
50		315	194	103	75
100		228	136	70	58
200		155	98	45	39
500		69	38	21	18

Tariff Duty on Chemicals

Cresylic Acid—By Presidential proclamation the tariff duty on cresylic acid has been decreased from 40 per cent ad valorem and 7 cents per pound to 20 per cent ad valorem and 3¹/₂ cents per pound. The reduction was made upon recommendation of the Tariff Commission, which conducted hearings and made an investigation of costs of production in the United States and Great Britain, which is the principal competing country. The domestic production in 1925 was estimated at about 1,600,000 gallons. Imports for the same period were about 965,000 gallons.

Fluorspar Duty—On July 22 and 23 the Tariff Commission conducted hearings in the fluorspar cost of production investigation. The investigation was instituted by the Commission upon application of James A. Green, Cincinnati, Ohio, and the Lungren Stevens Co., Chicago, Ill., who requested a 50 per cent increase in the present duties on imported fluorspar. Witnesses for the complainants testified that they have been shut out of eastern markets, and that foreign producers of fluorspar were crowding them out of the Pittsburgh steel district. They stated that an increase in tariff rates would not result in an increase in price, but would have the effect of increasing domestic production.

C. A. Buck, vice president of the Bethlehem Steel Company, appeared in opposition to this increase, and claimed that it would result in a discriminatory burden upon eastern steel manufacturers. He claimed that eastern steel producers are dependent upon the imported product because of the greater transportation cost of the domestic product to them. It was his opinion that increased tariff would not result in an increased domestic production, but would have a tendency to decrease English importations and increase those from Germany and probably other foreign countries. He admitted that the English had an advantage of $2.50 per ton in the production of fluorspar over domestic producers. However, he does not believe that, even if an increase of $2.50 per ton were granted, the domestic producers could compete with the foreigners because of transportation costs between Kentucky and southern Illinois producing points and points on the Atlantic seaboard.

A Principle for Testing the Durability of Paints as Protective Coatings for Wood[1]

By F. L. Browne

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The purpose of this paper is to set forth the basic principle of a technic for measuring, independently of the personal bias of the operator, the degree of protection afforded by paint coatings against the weathering of wood and the change in their protective power as the coatings themselves deteriorate during exposure. Illustrative data are taken from experiments, some of which were started more than six years ago with equipment and routine designed for a somewhat different purpose. Details of the experimental procedure are being improved materially in the work now in progress, but the fundamental principle remains the same. Discussion of minor changes in method and comparison of results obtained with paints of specified composition are reserved for future publication; for the present purpose the composition of the three paints used in obtaining the illustrative data is unimportant.

PROTECTION and decoration are usually given as the two principal reasons for painting exterior woodwork. The paint industry considers protection so important that its coöperative advertising slogan is based upon that idea. Yet, in the many paint exposure tests on wood that have been conducted during the last quarter-century, the investigators have been content with describing roughly the changes in such properties of the paint film as gloss, opacity, dirt collection, fading, chalking, checking, cracking, flaking, and scaling. Attempts to integrate the results into a general judgment of the condition of the coating and to fix the end point of its service life have failed of acceptance because of the inability of different workers to agree on the significance and relative importance of the several factors involved. No serious effort has been made to determine experimentally how long coatings continue to protect wood against deterioration. On the contrary, paint technologists in their tests are prone to ignore completely such evidences of wood-weathering as wood checks, loose grain, cupping, warping, and loosening of nail fastenings, on the ground that they are "wood defects," not "paint defects." Even the failure of paint over the summerwood earlier than that over the neighboring springwood is sometimes dismissed as "wood defect" and, when traditional painting methods are found to give less satisfactory coatings on some kinds of wood than on others, the poor results are likely to be ascribed to the "refractory nature of the wood" rather than to inappropriate painting procedure.

The writer does not purpose to exaggerate the importance of protection as the object in painting wood. Perhaps decoration is a motive so much more urgent that paint technologists may be justified in paying very little attention in their tests to protection; that is a point to be decided by psychological rather than by technological inquiry. But as long as the paint industry insists upon and the paint user acquiesces in the view that protection is one of the major, if not the major, reason for painting, it seems to be incumbent upon technologists conducting paint tests to devise some method for measuring the length of time coatings guard wood against the elements.

Paint Protection a Matter of Resistance to Moisture Movement

The weathering of wood and its prevention by paint coatings were first studied theoretically by Tiemann[2] and experimentally by the author.[3] Weathering is attributed principally to the disintegrating effect of internal stresses set up in the wood as the result of fluctuating moisture content of those portions exposed directly to the weather. The hygroscopic, swelling character of wood and the slow transfusion of moisture through it give rise to a "working" of the wood near the exposed surface against the more sluggishly changing interior. Other factors, such as mechanical abrasion and photochemical oxidation of the cellulose, doubtless play parts in the weathering process, but swelling and shrinking in response to changing atmospheric conditions are thought to take the leading part.

Paint coatings protect wood against weathering by retarding the passage of moisture into or out of the wood sufficiently to damp out extreme fluctuations in moisture content near the surface. They need not prevent transfusion completely. It is impossible to say as yet just how retardant to moisture coatings must be; this probably depends upon various extrinsic factors, such as species of wood and climatic conditions. But, as will be seen, it is not necessary to fix the degree of retardation exactly in order to apply the technic suggested herein to the comparison of the protective values of different paints when applied to wood.

Measuring Moisture-Retarding Effectiveness

Thus moisture-retarding effectiveness of paint coatings is the physical property upon which their protective value for wood depends, and a means for following changes in that property during the life of coatings should constitute a measure, at least for comparative purposes, of their durability as protective agents. Dunlap[4] has described such a means which, essentially, is the technic of the investigation here reported.

In carrying out this technic, wood specimens $^{5}/_{8}$ by 4 by 8 inches (1.6 by 10 by 20 cm.), with all sharp edges and corners rounded off, are seasoned in a room at 60 per cent relative humidity and 80° F. (27° C.) and are coated similarly on all surfaces. They are then subjected repeatedly to the follow-

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[1] The principle for paint testing herein suggested, together with a part of the data, was presented before the Midwest Regional Meeting and the Meeting of the Section of Paint and Varnish Chemistry of the American Chemical Society, Madison, Wis., May 27 to 29, 1926. The first draft of a paper on the subject was received in the office of This Journal, June 11, 1926.

[2] *Sci. Am.*, **130**, 314 (1924); see also Browne, *Am. Paint J.*, **9**, 56 (1925); and *Drugs, Oils, Paints*, **41**, 88 (1925).

[3] *Paint Mfrs.' Assocn. U. S., Tech. Circ.* **238**, 289 (1925).

[4] This Journal, **18**, 1230 (1926); *Mech. Eng.*, **48**, 1457 (1926).

ing cycle of conditions, being weighed before and after each exposure to step (2):

(1) 60 per cent relative humidity, 80° F., for 2 weeks
(2) 95 to 100 per cent relative humidity, 80° F., for 2 weeks
(3) 60 per cent relative humidity, 80° F., for 2 weeks
(4) Outdoor exposure facing south, at an angle of 60 degrees[5] to the horizontal, for 6 weeks

Step (4) secures the actual weathering; step (2) provides the means for measuring the result; steps (1) and (3) merely return the specimens to a standard moisture content before their reëxposure to the conditions of the other two parts of the cycle. The gain in weight during step (2) is the amount of moisture absorbed through the coating. Plotting moisture absorbed against time of exposure to the outdoor weathering conditions gives a graphical representation of the history of the coating, and comparison of the moisture absorbed through different coatings shows their relative effectiveness in protecting wood against weathering. As will be shown later, the moisture absorption by an adequately coated panel is a characteristic of the coating and not of the wood, at least until the coating has begun to disintegrate seriously, so that within the experimental error a given paint allows the same absorption regardless of the wood on which it is applied.

Note—Dunlap computes the "efficiency" of the coating by subtracting the absorption by the coated panel from that by uncoated panels of the same wood, expressing the difference as a percentage of the absorption by uncoated wood. That procedure is more elegant than the method employed here and is reasonably convenient when studying different coatings on the same kind of wood. It becomes cumbersome and confusing, however, when the same coating is studied on different woods, because, although the permeability of the coating may be independent of the wood, the base of the percentage calculation is not.

Typical Results

Figure 1 is constructed from data obtained by Dunlap[6] in the course of a study of moisture-retardant finishes for aircraft propellers. Yellow birch panels were employed, two of them painted with three coats of a widely used type of white house paint which will be designated paint *A*, two painted with paint *A* using slightly different reductions with oil and thinner for the priming and second coats, and two painted with three coats of another white paint representative of common practice, which is designated as paint *B*. The panels with paint *A* were in the test cycle from October, 1921, to June, 1926; those with paint *B* from November, 1921, to November, 1926. Of that period of approximately 5 years about 2$^1/_2$ years were spent in step (4) of the test cycle, the rest of the time in steps (1), (2), and (3). Figure 2 shows the exposed faces of the panels at the end of the test.

Both types of paint at first became less permeable to moisture on aging, and at their maximum effectiveness (the minimum of the curves) they differed from each other only very slightly in this quality. Paint *B* retained its maximum resistance to the passage of moisture for a fairly long time, however, whereas paint *A* soon began to fall off and continued to become increasingly permeable during the rest of its history.

Chalking became noticeable earlier in the case of paint *A* than in that of paint *B*, but in both cases it antedated materially the beginning of deterioration in effectiveness of the coating as measured by the moisture absorption. Disintegration of the coating, leaving bare areas of wood readily visible to the unaided eye, also began earlier with paint *A* than with paint *B*. With paint *B* disintegration was a close precursor of loss in moisture-retarding effectiveness, but with paint *A* the resistance of the coating to moisture decreased materially before disintegration began.

In December, 1924, 84 panels, 4 panels of each of 21 different species of wood, 2 painted with paint *A* and 2 with paint *C*, which was similar but not quite identical in composition with paint *B*, were started in their first test cycle. The results obtained so far are given in Figure 3. The woods are divided, on the basis of present information regarding their painting characteristics, into three groups, which will be called the "cedar group" (7 woods), the "white pine group" (8 woods), and the "yellow pine group" (6 woods). The graphs show the average absorption of all the panels in each of these groups, which were painted with paint *A* or with paint *C*, respectively. Thus each point in the figure represents an average value for 14, 16, or 12 test panels depending upon whether it is the "cedar," "white pine," or "yellow pine" group.

As far as they have gone, the new experiments give results very similar to the old ones. Both paints reached a minimum moisture absorption, of roughly 6 grams per panel, after about 24 weeks' exposure. Paint *A* then began to become more permeable while the permeability of paint *C* remained practically unchanged. The species of wood, therefore, seems to affect the resistance of the coating to moisture only very slightly, if at all, during the early part of its history, which is in confirmation of Dunlap's previous findings. Later, however, the influence of the wood apparently begins to express itself and the three wood groups give evidence of separating, the decline in resistance of the coating to moisture being more rapid on the yellow pine group than on the white pine group, and least rapid on the cedar group. Some such development should be expected since we know that the common painting method employed for all the woods is best adapted to the characteristics of the cedar group and least well adapted to those of the yellow pine group.

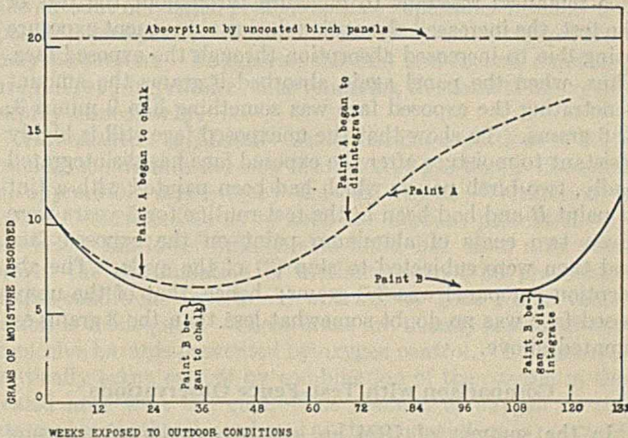

Figure 1—Variation, under Weathering, in the Moisture-Retarding Property of Paints on Yellow Birch Panels

Chalking began on all the panels during the third 6-week period of exposure to the weather—that is, somewhat before the coatings seemed to have attained their minimum permeability. Very little coating disintegration has been observed thus far. Of the 84 panels, 74 are rated "good" with respect to coating integrity, 5 with paint *C* and 3 with paint *A* are rated "fair," and 2 with paint *C* are rated "poor" in this respect. (All the 6 panels in Figure 2 are rated "bad.")

At the end of 60 weeks' exposure to the weather there was clear evidence of wood-weathering in a number of panels on which the paint coatings were rated "good" in integrity. Of the 42 panels with paint *A*, 29 showed no visible evidence of wood-weathering and had an average absorption of 9.0 grams per panel, while 13 panels with an average absorption of 11.2 grams showed distinct evidence of wood-weathering in the form either of wood checks or pronounced cupping.

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[5] 45 degrees would be better; see Walker, This Journal, 16, 528 (1924).

[6] Unpublished data of the Forest Products Laboratory.

Of the panels with paint *C*, 35 having an average absorption of 7.1 grams showed no evidence of wood weathering and 7 with an absorption of 8.7 grams showed some wood checking. It seems, then, that with woods which weather easily paint coatings cannot deteriorate in moisture-retarding effectiveness very much without becoming inadequate protective agents.

In considering Figure 3, remember that an absorption of 9 grams at the end of 60 weeks' exposure indicates a much greater permeability of the *exposed face* of the panel than the same absorption before exposure to the weather. The 9 grams absorbed at the beginning were divided evenly between the front and back surfaces (neglecting ends and edges), giving 4.5 grams per face. On aging, the coating became less permeable, until at its best only about 6.0 grams per panel or 3.0 grams per face were absorbed. The back or unexposed face remained resistant to moisture throughout the rest of the test, the increased absorption during subsequent exposure being due to increased absorption through the exposed face. Thus, when the panel again absorbed 9 grams the amount penetrating the exposed face was something like 9 minus 3, or 6 grams. To show that the unexposed face still is highly resistant to moisture after the exposed face has disintegrated badly, two birch panels which had been painted with a tint of paint *B* and had been in the test routine for 5 years were given two coats of aluminum paint on the exposed face and then were subjected to step (2) of the cycle. The absorption per panel was 3.6 grams; hence, that of the unexposed face was no doubt somewhat less than the 3 grams estimated above.

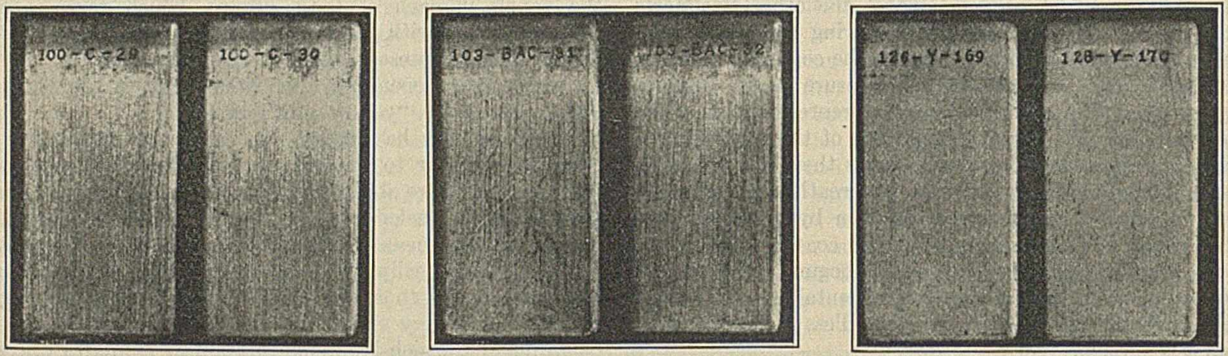

Figure 2—Panels of Figure 1 at End of Test. Panels 100-C and 103-BAC Painted with Paint *A*; Panels 126-Y Painted with Paint *B*

Comparison with Test-Fence Observations

In the summer of 1924 an extensive series of exposure tests,[7] using paints *A* and *C* on edge and flat grain surfaces of 18 of the woods already mentioned, were started on 11 test fences in as many different parts of the country. More than 700 panels were exposed. The writer inspects all of them at least once a year; those at Madison are observed at much shorter intervals. Before he was acquainted with the data now presented in Figures 1 and 3, and acting solely on the basis of visual inspection of these test fences, he had expressed the tentative opinion that although paint *C* as applied in this study showed signs of coating disintegration, especially on woods of the yellow pine group, earlier than paint *A*, nevertheless paint *C* seemed to afford adequate protection against wood weathering for a longer period than paint *A*. It was also clear that wood-weathering started in many panels before disintegration of the coating laid bare any appreciable areas of wood.

These opinions are not accepted by some paint technologists who have inspected one or two of the test fences in question. That, of course, is not surprising in view of the facts that test-fence inspections rely entirely upon the personal opinions of the inspector and that agreement between experts concerning results has never been possible in past experiments. The writer's opinions are given here because, having been formed before he had knowledge of the comparative history of the two paints in question with respect to moisture-retarding effectiveness, and agreeing in striking manner with the results of the absorption test, they constitute an experimental verification of the theory upon which the new technic of paint-testing is based.

That one of the protective functions of paint is the exclusion of moisture has long been accepted as a matter of theory, but to the best of the writer's knowledge no effort previous to Dunlap's had been made to find out how well the paints perform it and how long they retain their effectiveness. One or the other of the two very different assumptions following has been made, though neither seems to find clear-cut expression in the technical literature:

> (1) It is generally accepted that the protection which a paint film gives a structural surface depends on how completely the paint maintains an unbroken coating, adhering closely to the surface underneath. Protection continues to be maintained as long as the paint film does remain intact as an unbroken, closely adhering coating and protection is destroyed when and where a break occurs in the paint film which exposes the surface underneath to the action of the weather. * * * The protective value of the paint is its ability to maintain an unbroken, closely adhering coating and its degree of protection can be judged only by the extent to which it meets this requirement.[8]
>
> (2) Rub your fingers across the (painted) surface (of a frame house). If the paint comes off in a powdery substance, or shows signs of cracking, it is time to paint.[9]

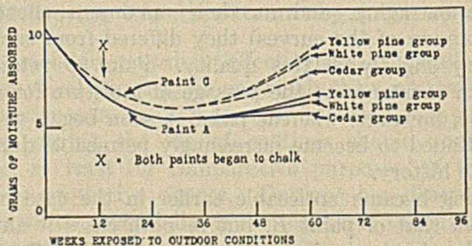

Figure 3—Variation, under Weathering, in Moisture-Retarding Property of Paints on Panels of 21 Different Woods

Even the limited data so far available seem sufficient to show that neither of these views can be accepted. Certainly, some paints continue to retard the absorption of moisture for a long time after they begin to chalk. On the other hand,

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Browne, *Paint Mfrs.' Assocn. U. S., Tech. Circ.* **219**, 124 (1924).

[8] From a letter to the Forest Products Laboratory from the research laboratory of a very large manufacturer in the paint industry.

[9] Back cover of *Save the Surface Magazine* for July, 1927.

some paints just as certainly fail to furnish adequate protection for the wood long before coating disintegration becomes noticeable. If paints are regarded seriously as protective coatings for wood, their durability in that respect must not be left to deduction from assumptions, but must be measured definitely. Although the routine herein suggested may be cumbersome, the principle involved is sound and a more convenient and more rapid technic embodying it is being developed in this laboratory.

Conclusions

1—Since paint coatings protect wood against weathering by retarding the exchange of moisture between wood and air, their durability as protective coatings can be measured by observing their effectiveness in retarding the absorption of moisture from saturated air by painted wood panels, at intervals during the exposure of the panels to the weather.

2—Paints of different composition may have very different life histories with respect to moisture-excluding effectiveness and neither the time of initial chalking nor of initial exposure of wood through coating disintegration can be relied upon as a general indication of the durability of the coating's effectiveness.

3—During the early part of the life history of an initially adequate protective coating the amount of moisture absorbed by coated wood panels is a characteristic of the coating rather than of the wood; that is, the absorption is about the same regardless of the kind of wood coated. During the latter part of the life history of the coating the influence of the wood becomes noticeable.

4—The observations of the change in moisture-excluding effectiveness during exposure confirm inferences previously drawn by the writer as a result of his inspections of test fences on which panels of the same woods and paints were exposed. In the test-fence results indications of the deterioration in moisture-excluding effectiveness of the coatings were given by the obvious beginning of wood-weathering under coatings that still remained intact.

Oxygen Required for the Propagation of Hydrogen, Carbon Monoxide, and Methane Flames[1]

By G. W. Jones and G. St. J. Perrott

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

GENERALLY speaking, three factors are essential for the development of gas or dust explosions: (1) combustible substances, (2) oxygen supply, and (3) igniting source. The elimination or proper control of any one of these may be used as a means of preventing explosions.

The combustible substances usually contain hydrogen, or combinations of the two, and may be in the form of gases or dusts. Sulfur, usually in the form of a sulfide, and the metallic dusts, such as aluminum powder, are also capable of developing explosions.

The oxygen supply is generally that furnished by the air present. Normal air consists of 20.93 per cent oxygen, 0.03 per cent carbon dioxide, and 79.04 per cent nitrogen by volume. The nitrogen includes small amounts of the rare gases argon, neon, and krypton.

The igniting sources are gaseous or solid substances which are maintained at a temperature sufficiently high for a period long enough to ignite the gas mixture in question. A heated substance, gaseous or solid, several hundred degrees above the ignition temperature of the gas under investigation will fail to ignite the gas if the period of application of this heat is too short. On the other hand, a heat source at or only a few degrees above the ignition temperatures will ignite the mixture, provided the application of the heat is sufficiently long in duration. Ignition by flames is one of the most certain and positive methods for igniting gas mixtures. Other sources of ignition are electric sparks, arcs, and incandescent materials. Any of these, if of sufficient temperature and duration, will ignite explosive mixtures.

Methods of Preventing Explosions

Confining our attention to gases, and more especially those found in mines, the engineer has the choice of three methods of preventing explosions: (1) He may eliminate the accumulation of gas so that the proportions present never reach a percentage high enough to become explosive; (2) he may remove all possible sources of ignition; and (3) he may control the amount of oxygen present so that explosions become impossible, irrespective of the amount of combustible gas that may be present. In general, the first and second requisites are followed in practice, thus rendering the control of oxygen supply unnecessary.

Ventilation of Mines—Under normal conditions of coal-mining, methane is the only combustible gas that is liberated in appreciable amounts by the coal strata. Ventilation is usually controlled so as to keep the amount present in the air below the lower inflammable limit, but cases may arise where the accumulation of methane cannot be prevented. These conditions arise in old workings or gobs where ventilation is inadequate. These areas are usually sealed off and explosive hazards prevented by oxygen control. This is automatically taken care of by combination of the oxygen in the sealed area with the coal. The amount of oxygen in the atmosphere is thereby reduced so that the mixture is rendered non-explosive. As will be shown later, when the oxygen present in atmospheres containing methane is reduced to 12 per cent, all mixtures of methane are rendered non-explosive.

Under abnormal conditions in mining—as, for example, after mine explosions, mine fires, or through liberation of gases from explosives used in mining—other combustible gases are added to the mine atmosphere. Hydrogen and carbon monoxide may be present as partial combustion products along with varying proportions of black damp (carbon dioxide and nitrogen). The question arises—to what extent must the oxygen in such atmospheres be reduced to render the atmosphere non-explosive? This is of particular importance in the case of mine fires where sections of a mine are sealed, where fire is in progress, in order that safe and efficient recovery work of the sealed area may be carried out.

These gases from mine fires may contain rather large proportions of hydrogen and carbon monoxide, especially soon after closing the area under fire.

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[1] Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927. Published with approval of the Director, U. S. Bureau of Mines.

Previous Data on Oxygen Requirements for Flame Propagation

Data as to the oxygen required for the propagation of methane flames have been obtained by Coward and Hartwell[2] in connection with problems on the extinctive action of inert gases on methane. These tests were made under conditions whereby the results obtained very closely represent conditions which may occur in actual practice, where the gases are intimately mixed with the oxygen required for combustion.

Little information is available as to the amount of oxygen required for the propagation of carbon monoxide and hydrogen flames, at all concentrations from the lower to upper inflammable limits. Eitner[3] made some experiments with hydrogen and with carbon monoxide in a Bunte buret and showed the narrowing of the range of inflammability of mixtures in atmospheres in which (1) the oxygen was gradually replaced by carbon dioxide, and (2) when increasing amounts of carbon dioxide were added to air. In the first, no inflammable mixture could be made with either hydrogen or carbon monoxide when the oxygen was reduced to 7 per cent (carbon dioxide, 14 per cent). In the second case no inflammable mixture could be made with hydrogen in an atmosphere composed of 48 per cent air and 52 per cent carbon dioxide; with carbon monoxide the proportions were 47 per cent air and 53 per cent carbon dioxide.

Tests were made by Clowes and Feilmann,[4] in which a jet of hydrogen was burned in an enclosed space. The "residual" atmosphere when the flame was extinguished contained 5.5 per cent of oxygen. Similar tests with carbon monoxide caused the flame to be extinguished when the oxygen content was reduced to 13.35 per cent. The effect of variation of concentration of hydrogen and carbon monoxide was not determined.

Similar tests are reported by Rhead[5] in which hydrogen and carbon monoxide issuing from a quartz jet were burned in a 12-liter bottle, and the oxygen content of the residual atmosphere which extinguished the flame determined. Under these conditions the oxygen content of the residual atmosphere which extinguished hydrogen was found to be 5.6 per cent and for carbon monoxide under similar conditions 10.2 per cent.

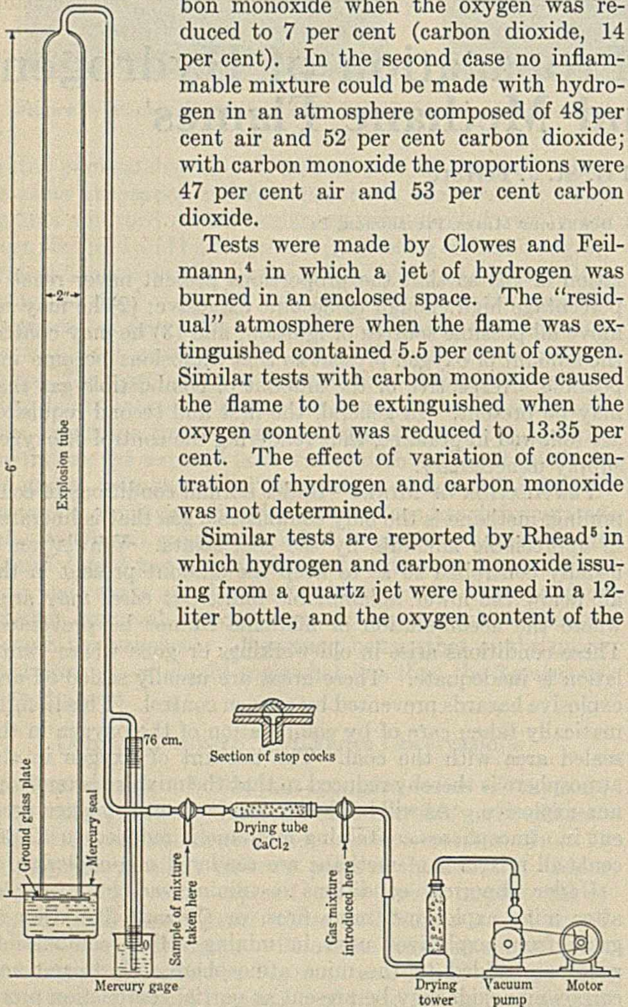

Figure 1—Flame Propagation Apparatus

Results obtained by this method will vary with the experimental conditions. For example, tests were conducted by the senior author[6] on space heaters burning natural gas in a closed room. For a heater of the yellow flame type, in which no primary air is mixed with the gas issuing from the burner ports it was found that the flames were extinguished when the oxygen in the closed room was reduced to 17.7 per cent. In similar tests made with another type of radiant heater, in which approximately 70 per cent of the primary air necessary for combustion of the gas was introduced into the gas before issuing from the burner ports, the flame continued to burn in the closed room until the oxygen was reduced to 13.8 per cent. The most favorable condition for minimum oxygen requirements is that in which all the air required for combustion is intimately mixed with the combustible gas. It is under these conditions that the following experiments were conducted and hence the values given are lower than those reported where flames burn from jets in a confined space.

Burgess and Wheeler[7] have shown that the size of the experimental apparatus has a marked effect on the results obtained. The test apparatus should be 2 inches (5 cm.) or more in diameter in order to obtain results comparable to those in large spaces. Therefore, the results obtained by Eitner in a small narrow buret cannot be directly applied to conditions in practice where large volumes of gases are involved.

Experimental

The investigation herein conducted consisted in determining the oxygen required to propagate hydrogen and carbon monoxide flames over the complete range of inflammability and under conditions wherein the inert gas consisted of (1) nitrogen, and (2) carbon dioxide plus the nitrogen associated with the added air.

The test procedure followed the method used by Coward and Hartwell[2] and possessed the following requisites: (1) a tube sufficiently large in diameter so that the cooling effect of the walls is largely eliminated; (2) a tube long enough for the observer to be certain that true propagation takes place and continues after the effect due to the ignition source had been removed; (3) use of a flame to insure a positive ignition source; (4) tests made under conditions of atmospheric pressure and temperature; and (5) the propagation of flame taking place under conditions largely free from turbulent effects.

APPARATUS—The apparatus (Figure 1) consisted of a cylindrical glass tube 2 inches (5 cm.) in diameter and 6 feet (1.8 meters) long placed in a vertical position. The gas mixtures were ignited from the lower end and propagation of flame took place in an upward direction. Glass shell tubing, fused to the top, connected with a calcium chloride drying tube as shown. Three-way T-bore capillary stopcocks were connected at each end of the drying tube. From this tube connection was made to another large drying tower and Hi-Vac pump. A manometer was sealed to the glass tube leading from the explosion tube. The bottom of the explosion tube was sealed with a ground-glass plate. This was slightly coated with a rubber preparation and further guarded against leakage by placing a mercury seal around the bottom of the tube.

In conducting a test the apparatus was evacuated by the pump until the manometer on the apparatus failed to rise further after 15 minutes of evacuation and registered within 1 mm. of the prevailing barometric pressure at the time of the experiment; correction was made for meniscus error due to the difference in size of tubing on the manometer. When the apparatus was sufficiently evacuated, the prepared gas mixture was introduced through the right-hand cock as indicated. Introduction of the gas mixture was continued until the pressure was slightly above atmospheric. Then the excess of gas was released by connecting

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[2] *J. Chem. Soc.* (*London*), **129**, 1522 (1926).

[3] *J. Gasbel.*, **45**, 21, 69, 90, 112 (1902).

[4] *J. Soc. Chem. Ind.*, **13**, 1155 (1894).

[5] *Fuel Science Practice*, **6**, 37 (1927).

[6] Jones, Berger, and Holbrook, *U. S. Bur. Mines, Tech. Paper* **337** (1923).

[7] Safety in Mines Research Board, London, *Paper* **15** (1925).

a water seal (not shown in drawing) to left-hand three-way stopcock and opening to the outside air. This procedure was followed to insure that the gas in the explosion tube was at atmospheric pressure when the test was made. The mercury seal was then removed and the mixture tested for inflammability by sliding off the ground-glass plate and at the same time passing the flame from a small alcohol lamp across the open end of the tube. The mode of propagation was then observed. A mixture close to the extinction point may propagate a foot or so before being extinguished as a result of the heat imparted to the mixture from the flame used for igniting the mixture. In the method followed, there was first found by trial and error a mixture which would just propagate flame. This was then changed slightly until flame would no longer propagate. The average of these two values was taken as the limit mixture.

Inflammability tests made with methane-air[8] mixtures with this apparatus gave results almost identical with those obtained in Great Britain with similar apparatus.

GASES USED—*Hydrogen.* The hydrogen supply was obtained in high-pressure cylinders. Analysis of this gas on a Bone and Wheeler apparatus gave a hydrogen content of 99 per cent, 1 per cent oxygen and nitrogen, and no combustibles other than hydrogen.

Carbon Monoxide. The carbon monoxide was prepared by the action of concentrated sulfuric on formic acid. The carbon monoxide formed by the reaction was passed through a Cardoxide filter to remove carbon dioxide and then through a filter containing activated charcoal to remove vapors of formic acid. The apparatus was thoroughly purged before collecting the gas in order to obtain an air-free product. Analysis of this gas gave 99.3 per cent absorption in acid cuprous chloride solution.

Nitrogen. The nitrogen was obtained in high-pressure cylinders. Analysis of this mixture indicated 99.5 per cent nitrogen and 0.5 per cent oxygen.

Carbon Dioxide. The commercial product, contained in high-pressure cylinders, was used in the experiments, but before samples were taken most of the contents was allowed to escape. Analysis of the remaining portion, which was used in the experiments, showed a carbon dioxide content of nearly 100 per cent.

METHOD OF CONDUCTING TESTS—A supply of hydrogen or carbon monoxide was stored in an 80-liter gasometer sealed with a 50-50 mixture of water and glycerol. The upper limit of inflammability was then determined by drawing definite amounts of the gas into 12-liter calibrated aspirator bottles containing a 50-50 mixture of water and glycerol and then drawing various amounts of air into the bottle. The gas-air mixture was well shaken over the water-glycerol solution and the mixture then added directly to the evacuated explosion apparatus as previously described. When the apparatus became filled, samples of the mixture were taken for analysis from the left-hand stopcock, over mercury in small test tubes, and a complete analysis of the mixture made. Although some change in the mixture resulted from the shaking in the aspirator bottles, the sample of gas analyzed was approximately that of the mixture in the test apparatus, as the sample taken for analysis was taken from the apparatus rather than from the aspirator bottles. As the inflammable limits had been determined for the mixture of pure gas and air, a definite amount of nitrogen was added to the hydrogen in the gas holder and tests for inflammability were likewise run on this mixture. In this manner the complete range of inflammability for hydrogen, nitrogen, and oxygen for many mixtures between the lower and upper inflammable limits was determined.

The oxygen requirements for the propagation of hydrogen flames in mixtures containing various percentages of nitrogen and ranging from the lower to upper limits of inflammability are given in Figure 2. The results of tests conducted in a similar manner with carbon monoxide, nitrogen, and oxygen mixtures are also shown graphically in Figure 2. The values for methane are taken from published data by Coward and Hartwell.[2]

Discussion of Results

METHANE—It is seen that for methane the oxygen required for the propagation of flames depends markedly upon the amount of methane present in the mixture. At the lower limit, 5.25 per cent methane, the oxygen necessary for flame propagation is 19.8 per cent. As the methane increases to 6.1 per cent the oxygen required falls rapidly to 12.1 per cent and it is at this point that the ratio between oxygen and methane is that required for complete combustion, $2O_2:CH_4$. It is at this point that the minimum amount of oxygen is required for flame propagation. As the methane present is increased above 6.1 per cent, the oxygen required for flame propagation increases. When the upper inflammable limit for methane in air (14 per cent) is reached, the oxygen required is 18 per cent. Therefore, if the oxygen in a methane-nitrogen-air atmosphere is reduced below 12.1 per cent, flame propagation and explosions are impossible under the test conditions, no matter what proportions of methane are present.

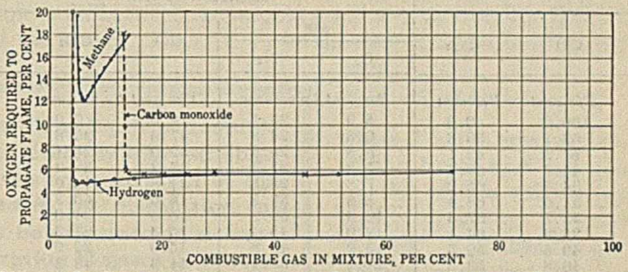

Figure 2—Oxygen Required to Propagate Carbon Monoxide, Hydrogen, and Methane Flames–Inert Gas, Nitrogen

HYDROGEN—In the case of hydrogen, starting at the upper limit (72 per cent) we find that only 5.9 per cent oxygen is necessary to propagate flame, and as the hydrogen is reduced and the inert nitrogen increased the amount of oxygen necessary for flame propagation falls slightly and gradually until at near the lower limit for hydrogen (4.3 per cent) only 5.1 per cent oxygen is necessary. The curve over the entire range is almost flat and nearly a straight line, and requires markedly less oxygen for flame propagation than in the case of methane.

Table I—Extinction of Hydrogen Flames by Carbon Dioxide

TEST MIXTURE		COMPOSITION OF LIMIT MIXTURE AFTER ADDITION OF AIR			
		AIR			
H_2	CO_2	O_2	N_2	H_2	CO_2
Per cent	*Per cent*	*Per cent by volume*		*Per cent by volume*	
100.0	0.0	5.9	22.1	72.0	0.0
69.6	30.4	6.2	23.5	48.9	21.4
51.3	48.7	6.6	24.8	35.2	33.4
40.0	60.0	6.9	26.1	26.8	40.2
30.0	70.0	7.0	26.7	19.9	46.4
25.6	74.4	7.1	26.9	16.9	49.1
21.1	78.9	7.3	27.7	13.7	51.3
15.1	84.9	7.3	27.8	9.8	55.1
13.5	86.5	7.6	28.7	8.6	55.1
11.5	88.5	7.6	28.9	7.3	56.2
9.6	90.4	7.8	29.7	6.0	56.5
9.1	90.9	8.3	31.3	5.5	54.9
8.9	91.1	8.4	32.0	5.3	54.3
11.6	88.4	11.7	44.4	5.1	38.8
18.3	81.7	16.1	61.0	4.2	18.7
29.5	70.5	17.9	67.9	4.2	10.0
38.4	61.6	18.7	70.6	4.1	6.6
100.0	0.0	20.1	75.9	4.0	0.0

CARBON MONOXIDE—Tests with carbon monoxide show similar results; in fact, in the mixtures containing high percentages of carbon monoxide the oxygen requirement is very

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[8] Coward and Jones, *Bur. Mines, Repts. Investigations* **2757** (1926).

nearly the same as that for hydrogen; the difference is that carbon monoxide has a slightly higher lower inflammable limit and makes a sharp turn upward at this point.

Extinctive Effect of Carbon Dioxide—The extinctive effect of carbon dioxide when added to hydrogen and air mixtures is best shown by Table I.

Starting with the upper inflammable limit mixture of hydrogen and air, it is seen that 5.9 per cent oxygen is required to propagate flame. As increasing amounts of carbon dioxide are added to the hydrogen, the oxygen required to propagate flame gradually increases. When the hydrogen in the test mixture is reduced to 5.3 per cent and more than 50 per cent carbon dioxide is present, the oxygen required for propagation has been raised to 8.4 per cent. With further reduction of the hydrogen percentage in the test mixture from 5.3 to 4.0 (the lower limit of inflammability), the oxygen required for flame propagation increases rapidly from 8.4 to 20.1 per cent.

Similar tests with carbon monoxide, carbon dioxide, and air mixtures are given in Table II, and follow closely the values for hydrogen for these mixtures in which carbon monoxide is present in large amounts.

Table II—Extinction of Carbon Monoxide Flames by Carbon Dioxide

Test Mixture		Composition of Limit Mixture after Addition of Air			
		Air			
CO	CO_2	O_2	N_2	CO	CO_2
Per cent	*Per cent*	*Per cent by volume*		*Per cent by volume*	
100.0	0.0	5.9	22.1	72.0	0.0
69.7	30.3	6.5	24.8	47.9	20.8
57.9	42.1	6.8	25.8	39.0	28.4
41.7	58.3	7.2	27.3	27.3	38.2
34.8	65.2	7.8	29.5	21.8	40.9
31.6	68.4	8.6	32.5	18.6	40.3
32.7	67.3	10.3	39.2	16.5	34.0
35.9	64.1	12.0	45.4	15.3	27.3
40.5	59.5	13.2	49.8	15.0	22.0
46.8	53.2	14.4	55.1	14.3	16.2
67.5	32.5	16.6	62.7	14.0	6.7
100.0	0.0	18.1	68.6	13.3	0.0

Starting with the upper limit of carbon monoxide (72 per cent CO) in air, it is seen that 5.9 per cent oxygen is required for the propagation of flame. As carbon dioxide is added to the carbon monoxide, the amount of oxygen required to propagate flame increases as the carbon dioxide increases. When the carbon monoxide in the limit mixture has been reduced to 16.5 with 40.3 per cent carbon dioxide present, the oxygen required for propagation of flame equals 8.3 per cent. From this point on down to the lower inflammable limit (13.3 per cent) the oxygen required increases rapidly to 18.1 per cent when the lower limit is reached. These results show that if carbon dioxide is present along with nitrogen in the inert gases, the values given in Figure 2 for the propagation of flames will be raised somewhat.

Black Damp in Coal Mines

A compilation of the composition of black damp from mines all over the United States, made by Burrell and others,[9] shows that it consists largely of nitrogen. In the majority of cases the nitrogen present amounts to 85 to 95 per cent by volume; the remainder is carbon dioxide. Although the addition of carbon dioxide to the mixtures somewhat raises the oxygen required to propagate flames, as nitrogen is the prevailing inert gas in the black damp the values given in Figure 2 should apply fairly closely for the usual mining conditions.

Effect of Inert Gases on Flammable Gases

It is of interest to compare the amounts of the inert gases—nitrogen, carbon dioxide, and helium—which must be added to hydrogen, carbon monoxide, and methane in order to produce a mixture which is non-inflammable no matter what proportions of air are added to the mixture. These data have been obtained in connection with another problem under investigation by the Bureau of Mines dealing with the inflammability of complex gases. Table III gives the amounts of inert gas which must be added to the different gases.

Table III—Inert Gas Required for Extinction of Hydrogen, Methane, and Carbon Monoxide Flames

Combustible Gas	Added Inert Gas	Volumes Inert Gas per Volume Combustible Gas	Gas in Limit Mixture after Addition of Air	
			Combustible	Oxygen
			Per cent	*Per cent*
Hydrogen	Nitrogen	16.55	4.3	5.1
Hydrogen	Carbon dioxide	10.20	5.3	8.4
Hydrogen	Helium	10.50	6.1	6.2
Methane[a]	Nitrogen	6.00	6.1	12.1
Methane[a]	Carbon dioxide	3.20	7.3	14.6
Methane	Helium	6.07	6.0	12.0
Carbon monoxide	Nitrogen	4.12	13.9	6.0
Carbon monoxide	Carbon dioxide	2.16	18.6	8.6

[a] From published data by Coward and Hartwell.[2]

Referring to the values given, we find that 16.55 volumes of nitrogen may be added to hydrogen and such a mixture when added with the proper amount of air will just propagate flame. If the volume of nitrogen to hydrogen is increased above 16.55, however, the mixture is rendered non-inflammable. The amount of hydrogen in this limiting mixture after addition of the proper amount of air is seen to equal 4.3 per cent and the oxygen present in the mixture, 5.1 per cent. When the carbon dioxide is substituted for nitrogen, only 10.20 volumes are required, as compared with 16.55 in the case of nitrogen. Results for methane and carbon monoxide also show the greater extinctive effect of carbon dioxide. The higher extinctive effect of carbon dioxide appears to be due largely to its higher heat capacity. The extinguishing effect of helium on hydrogen is of interest, largely in connection with the use of mixtures of these two gases in dirigibles. The greater extinguishing effect of helium has been attributed to its higher thermal conductivity.[2,7]

Table III shows that much more inert gas must be added to hydrogen to render the mixture non-inflammable than to methane, while methane requires more inerts than carbon monoxide.

Another interesting point in Table III is that when either nitrogen or carbon dioxide is added to methane until all mixtures become just extinctive when mixed with air, the ratio between oxygen and methane is that required for complete combustion, or 2:1. If this same relation held for hydrogen, then for complete combustion two volumes of hydrogen should be present to one of oxygen in the final extinctive mixture. The data show that this is not so, and that oxygen is present in proportions much greater than that required for complete combustion. In the case of carbon monoxide two volumes of the gas require one volume of oxygen for complete combustion. The data show that for this gas the oxygen is deficient for complete combustion.

In other words, when either nitrogen or carbon dioxide is added to each of the three gases to the extinctive point, they behave differently with respect to completeness of combustion of their limiting mixtures. No explanation is offered at the present time for these variations

Summary

The applications of the results of this study to mining conditions are as follows:

1—When methane is the only inflammable gas present, as for the normal conditions in mine atmospheres, flames and explosions may be prevented by reducing the oxygen in the atmosphere to 12 per cent.

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[9] Burrell, Robertson, and Oberfell, *Bur. Mines, Bull.* **105** (1916).

2—In the case of abnormal conditions where combustion processes have taken place, not only may methane be present but also carbon monoxide and hydrogen. Under these conditions, to render the atmosphere safe from flame propagation and explosions, the oxygen present in the area must be reduced well below 12 per cent to render the atmosphere non-inflammable. The extent to which this reduction should be made depends upon the relative amounts of carbon monoxide and hydrogen present. The results suggest that in order that all sealed areas be safe under all conditions, the oxygen present should be reduced to 5 per cent. Under such conditions all atmospheres containing methane, hydrogen, or carbon monoxide would be non-inflammable at such temperatures as could be tolerated by rescue workers entering such areas.

At very high temperatures these conclusions will not apply because the oxygen required for the propagation of flame at elevated temperatures may be somewhat less than that required at the ordinary temperatures.

Tower Absorption Coefficients[1]

By R. C. Cantelo, C. W. Simmons, E. M. Giles,[2] and F. A. Brill[3]

Lehigh University, Bethlehem, Pa.

THE rate of solution in an absorbing liquid of a soluble gas from an inert carrier may be expressed by the differential equation $dm/dt = -K_2 f(m)$, where m is the concentration of the gas in the carrier, expressed either in terms of volume concentration or of partial pressures, K_2 is the dissolution coefficient, and for a given set of conditions K_2 is constant. The problem then resolves itself into two parts—(1) the determination of the form of $f(m)$, and (2) the determination of the variables of which K_2 is a function.

The rate of solution in an absorbing liquid of a soluble gas from an inert carrier is given by the equation $dm/dt = -K_2 f(m)$, m being the concentration of the soluble gas in the carrier, and K_2 the dissolution coefficient. This equation may be expressed in a form suitable for the study of absorption of gases in towers.

The dependence of K_2 upon the rate of gas flow, composition of gas, and rate of flow of absorbing liquid has been determined by experiments in which carbon dioxide and sulfur dioxide have been used as soluble components in air as the inert carrier. These experiments show that K_2 is independent of the rate of flow of gas and of the gas composition; and that K_2 varies linearly with the rate of flow of the absorbing liquid.

Forms Proposed for $f(m)$

Donnan and Masson[4] suggest as a general form $f(m) - n$, where the equilibrium conditions for a constant temperature are expressed by the equation $n = f(m)$, and n is the concentration of the soluble component in the absorbing liquid. For a gas which obeys Henry's law, the differential equation then becomes $dm/dt = -K_2 (km - n)$, where k is the Henry coefficient defined by $n = fm$.

Lewis,[5] and Whitman and Keats[6] express $f(m)$ in the form $(P_g - P_1)$, where P_g is the partial pressure of the soluble component in the inert carrier and P_1 is its partial pressure over the solvent. It is evident that for a gas which obeys Henry's law—i. e., $P = kc$—this function $(P_g - P_1) = K(C_g - C_1)$, where C is the concentration corresponding to P. This form bears a close similarity to Donnan and Masson's $f(m) = (km - n)$, and the two forms approximate each other.

In the cases of gases that are very soluble $f(m)$ is a much simpler expression, and Lewis and Whitman[7] have shown that it becomes equal to P_g, the partial pressure of the soluble component in the inert carrier.

PART I—ABSORPTION OF CARBON DIOXIDE

This section deals only with the absorption of carbon dioxide from air as the inert carrier. Therefore, any of the forms for $f(m)$ given above for a gas obeying Henry's law may be applied. Use has been made of the form $K_2 (km - n)$, as it admits the readily determined form of the integral equation involving m and n.

Variables of Which K_2 is a Function

Consider a small element of volume of a packed absorption tower between the heights x and $x + dx$ from the bottom of the tower. Then,[8] if V_l be the flow of liquid in liters per hour

$$V_l dn = K_2 rA dx (km - n) \quad (1)$$

where A is the cross section of the tower and r is the fraction of free volume per cubic decimeter of gross volume. K_2 is then the dissolution coefficient for the given tower in grams absorbed per hour per cubic decimeter of free volume per concentration deficit from equilibrium of one gram per liter. This equation permits a consideration of the variables which will affect K_2. Obviously $rAdx$ is a constant term for a given tower, and the variables are therefore k, m, and n. Henry's coefficient k is a function of the temperature; K_2, therefore, is some function of the temperature of the absorbing liquid, T_l. The importance of this factor has been pointed out previously by Van Arsdale.[8] The dependence of K_2 on m must be determined experimentally, and obviously n will vary with V_l so that K_2 also will vary with V_l. Equation (1) may be written

$$V_l dn = V_g dm \quad (2)$$

Hence the left-hand term in equation (1) may be varied by varying V_g. Hence K_2 is a function of V_g, the velocity of gas flow in liters per hour. We may combine V_g and V_l in the form of a ratio $V_g/V_l = f =$ the flow ratio.

Finally $K_2 = \phi (T_l, m, f)$, the form of the function in each case to be determined experimentally, and the dependence of K_2 upon the numerator and the denominator of f, to be determined separately. Now it will be much more convenient for the purpose of experimental investigation to transform the equation $dm/dt = -K_2 (km-n)$ into one involving dm/dx, and in a recent paper one of the writers[9] has developed this transformation. For a gas which obeys Henry's law this integral equation has the form:

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[1] Part I received May 10, 1927; Part II received July 2, 1927.

[2] Part-time assistant in work of Part I.

[3] Part-time assistant in work of Part II.

[4] *J. Soc. Chem. Ind.*, **39**, 236T (1920).

[5] This Journal, **8**, 825 (1916)

[6] *Ibid.*, **14**, 186 (1922).

[7] *Ibid.*, **16**, 1215 (1924).

[8] Van Arsdale, *Chem. Met. Eng.*, **28**, 889 (1923).

[9] *Ibid.*, **33**, 680 (1926).

$$\frac{1}{a(k-f)+fM^1} 2.303 \log \frac{(a-M^1)[(k-f)M_0+f(M^1)]}{kM^1(a-M_0)} = \frac{K_2h}{B(1-p^1w-p^1)} \quad (3)$$

where $a = \frac{M}{0.0821\ T_w(1-p_w)}$ $B = \frac{MU}{0.0821\ r\ AT^1}$

$f = \frac{\text{velocity of inlet gas}}{\text{velocity of liquid}} = \text{flow ratio}$

M^1 = grams per liter of soluble component in outlet gas
M_0 = grams per liter of soluble component in inlet gas
T_w = temperature of extractor in ° K.; T^1 = temperature of outlet gas in ° K.
p^1 = partial pressure of soluble component
M = molecular weight of soluble component
p_w = vapor pressure of extractor in atmospheres at T_w
U = liters of gas per hour issuing from the tower
r = fraction of free volume per cubic decimeter of gross volume
A = cross section of tower in square decimeters
h = height of tower in decimeters
k = Henry's coefficient
K_2 = dissolution coefficient = grams of soluble component absorbed per hour per cubic decimeter of free volume per concentration deficit from equilibrium of one gram per liter
p^1_w = vapor pressure of extractor in atmospheres at T^1

Note—It should be noted that K_2 will have the same numerical value whether metric or English units are used. In the second case K_2 = pounds of soluble component absorbed per hour per cubic foot of free volume per concentration deficit from equilibrium on one pound per cubic foot.

Apparatus and Manipulation

The experimental tower was constructed of a fiber tube 1.6 meters long and 9.1 cm. outside diameter, and had been treated with an inert filler to render it gas-tight. The outlet and inlet fittings were soldered to metal caps and these caps were sealed on each end of the tower with a sulfur-resin mixture. Small Raschig rings made from glass tubing filled the tower to an effective height of 86 cm. This packing gave a free volume ratio of 0.663 per cubic decimeter of tower volume.

The water was led through a valved 1/2-inch (13-mm.) pipe from a constant level reservoir 3.6 meters above the top of the tower to a spray nozzle just above the surface of the tower packing. This distributor was arranged to spray the water on the filler but not on the tower wall. The water was discharged at the bottom of the tower through a 3/4-inch (19-mm.) pipe shaped to form a water seal and fitted with a glass gage to indicate any tower flooding. The outlet discharged into a measuring tank. Temperatures of the water were determined at the top and bottom of the tower. (Figure 1)

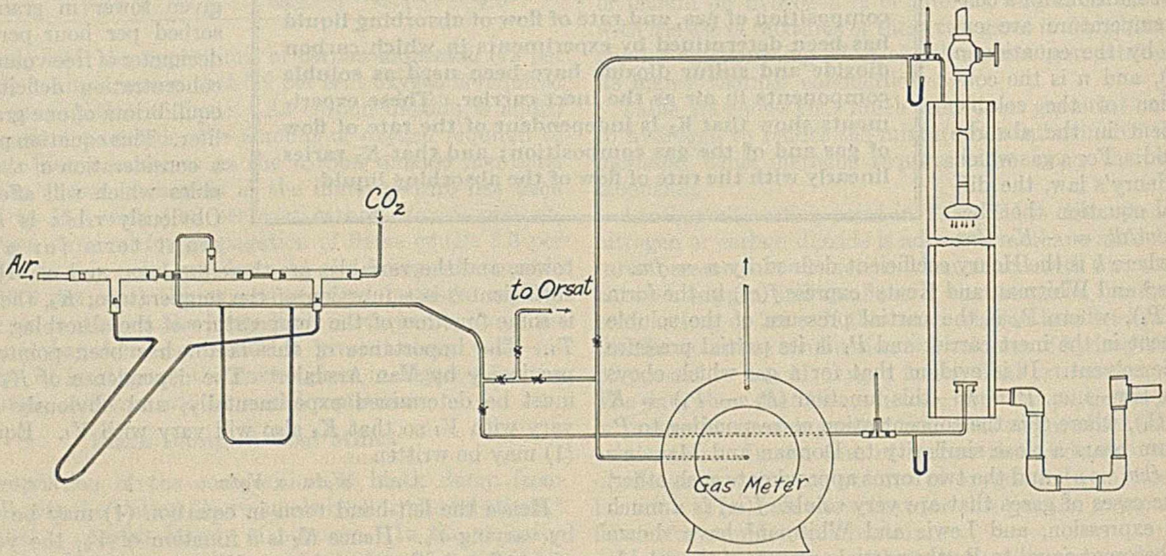

Figure 1

Air at constant pressure was supplied by a compressor. Carbon dioxide was supplied from a cylinder of the liquefied gas. The air and carbon dioxide were led through inclined U-tube flowmeters which registered the differential flow of the two gases. These flowmeters were used in approximate regulation and served as an efficient mixing unit as well as an indicator of gas-flow constancy. The gas mixture was led to the bottom of the tower and entered the tower through a distributor placed slightly above the water outlet. The gas mixture passed up through the packing and, after discharging at the top of the tower, was led through a wet test meter which accurately registered the volume of the exit gas. The maximum gas rate was limited by the pressure in the gooseneck water outlet and the minimum by the sensitiveness of the gas meter. With a bleeding system samples of either inlet or outlet gas could be run directly to an Orsat gas apparatus without disturbing the gas circuit. Temperatures of the inlet and exit gas were taken and after a few runs the air in the room was circulated to maintain an approximately uniform temperature. Barometric pressure and the static head at the gas inlet and exit were recorded.

In operating the absorption tower the water inlet valve was regulated to give the required rate measured at the tower outlet. The desired carrier gas rate was regulated and recorded on the gas meter at the gas exit. Then by regulation of the carbon dioxide supply and controlling with Orsat analysis a gas mixture of definite composition was obtained. The outlet gas was analyzed and its volume per minute recorded. Thus from the composition of the inlet gas and the composition and volume of the outlet gas, the volume of the inlet gas under operating conditions was calculated.

Experimental

Since the solubility of a gas as expressed by Henry's coefficient is a function of the temperature, the determination of the effects of gas rate, gas composition, etc., must be made at constant water temperature.

Series I—Effect of variation in volume of inlet gas on the value of K_2. In this series the composition of the inlet gas and the water rate were kept constant, and care was taken to keep the water temperature, and thus Henry's coefficient, constant. By so doing, the only experimental variable was the gas rate.

Table I—Effect of Variation in Volume of Inlet Gas

Test	CO_2 Inlet Gas	Temp. Inlet Gas	Inlet Gas Rate	CO_2 Exit Gas	Temp. Exit Gas	Exit Gas Rate	Water Rate	Water Temp.	K_2
	Per cent	° *C.*	*Liters per min.*	*Per cent*	° *C.*	*Liters per min.*	*Liters per min.*	° *C.*	
1	18.6	21.0	3.76	7.4	22.6	3.31	7.5	6.4	42.30
2	19.2	21.0	4.34	8.5	22.0	3.82	7.5	6.4	42.02
3	19.0	17.4	3.31	7.2	16.4	2.88	7.5	7.0	40.47
4	18.8	17.0	4.47	9.2	16.0	3.99	7.5	7.2	41.10
5	18.6	19.2	3.68	7.2	17.6	3.23	7.5	6.6	43.10
6	18.6	17.0	2.97	6.4	15.6	2.58	7.5	6.6	38.73
7	18.4	18.4	4.81	9.4	18.0	4.33	7.5	6.8	41.30
8	18.4	17.0	4.22	8.8	15.6	3.76	7.5	6.8	40.02
9	19.4	15.4	3.45	8.0	14.4	3.03	7.5	6.8	42.10

The results (Table I) indicate a constant value for K_2 with a variation in gas rate.

Series II—Effect of varying gas composition on the value of K_2. The water rate and water temperature were kept constant; and the volume and composition of the inlet gas varied.

Table II—Effect of Varying Gas Composition

Test	CO_2 Inlet Gas	Temp. Inlet Gas	Inlet Gas Rate	CO_2 Exit Gas	Temp. Exit Gas	Exit Gas Rate	Water Rate	Water Temp.	K_2
	Per cent	° *C.*	*Liters per min.*	*Per cent*	° *C.*	*Liters per min.*	*Liters per min.*	° *C.*	
1	13.4	17.2	3.70	5.4	16.2	3.39	7.6	9.2	41.08
2	33.1	16.3	4.53	17.8	15.0	3.68	7.6	8.5	38.40
3	15.4	21.0	3.80	6.8	24.0	3.45	7.6	8.8	42.76
4	34.6	21.0	4.81	19.4	24.0	3.90	7.6	8.8	38.44
5	16.0	21.4	3.94	7.2	22.4	3.56	7.6	8.8	42.68
6	17.2	14.2	4.13	8.2	14.2	3.73	7.6	9.0	43.38
7	11.8	15.4	4.05	5.6	14.6	3.79	7.6	9.0	43.33
8	29.2	17.0	4.95	16.4	16.2	4.19	7.6	9.0	38.26
9	18.2	17.0	4.36	9.6	16.0	3.93	7.6	9.0	38.54
10	22.6	17.0	4.61	12.0	15.8	4.04	7.6	9.0	40.00

The results (Table II) indicate a constant value for K_2 with variation in gas composition and gas flow. Thus, since K_2 is constant with varying gas flow (Table I), it follows that K_2 is also constant with varying gas composition.

Series III—Effect of varying water rate on the value of K_2. Table III gives the results of this series in which the flow ratio was varied over the wide range of 0.463 to 3.022 with a variation in inlet gas composition of 11.8 to 26.4 per cent carbon dioxide. The differences in water temperatures noted were due to uncontrollable climatic conditions.

Table III—Effect of Varying Water Rate

Test	CO_2 Inlet Gas	Temp. Inlet Gas	Inlet Gas Rate	CO_2 Exit Gas	Temp. Exit Gas	Exit Gas Rate	Water Rate	Water Temp.	Flow Ratio	K_2
	Per cent	° *C.*	*Liters per min.*	*Per cent*	° *C.*	*Liters per min.*	*Liters per min.*	° *C.*		
1	20.8	10.4	3.91	10.6	10.8	3.46	6.13	7.4	0.639	35.56
2	13.6	14.0	3.57	7.8	13.6	3.34	5.05	6.4	0.707	26.08
3	15.2	18.8	3.40	8.2	18.4	3.14	4.39	6.8	0.775	27.61
4	21.4	21.2	3.91	17.2	21.0	3.71	1.29	7.0	1.068	12.86
5	21.6	21.2	3.88	12.0	21.0	3.46	5.21	7.0	3.022	28.72
6	25.4	11.6	4.02	18.0	11.0	3.66	2.72	7.0	1.476	19.38
7	25.6	12.0	4.05	13.4	11.2	3.48	6.06	7.2	0.667	34.20
8	23.6	12.2	3.85	10.4	11.4	3.29	8.34	7.2	0.463	40.40
9	13.8	17.6	3.85	10.6	16.8	3.70	1.72	8.4	2.339	15.92
10	11.8	18.2	3.46	7.2	17.6	3.29	2.94	8.2	1.169	25.94
11	13.8	18.8	3.57	9.8	18.0	3.39	1.73	8.6	2.065	16.41
12	13.8	18.4	3.57	8.6	17.2	3.37	3.20	8.4	1.112	25.04
13	18.4	15.4	3.38	12.3	15.0	3.06	2.57	9.0	1.278	20.08
14	17.8	15.6	3.38	12.4	15.2	3.08	2.24	9.2	1.462	16.20
15	26.4	16.6	3.48	20.6	16.6	3.23	1.56	9.2	2.232	16.28
16	24.6	17.4	3.54	18.2	17.2	3.25	2.04	9.2	1.772	16.40
17	25.8	17.4	3.63	16.0	17.2	3.19	3.26	9.2	1.113	20.36

The results (Table III) show a marked variation in K_2 with a variation in water rate. The relationship between K_2 and the water rate is shown graphically by Figure 2. It is evident that K_2 decreases rapidly with increase in flow ratio until a critical flow ratio is reached, whereupon the value for K_2 remains substantially constant. This means that K_2 decreases with decrease in water rate.

Conclusion

The dimensions of the tower used in these experiments together with the linear velocity of gas flow varying between 42.7 and 91.5 cm. (1.4 and 3 feet) per minute are such that the results obtained are comparable with commercial practice. These results show that the gas velocity and composition are of slight importance for a given flow ratio. The important factors to be considered in the design and operation of absorption towers for the removal of gases which obey Henry's law are:

(1) The rate of flow of the absorbing liquid. The rate of solution of a soluble component from an inert carrier is shown to decrease rapidly with decrease in the rate of flow of the absorbing liquid until a critical flow ratio is reached, whereupon the rate of solution remains substantially constant. The determination of this critical flow ratio becomes, therefore, of fundamental importance in the efficient operation of absorption towers.

(2) The temperature of the absorbing liquid.

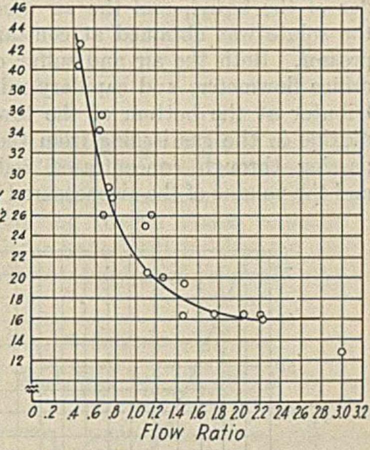

Figure 2—Variation of K_2 with Water Rate (CO_2 Absorption)

PART II—ABSORPTION OF SULFUR DIOXIDE

Part II deals with the absorption of the very soluble gas, sulfur dioxide, from air as the inert carrier. The rate of absorption of sulfur dioxide may be expressed by the equation $dp/dt = -K_4p$, and equation (3) has the form:

$$\frac{1}{a}\log\frac{p_0(a-p^1)}{p^1(a-p_0)} = K_4Bh \tag{4}$$

a = $(1-p_w)$
p_0 = partial pressure of solute gas in entering gas
p_1 = partial pressure of solute gas in exit gas
B = $\dfrac{rAT^1}{UT(1-p^1_w-p^1)}$
K_4 = dissolution coefficient
V_c = velocity of carrier
V_ι = velocity of extractor
Other symbols have significance given in Part I

This equation has the disadvantage that it does not contain the quantity *f*, the flow ratio, expressed as V_c/V_ι. Again it is impossible to give K_4 a physical significance, as was done for K_2.

Therefore, it was decided to examine how closely aqueous solutions of sulfur dioxide obeyed Henry's law.

Sims's[10] data for 7° and 20° C. gave values for *k*, the Henry coefficient, for solutions of concentration above 25 and 13 grams per liter, respectively, which varied from the average values by 7.1 and 6.0 per cent. Through the courtesy of W. B. Campbell results obtained in the Forest Products Laboratories of Canada[11] were examined. These determinations show that at the higher temperatures aqueous solutions of sulfur dioxide follow Henry's law closely, while at the lower temperatures the deviation is of the order of 7 per cent. For example, at 25° C. the maximum deviation from the average value of *k* for solutions above 35 grams per liter is 5.8 per cent; whereas at 80° C. it is 1.5 per cent. Figure 3 shows graphically the variation of these average values of *k* with the temperature.

It appears, then, that with small error, equation (3) may be applied to the experimental results obtained for the absorption of sulfur dioxide. Values for K_2, for sulfur dioxide, so obtained are given in Table IV, while the values for K_4 given in the same table were calculated by the use of equation (4).

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[10] *J. Chem. Soc. (London)*, **14**, 1 (1862).

[11] Not yet published.

Apparatus and Manipulation

The experimental absorption tower was similar to that used in Part I (Figure 1), except as indicated below. The sulfur dioxide was obtained from a 50-pound (23-kg.) cylinder of the liquid, and the air used as the inert carrier of the solute was obtained at constant pressure from a compressor. Both the air and sulfur dioxide were led through orifice flowmeters and capillary mixing apparatus to a distributor at the bottom of the tower. The residual sulfur dioxide in the gas issuing from the tower was removed by passing through concentrated sodium hydroxide solution and the volume of the air measured by a wet test meter. Inlet and outlet gas samples were bled from the system through standard iodine solution by an aspirator bottle.

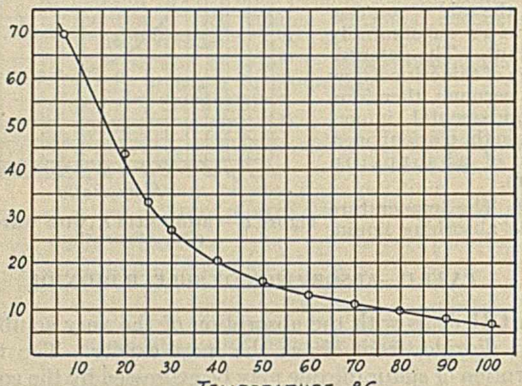

Figure 3—Variation of *k* with Temperature (SO_2 Absorption)

In operating the absorption tower the water inlet valve was regulated to give the required water rate. The desired inlet gas composition was obtained and the volume of exit air recorded. From these and the composition of the outlet gas the volumes of the inlet and outlet gas under operating conditions were calculated. The temperatures of the inlet gas, outlet gas, and water were recorded.

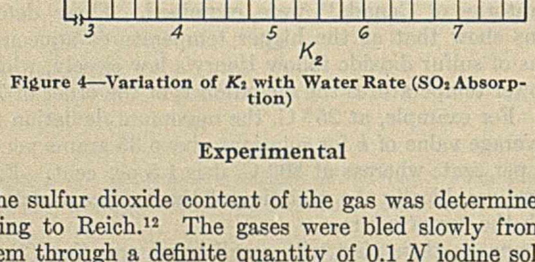

Figure 4—Variation of K_2 with Water Rate (SO_2 Absorption)

Experimental

The sulfur dioxide content of the gas was determined according to Reich.[12] The gases were bled slowly from the system through a definite quantity of 0.1 *N* iodine solution by means of aspirator bottles until a starch color was discharged. From the quantity of iodine and the volume of solution discharged from the aspirator bottle, the volume percentage sulfur dioxide may be calculated according to the following formula:

$$\text{Per cent } SO_2 = \frac{11.17}{V_0 + 11.17}$$

$$\text{where } V_0 = \frac{V(p - pw)}{760(1 + 10.00367T)}$$

V = measured volume

P = observed barometric pressure

pw = aqueous tension at T

T = temperature of gas

11.17 = cubic centimeters of SO_2 equivalent to 10 cc. of 0.1 *N* iodine solution

Determinations were made on a gas containing as little as 0.01 per cent sulfur dioxide and the slow bleeding over a period of 10 to 15 minutes insures a representative sample.

Table IV—Absorption of Sulfur Dioxide

Test	SO_2 Inlet	SO_2 Outlet	Air	Water	Temp. Inlet Gas	Temp. Outlet Gas	Water Temp.	Flow Ratio	K_4	K_2
	%	%	*Liters per min.*	*Liters per min.*	° *C.*	° *C.*	° *C.*			
1	21.0	0.27	3.88	1.00	20.0	21.0	19.0	5.00	301.9	7.22
2	24.0	0.11	2.97	0.93	20.0	21.0	19.0	4.30	286.0	6.72
3	27.0	0.01	2.12	1.04	19.0	20.0	19.0	2.86	293.0	6.90
4	16.52	4.50	3.82	0.20	19.0	21.0	19.0	22.70	93.0	3.31
5	18.72	2.63	3.54	0.255	20.0	21.5	19.0	17.43	128.8	3.65
6	29.50	0.65	1.67	0.27	21.0	22.0	19.0	8.93	128.0	3.34
7	16.90	1.00	3.17	0.342	17.0	19.0	19.0	11.38	161.9	4.33
8	14.67	1.64	3.85	0.333	17.0	19.0	19.0	13.81	152.8	4.20
9	16.0	1.48	3.37	0.317	17.5	19.6	19.0	12.85	136.8	3.93
10	18.4	0.90	2.66	0.302	18.0	20.0	19.0	11.01	145.1	3.87
11	24.0	0.80	2.07	0.271	19.0	20.5	19.0	10.25	129.1	3.41
12	29.25	0.42	1.67	0.265	19.4	20.8	19.0	9.08	130.1	3.38
13	13.9	2.85	4.53	0.263	20.0	21.0	19.0	20.44	131.3	3.77
14	18.44	0.53	2.83	0.448	18.0	19.5	19.0	7.91	180.8	4.58
15	18.44	0.20	2.83	0.720	18.0	19.5	19.0	4.91	228.1	5.62
16	18.44	0.35	2.83	0.530	18.0	19.5	19.0	6.68	295.4	5.01

The experimental results are shown in Table IV and the variation of K_2 with water rate is shown graphically in Figure 4. It is interesting to note that K_4 also varies linearly with the water rate.

Conclusion

The principal factor determining the rate of absorption of sulfur dioxide is the water rate. K_2, the dissolution coefficient, varies linearly with the rate of flow of the extractor.

Acknowledgment

This investigation (Parts I and II) was carried out under the Henry Marison Byllesby Memorial Research Fellowship in Engineering.

Calendar of Meetings

American Chemical Society—74th Meeting, Detroit, Mich., September 5 to 10, 1927.

Division of Organic Chemistry—Second National Symposium on Organic Chemistry, Columbus, Ohio, December 29 to 31, 1927.

American Electrochemical Society—Fall Meeting in the form of an excursion through the Northwest, September 4 to 20, 1927.

American Refractories Institute—Clifton Hotel, Niagara Falls, Canada, September 15, 1927.

American Welding Society—Book-Cadillac Hotel, Detroit, Mich., September 19 to 23, 1927.

Sixteenth Annual Safety Congress—Chicago, Ill., September 26 to 30, 1927.

Eleventh Annual Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 26 to October 1, 1927.

Association of Dairy, Food, and Drug Officials of the United States—31st Annual Conference, West Baden Springs, Ind., October 11 to 14, 1927.

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[12] Scott, "Technical Methods of Metallurgical Analysis," p. 554 (1924).

Experiments in Wood Preservation[1,2]

II—Arsenites of Copper and Zinc

By Leo Patrick Curtin

ENGINEERING LABORATORIES, WESTERN UNION TELEGRAPH CO., NEW YORK, N. Y.

Formulas and procedures are given for the impregnation of wood by a one-movement process, with the following substances—zinc meta-arsenite, copper ortho-arsenite, copper aceto-arsenite, copper fluoride, and copper basic chloride. The first three compounds have important applications as commercial wood preservatives.

It is shown that the meta- and ortho-arsenites of zinc and copper are soluble in acid solutions of pH 5 and, therefore, soluble in the presence of growing wood-rotting fungi, which evolve acid of this strength.

Boiling tests are described which show that the arsenites of zinc and copper are highly resistant to leaching effects.

Data are given on toxicity tests in the field and in the laboratory which show that the preservatives are as toxic as theoretical considerations indicate.

IN THE preceding paper[3] it was shown that the growths of wood-rotting fungi were attended by immediate production of acid, the hydrogen-ion concentration being approximately pH 5. The present paper will describe several salts of value as wood preservatives which are of extremely low solubility in water but are soluble in solutions of pH 5 or less. Because of their lack of solubility, these salts are not leached out of the wood to an appreciable extent by rains and, by their property of dissolving in acidic solutions, they are effective fungicides and insecticides. It was decided to limit the investigation to preservative solutions which could be used in a one-movement process—that is, a treatment which requires but one treating liquid and one handling of the wood.

The preservative salt must, of course, contain at least one toxic ion; otherwise it would have little or no preservative effect. It must also be obtainable cheaply and in large quantities. For pressure treating, the salt solution must be non-corrosive toward iron, since the treating cylinder and other equipment are of iron or steel. This consideration is not so important in open-tank treating, where the treating tanks may be of wood or concrete.

The salts of iron and the metals below it in the electromotive series are all corrosive toward iron. In this group copper salts were considered to be the most promising as wood preservatives. Mercury and, to a lesser extent, nickel salts are highly toxic but are expensive, while ferrous and ferric salts tend to pass into iron rust when exposed to the elements. In the non-corrosive group zinc, already widely known in the form of zinc chloride as a wood preservative, appeared to be the only metallic ion worthy of consideration. Of the negative ions, arsenites, fluorides, and borates appeared to be possibilities. The others were rejected because of lack of toxicity, high cost, or for chemical reasons.

Table I—Toxicities of Various Salts toward *Fomes annosus*

SALT	KILLING POINT *Per cent*
Zinc chloride	0.35
Copper sulfate	0.15
Copper fluoride	0.08
Sodium fluoride	0.25
Sodium arsenite	0.025
Arsenious oxide	0.015
Mercuric chloride	0.015

The toxicities of materials containing certain of these ions are given in Table I. The killing point is the lowest concentration of the salt in a nutrient medium at which the growth of the wood-destroying fungus *Fomes annosus* is totally inhibited. As a later paper will be devoted solely to the toxicity of preservatives, very brief reference will be made to it here.

Arsenites of Copper

The first experimental work had for its object the impregnation of wood with toxic, difficultly soluble salts of copper. For more than fifty years chemists in the copper industry have known that cuprous chloride, although of very low solubility in water, is quite soluble in the presence of considerable chloride ion, particularly at elevated temperatures. This property has been made the basis of several processes for copper-refining. Complex ions are formed in which the copper appears in the negative radical, $(CuCl)^-$ being the simplest type.

Cupric ion is readily reduced to the cuprous condition by many reagents, sodium bisulfite being one of the best for this purpose. If the reduction is done in the presence of small amounts of chloride ion, white, crystalline cuprous chloride is precipitated; if considerable chloride is present, there is no precipitate, the complex ion $(CuCl_2)^-$ being formed. This solution is readily oxidized by atmospheric oxygen with formation of basic chlorides of copper.

The reduction and subsequent oxidation occur substantially as follows:

$$2CuSO_4 + NaHSO_3 + 2NaCl + 3NaOH \longrightarrow 2CuCl + 3Na_2SO_4 + 2H_2O$$

$$2CuCl + O \longrightarrow CuO + CuCl_2$$

Sodium hydroxide or soda ash is added to neutralize partly the sulfuric acid liberated by the reduction; otherwise, oxidation would regenerate copper sulfate or chloride with no production of basic copper. In practice a slightly smaller quantity of base must be used than is indicated in the equation. Cuprous hydroxide starts to precipitate before true neutrality is reached and the solution must be left faintly acid to keep the copper in solution. A slight excess of bisulfite is used to protect against premature oxidation.

Laboratory experiments showed that a solution of sodium cuprochloride readily penetrated small sticks of yellow pine and that a large part of the copper was precipitated as rapidly as atmospheric oxygen diffused through the wood. The precipitate was largely a mixture of basic chlorides, eighteen of which are known, the simplest and least basic being

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[1] Received April 11, 1927.

[2] The various processes, preservatives, and products described in this and successive papers are protected in the United States and foreign countries by patents and patent applications owned by the Western Union Telegraph Company and the Curtin-Howe Corporation.

[3] THIS JOURNAL, 19, 878 (1927).

$2CuO.CuCl_2$. In this case one-fourth of the copper will be present as soluble normal chloride or sulfate while, if the products of oxidation are $CuO + CuCl_2$, one-half of the copper will finally be in solution.

Although the copper oxide and basic chloride would no doubt have preservative properties, it is evident that the treatment might be improved by replacing the oxy or hydroxy group with a highly toxic ion, such as arsenite, and precipitating the soluble copper by fluoride ion. The precipitating reactions would then be as follows:

$$3CuO + 3CuCl_2 + As_2O_3 + 2H_2O + 6NaF \longrightarrow Cu_3(AsO_3)_2.2H_2O + 3CuF_2 + 6NaCl$$

It was found that the presence of arsenious acid and fluoride ion in the solution interfered in no way with the reduction of cupric ion by sodium bisulfite or with the subsequent oxidation by the atmosphere. The second reaction proceeded with precipitation of copper as yellowish green ortho-arsenite, Scheele's green, and pale blue copper fluoride.

One hundred white cedar (arbor vitæ) poles were butt-treated with the copper arsenite-fluoride solution, with very satisfactory results as far as the treatment itself was concerned. The solution containing fluoride ion was somewhat corrosive, even toward copper heating coils, and there also appeared to be a tendency for the cupric fluoride to hydrolyze into basic fluoride and free hydrogen fluoride. Since arsenite is both cheaper and more toxic than fluoride and is also non-corrosive, it was decided to discontinue the use of fluoride, replacing it with arsenious oxide.

As already stated, the treating solution is faintly acid, which means that arsenious oxide must be used as the free acid. Ortho-arsenious acid has a primary dissociation constant of 6×10^{-10} at 25° C., much lower than carbonic acid and in the class with boric and hydrocyanic acids. This fact, together with the insolubility of the arsenites of copper, suggested the use of acetic or other volatile acid as a means of precipitating the copper in the soluble copper salts. Starting with a solution containing cupric ion, acetate ion, and arsenious acid, the following reaction took place on evaporation of the solution:

$$4Cu^{++} + 8(CH_3COO)^- + 3As_2O_3 + 3H_2O \longrightarrow Cu_4(AsO_2)_6(CH_3COO)_2 + 6CH_3COOH$$

The precipitate, Paris green, was thrown down progressively as the solution lost acetic acid by evaporation.

The preservative solution was then modified by eliminating the fluoride and adding appropriate quantities of arsenious oxide and calcium acetate. When calcium acetate and copper sulfate are used, the resulting precipitate of calcium sulfate is discarded. Sodium or copper acetates may be used, but the calcium salt is the least expensive.

An experiment was also made to ascertain whether formate ion might be substituted for acetate ion in this last reaction. Formic acid, while four or five times more highly ionized, has a somewhat lower boiling point than acetic acid and also considerable tendency to oxidize to carbonic acid, which would permit quantitative precipitation of copper arsenite. The experiment showed that there was very little oxidation of the formic acid and the precipitation of the copper by this means was quite unsatisfactory. The very small amount of precipitate formed was lighter in color than Paris green.

Table II—Formula for Copper Arsenite Preservative Solution

Material	*Per cent*	*Mol*
Copper sulfate	2.80	0.0112
Sodium carbonate	0.75	0.0078
Arsenious oxide	1.25	0.0063
Sodium acetate	1.55	0.0114
Sodium chloride	4.00	0.0690
Sodium bisulfite	0.70	0.0067

The preservative solution is now being made according to the formula given in Table II.

The toxic precipitate is a mixture of cupric ortho-arsenite, $Cu_3(AsO_3)_2.2H_2O$, and cupric aceto-meta-arsenite, $Cu_4(AsO_2)_6(CH_3COO)_2$, Scheele's green, and Paris green. This formula gives a solution of approximately 2 per cent with respect to the toxic precipitate, calculated as $2CuO.As_2O_3$.

The bluestone is dissolved in half the water. The other materials are dissolved, in the order given, in the remainder of the water, which is at the boiling temperature. This second solution is added to the cupric solution, which is also very hot, and the mixture is held at the boiling point for 5 minutes. The resulting solution is faintly yellow with no precipitate and is ready for the treatment of wood. If the solution is water-white, not enough alkali has been added. If the treatment is to be made at 85° C. or higher, the percentage of sodium chloride may be reduced one-third. In any case some cuprous chloride settles out on cooling but redissolves when the solution is heated again.

Although the chemical reactions are fairly complex, the solution may be prepared readily by ordinary labor. It is desirable, however, to have reasonable accuracy in the weighing out of the chemicals.

The principal chemical reactions are as follows:

(1) Reduction reaction:

$$4CuSO_4 + 2NaHSO_3 + 8NaCl + 3Na_2CO_3 \longrightarrow 4Na(CuCl_2) + 6Na_2SO_4 + H_2O + 3CO_2$$

At this point the product is a faintly yellow liquid which is used to impregnate wood. Arsenious oxide and sodium acetate are also present in the solution but remain unchanged up to this point. The following reactions are typical of those which are believed to take place inside the wood, after it has been removed from the treating solution:

(2) Oxidation reaction:

$$4NaCuCl_2 + O_2 + 2H_2O \longrightarrow 2Cu(OH)_2 + 2CuCl_2 + 4NaCl$$

(3) Precipitation of Scheele's green:

$$3Cu(OH)_2 + As_2O_3 \longrightarrow Cu_3(AsO_3)_2.2H_2O$$

(4) Precipitation of Paris green:

$$4CuCl_2 + 8CH_3COONa + 3As_2O_3 + 3H_2O \longrightarrow Cu_4(AsO_2)_6.(CH_3COO)_2 + 6CH_3COOH + 8NaCl$$

Reactions (2) and (3) take place quickly, the treated wood showing a definite yellowish green 5 minutes after being removed from the treating bath. Reaction (4) takes place more slowly since its limiting factor is the rate of evaporation of acetic acid. By the time the wood has lost most of its moisture, the copper is completely precipitated as arsenite and aceto-arsenite.

Approximately four hundred cedar and chestnut poles were butt-treated by this process in 1926 under ordinary plant conditions. A film of oil was maintained on the surface of the preservative solution to retard oxidation and evaporation. These poles were later placed in Western Union lines in the Middle West.

To obtain some information as to the solubility of Scheele's green, the following experiment was performed:

> A dilute solution of copper sulfate was prepared and also a solution of sodium carbonate and arsenious acid which contained exactly enough arsenious acid to precipitate the copper as arsenite and three times as much carbonate as would be required to precipitate the copper as basic carbonate. When the second solution was poured into the solution of copper sulfate the copper was quantitatively precipitated as ortho-arsenite.

This would indicate that the solubility of the cupric ortho-arsenite is less than that of the basic carbonate. $Cu_2(OH)_2CO_3$ is known to have a solubility in cold water of approximately 5 p. p. m.

Toxicity tests showed that 4 parts of Scheele's green in

10,000 parts of nutrient jelly completely inhibited the growth of the wood-destroying fungus *Fomes annosus*. This is in accordance with the theory that the acid liberated by the fungus has a solvent effect on the arsenite.

In order to determine the nature of the yellowish green precipitate formed by the oxidation of cuprous ion in the presence of arsenious acid, analyses were made on two lots of precipitate from solutions prepared independently.

There has been some disagreement as to the formula of Scheele's green. Bloxham's[4] formula, which appears to be incorrect, was widely disseminated in the literature, particularly in his textbook. Sharples[5] did very thorough investigation in the same field and published results which agree fairly well with those given below. In the following analyses it will be noticed that, although the ratio of copper to arsenic in the solution was that of Bloxham's formula, the precipitate showed a ratio corresponding to Sharples' formula.

No acetate ion or fluoride ion was present in the solutions and the precipitate was fairly pure Scheele's green. Oxidation was accomplished by drawing air through the solution, which was at room temperature. Analyses of insoluble arsenicals generally show considerable variation from the mean (Table III).

Table III—Analysis of Copper Arsenite

Lot	Analysis of Ppt. As	Analysis of Ppt. Cu	Ratio of As:Cu In ppt.	Ratio of As:Cu In original soln.
	Per cent	*Per cent*		
1	28.4	36.2	0.666	1.00
2	30.6	37.2	0.696	1.00
Mean	29.5	36.7	0.681	1.00
Scheele's green:				
Sharples' formula, $Cu_3(AsO_3)_2.2H_2O$, by computation	31.7	40.4	0.667	
Bloxham's formula, $CuHAsO_3$, by computation	40.4	33.8	1.00	

Meta-Arsenites of Zinc and Copper

In reaction (4) it was shown that copper aceto-arsenite may be precipitated from a solution containing copper acetate and arsenious acid as a result of evaporation of acetic acid. It was decided to investigate the practicability of using this reaction as the basis of an independent method of wood preservation and, further, to investigate what metallic ions besides copper might be used.

Solutions of arsenious oxide, sodium acetate, and a soluble salt of the metal under test were prepared with sufficient free acetic acid to permit the formation of no more than a faint precipitate. The solution was then filtered and allowed to evaporate by exposure to air. The ratio of metal to arsenic in the solution was 1:1.

Lead and mercury acetates reacted satisfactorily, but both were discarded because of cost and the corrosive nature of their solutions. Cupric ion was a very satisfactory precipitant. Zinc was also satisfactory, precipitating the arsenic almost as well as copper. Copper has a slight advantage in that acetate ion is removed by precipitation as well as by evaporation while zinc does not precipitate acetate. In the case of barium there was no precipitate when half the water had evaporated. The other alkaline earths also failed to precipitate arsenic. The arsenites of this group, while but sparingly soluble, are too soluble to be deposited in the presence of traces of acetic acid. It appeared that, in addition to the cupric salt, an arsenite of zinc could also be readily precipitated by the evaporation of acetic acid. These two salts were therefore studied in considerable detail.

Copper Aceto-Arsenite (Paris Green)

It was observed that the arsenite of copper thrown down in the evaporation process under discussion was a deeper, richer green than that obtained in the oxidation process, its color being suggestive of the widely used insecticide and fungicide, Paris green.

Two formulas are given for Paris green—the first and correct one being $3CuO.(As_2O_3)_3.Cu(CH_3COO)_2$;[6] the second is $Cu_3(AsO_3)_2.Cu(CH_3COO)_2$.[7] It is seen that the second is a copper salt of ortho-arsenious acid. The first formula may be rewritten as $Cu_3(AsO_2)_6.Cu(CH_3COO)_2$. This makes it clear that Paris green is probably a derivative of meta-arsenious acid.

A solution of arsenious oxide in water probably contains the oxide in various degrees of hydration.

$$\underset{\text{Arsenious oxide}}{As_2O_3} \rightleftharpoons \underset{\text{Meta-arsenious acid}}{2HAsO_2} \rightleftharpoons \underset{\text{Ortho-arsenious acid}}{2H_3AsO_3}$$

Acetic acid is very much more highly ionized than ortho-arsenious acid, which is the weaker arsenious acid. A solution of arsenious oxide in presence of small concentrations of acetic acid would therefore contain a negligible proportion of the ortho acid. The salts precipitated under such conditions would be meta-arsenites, since these may be formed from the appreciable quantities of meta-arsenious acid, and, in some cases, from arsenious oxide itself.

Such has been found to be the case. If the solutions are neutral or basic, ortho salts are formed. For example, in a solution containing zinc chloride, sodium hydroxide, and arsenious oxide, it may be considered that (*a*) meta-arsenite or (*b*) ortho-arsenite may be formed.

$$3ZnCl_2 + 6NaOH + 3As_2O_3 \longrightarrow \begin{cases} (a) & 3Zn(AsO_2)_2 + 6NaCl + 3H_2O \\ (b) & Zn_3(AsO_3)_2 + 6NaCl + 2As_2O_3 + 3H_2O \end{cases}$$

Such a solution was prepared to check the correctness of the theory and it was found that reaction (*b*) took place. The zinc was precipitated quantitatively, leaving considerable arsenious oxide in solution. The filtrate was analyzed and found to contain two-thirds of the original arsenic. This shows that the formation of ortho-arsenite is the reaction in neutral or alkaline solutions.

To clear up the question of chemical composition and at the same time ascertain the correct formula for the wood-preserving solution, several analyses were made, with the results given in Table IV.

Table IV—Analyses of Copper Aceto-Arsenite Paris Green

(Prepared from cold solutions of cupric acetate and arsenious acid, precipitation occurring as result of evaporation of acetic acid)

Lot	Analysis of Ppt. As	Analysis of Ppt. Cu	Ratio of As:Cu In ppt.	Ratio of As:Cu In original soln.
	Per cent	*Per cent*		
1	42.4	22.3	1.61	1.00
2	42.2	25.6	1.40	0.50
3	43.6	24.8	1.49	1.50
Mean	42.7	24.2	1.50	
Paris green:				
Formula $3Cu(AsO_2)_2.$-$Cu(CH_3COO)_2$ by computation	44.4	25.0	1.50	
Formula $Cu_3(AsO_3)_2.$-$Cu(CH_3COO)_2$ by computation	24.3	41.1	0.50	

It is clearly evident from the analytical data that the precipitate obtained by the proper action of this wood-preserving solution is fairly pure Paris green.

Analysis of lot 3, from a solution containing the proper proportions of the reacting materials, brings this out clearly. Evaporation was accomplished by drawing through the solution a stream of air previously filtered through cotton. In spite of this precaution a few particles of dust were found

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[4] *J. Chem. Soc.* (*London*), **15**, 281 (1862).

[5] *Chem. News*, **35**, 89, 108 (1877).

[6] Thorpe, Dictionary of Applied Chemistry.

[7] Smith, "Inorganic Chemistry," and elsewhere.

in the precipitate, slightly depressing the percentage values but not altering the ratio of arsenic to copper.

The solution for the deposition of cupric aceto-arsenite in wood is made up as given in Table V.

Table V—Formula for Copper Aceto-Arsenite Preservative Solution

Material	Per cent	Mol
Sulfuric acid (sp. gr. 1.84)	0.67	0.0061
Bluestone	2.00	0.0080
Calcium acetate	2.25	0.0142
Soda ash	0.05	0.0005
Arsenious oxide	1.25	0.0063

The first three materials are dissolved together in cold water. The second solution is prepared by heating the soda ash and arsenic in approximately half the water and holding at the boiling temperature for 5 minutes. When both solutions are cold the arsenic solution is poured into the copper acetate solution. Nothing more than a faint trace of precipitate should be formed when the two solutions are brought together. If appreciable quantities of copper arsenite are formed, more acetic acid should be used. This solution is of approximately 2 per cent concentration with reference to the toxic material calculated as copper aceto-arsenite. It is suitable for treating at 30° C. or lower. If the treating temperature is to be higher, more acetic acid must be used to keep the copper in solution.

In 1926, one hundred poles were successfully butt-treated with this solution and set in Western Union lines.

Zinc Meta-Arsenite

This preservative was developed in an effort to find a material which would be as toxic, inexpensive, and permanent as the arsenites of copper and also have the advantage of being non-corrosive to iron. These objectives are all attained with this material.

Zinc meta-arsenite is precipitated from a solution containing zinc ion, acetate ion, and arsenious acid. It is but seldom mentioned in the literature of chemistry. Avery[8] has done the most important work in this field. His product proved, on analysis, to be the meta-arsenite of zinc. The present writer's results check those of Avery within reasonable limits (Table VI).

Table VI—Analysis of Zinc Meta-Arsenite

(Prepared by evaporation of acetic acid from a cold solution of zinc acetate and arsenious acid)

	Analysis of Ppt.		Ratio of As:Zn	
Lot	As	Zn	In ppt.	In original soln.
	Per cent	Per cent		
1	51.6	23.1	1.95	1.00
2	52.5	20.6	2.22	2.00
Mean	52.1	21.9	2.09	
Zinc meta-arsenite, $Zn(AsO_2)_2$, by computation	53.7	23.4	2.00	

Table VII—Formula for Preparation of Zinc Meta-Arsenite Solution, 2 Per Cent Strength

Material	Per cent	Mol
Sulfuric acid (sp. gr. 1.84)	0.20	0.0019
Zinc sulfate	2.00	0.0070
Calcium acetate	1.40	0.0089
Soda ash	0.05	0.0005
Arsenious oxide	1.50	0.0075

A solution is made of the first three materials in cold water and the resulting calcium sulfate discarded. The soda ash and arsenious oxide are dissolved separately in half the total quantity of water with heating, and when cool this solution is poured into the solution of zinc acetate. This formula is for treating at 30° C. or lower; if the temperature is higher, a slight increase in the acetic acid content in the solution must be made. It has been found that 0.3 per cent of additional glacial acetic acid will stabilize the solution against precipitation at 100° C. The disadvantage of this added acetate is that precipitation of zinc arsenite in the wood is more sluggish than if the formula had been followed.

The precipitation of arsenites by evaporation of acetic acid is a process requiring days and in some cases weeks for completion. Dryness and warmth cause it to take place in a few days.

The zinc-arsenic solution made according to the above formula has so little effect on iron that it may be regarded as non-corrosive toward that metal.

No corrosive effects were observed from contact of the solution with the iron treating cylinder and other steel and iron equipment. Qualitative tests with iron nails and other small pieces of iron and steel showed no corrosion and but a slight darkening of the brightly polished surfaces.

A quantitative test, in triplicate, against 5 per cent zinc chloride solution as a standard, was made on bright pieces of sheet iron at room temperature. The pieces of metal were immersed in the solutions for one week, without stirring or change of solution. At the end of that time the sheet iron in the zinc-arsenic solution showed no loss in weight while those pieces in the zinc chloride solution had lost 2.2 grams per square meter of surface.

Manufacturers of sulfuric acid are familiar with the fact that arsenious oxide in solution tends to make iron passive. Sulfuric acid made from pyrites[9] usually contains a small percentage of arsenious oxide and is of little or no value for the pickling of steel. The arsenic inhibits the usual reaction between the acid and the metal.

To learn the rate of precipitation of zinc arsenite the following materials were dissolved in 600 cc. of distilled water at room temperature: arsenious oxide 6, zinc chloride 4.1, sodium acetate 8.2, and glacial acetic acid 0.2 gram. A current of air was then passed through to cause evaporation. When the volume of the liquid had been reduced to 500 cc., the precipitate that had formed was collected, dried, and weighed. It was found that 41 per cent of the total possible yield of zinc meta-arsenite had been precipitated as a result of evaporation of 17 per cent of the solution. This sample was lot 2 in the analyses of zinc arsenite.

A similar test made with copper acetate and arsenious oxide showed that 34 per cent of the total possible precipitate had been thrown down when 12 per cent of the solution had evaporated. The Paris green precipitate is apparently of lower solubility than the zinc arsenite, and precipitates with even greater readiness than the foregoing figures indicate.

A solution of zinc arsenite is colorless and the salt is not easily seen when precipitated in wood. It seemed desirable, therefore, to devise some means by which the depth of penetration of the solution could be shown in a colorimetric manner. Two tests have been devised which are quite satisfactory. Both are tests for arsenite; the zinc ion present takes no part in the reactions. The first test requires wetting the block of wood to be tested with a solution of copper sulfate by carefully dipping or spraying with an atomizer. The block is allowed to stand for a few minutes, then is held for a moment in ammonia fumes. A characteristic grass-green precipitate of copper arsenite is formed. The second method gives a reddish brown coloration on the treated area due to the formation of silver ortho-arsenate. Silver nitrate crystals are dissolved in ordinary 3 per cent hydrogen peroxide. The wood under test is carefully dipped into this solution or sprayed with it. The characteristic color appears at once wherever arsenite has penetrated, but does not reach its maximum intensity until after several minutes. This color persists for a few days but gradually deteriorates owing to the decomposition of the silver salts when exposed to light. Both tests show up best on horizontal cross sections

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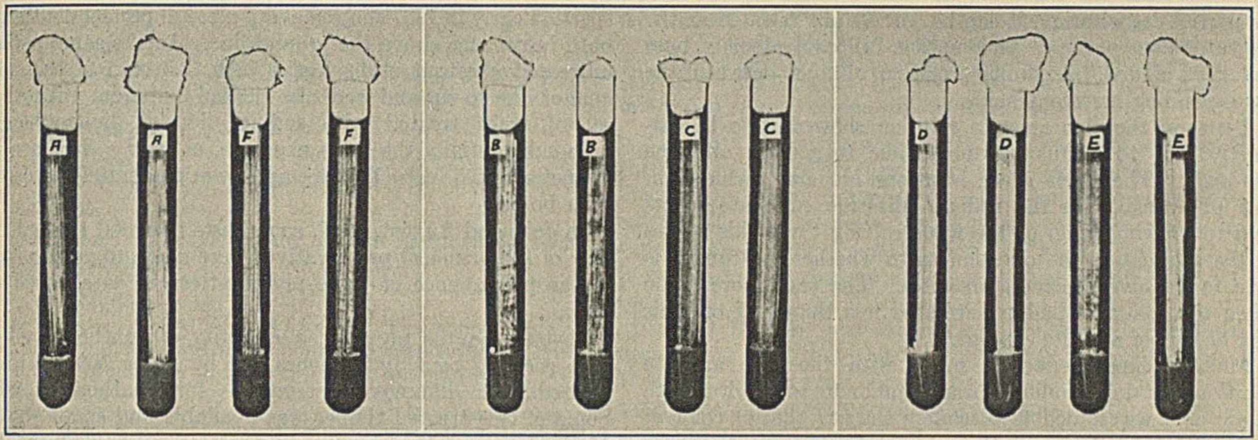
[8] *J. Am. Chem. Soc.*, **28**, 1161 (1906).

[9] Drefahl, Grasselli Chemical Co., private communication.

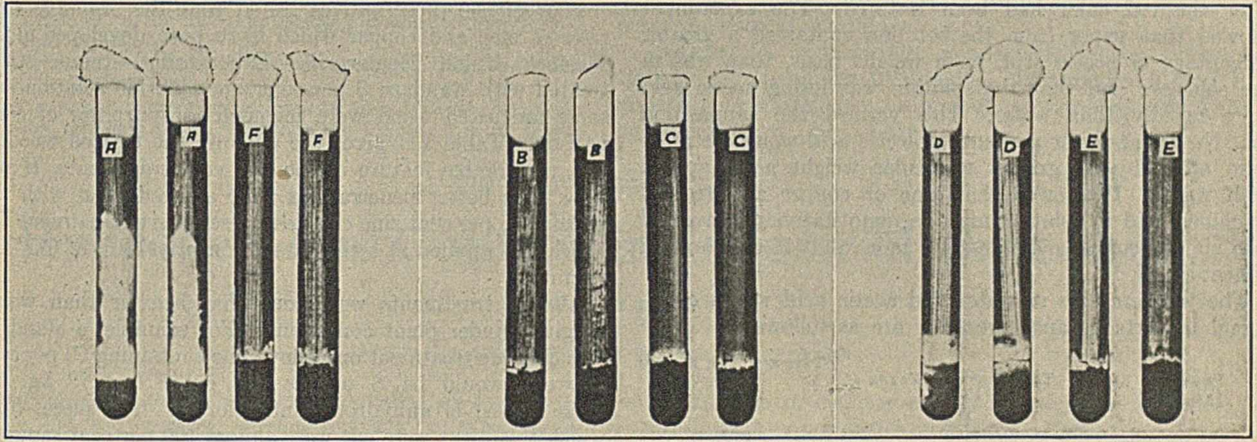


A—untreated
F—2% copper aceto-arsenite

B—2% copper arsenite
C—2% copper arsenite-fluoride

D—5% zinc chloride
E—2% zinc arsenite

One Day after Inoculation

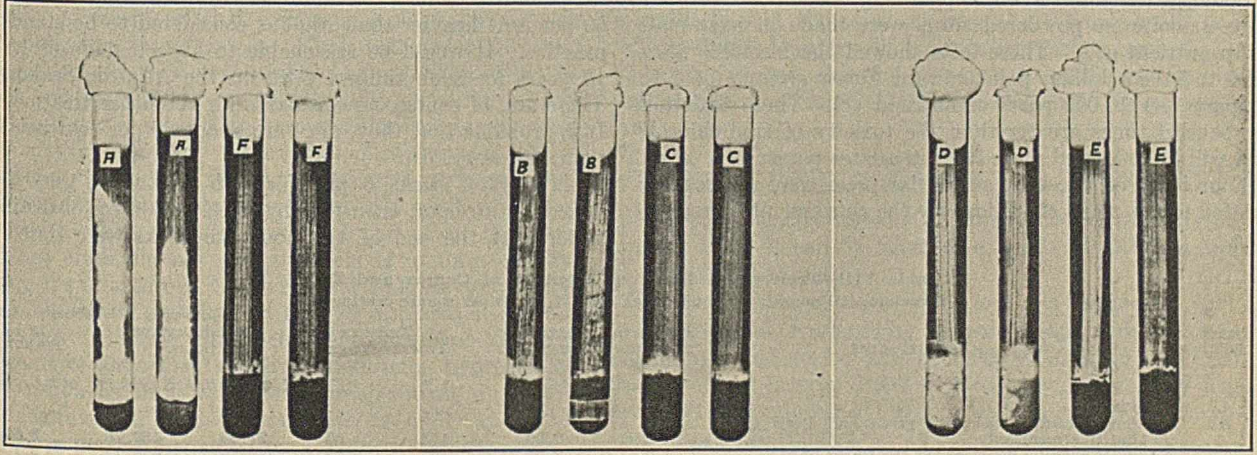


A—untreated
F—2% copper aceto-arsenite

B—2% copper arsenite
C—2% copper arsenite-fluoride

D—5% zinc chloride
E—2% zinc arsenite

Fifteen Days after Inoculation



A—untreated
F—2% copper aceto-arsenite

B—2% copper arsenite
C—2% copper arsenite-fluoride

D—5% zinc chloride
E—2% zinc arsenite

Twenty-Seven Days after Inoculation

of wood. The silver arsenate test is slightly more delicate than the other.

Previous studies of Scheele's green showed that this material is very toxic in spite of its low solubility. Scheele's green is an ortho-arsenite, whereas Paris green and zinc arsenite are meta-arsenites. Meta-arsenious acid is slightly stronger than ortho-arsenious acid, and for this reason there was a possibility that insoluble meta-arsenites would not be brought into solution by fungi.

Boric acid, which exists in the meta and ortho modifications, cannot be analyzed with phenolphthalein and standard alkali while in the ortho form. The indicator gives an alkaline reaction before a full equivalent of alkali is added. If, however, the ortho acid is converted into the meta form by partial dehydration, it can be successfully titrated as the indicator does not turn pink until a full equivalent of base has been added. A similar relation obtains between the corresponding arsenious acids.

Tests on the zinc arsenite solution showed it to be distinctly acid to litmus but non-acidic to sodium alizarine sulfonate. The Paris green solutions are also included in this pH range. As the sodium alizarine sulfonate reacts acid to growing fungi of the wood-rotting type, this settles in the affirmative the question as to whether the fungus is able to dissolve the meta-arsenites. The tests were made when the solutions had precipitated less than half of their zinc or copper arsenite content.

Another experiment was made with the zinc arsenite solution containing sodium alizarine sulfonate to which enough acetic acid was added to discharge the red (basic) color of the indicator. Air was then bubbled through to cause evaporation. The solution gradually passed through pink and light red until the basic color of the indicator was restored. No precipitation of zinc arsenite took place until after the red color had been restored. The experiment showed that vapor from the solution contained a greater percentage of acetic acid, on a weight basis, than was in the solution, and that the solution was losing acetic acid more rapidly than water. This verified the supposition that the lower vapor pressure of acetic acid would be more than offset by its greater molecular weight as compared with water. It showed that zinc or copper acetate and arsenious acid in solution may be quantitatively converted into zinc or copper meta-arsenite as a result of evaporation of acetic acid.

The temperatures of water and acetic acid which correspond to certain vapor pressures are as follows:

PRESSURE	TEMPERATURE WATER	TEMPERATURE ACETIC ACID
Mm. Hg	° *C.*	° *C.*
5	1.3	5.5
10	11.3	16.8
20	22.3	29.3
30	29.9	36.6

Toxicity Tests

Some toxicity tests on copper aceto-arsenite and zinc meta-arsenite in powdered form were made in agar–malt sirup nutrient gels. These tests showed the insoluble arsenites to have a killing point toward *Fomes annosus* of 4 to 10 parts per 10,000 parts of nutrient gel. These toxicities are several times greater than the toxicity of zinc chloride and will be discussed more fully in a later paper.

Four hundred chestnut and cedar poles were successfully treated under plant conditions by the zinc arsenite preservative.

Table VIII—Preservative Effect of Arsenites of Copper and Zinc
(Pressure, 100 pounds per square inch or 7031 grams per square centimeter)

TREATMENT	PRESERVATIVE	STRENGTH SOLUTION	DURATION TREATMENT	AV. TREATING TEMPERATURE		ABSORPTION PRESERVATIVE SOLN.		PRESERVATIVE IN TIMBER
		Per cent	*Hours*	° *F.*	° *C.*	*Lbs./cu. ft.*	*Kg./cu.m.*	*Oz./cu. ft.* or *Kg./cu. m.*
A	Untreated	.	..	..	..	..	..	..
B	Copper arsenite; Scheele's green and Paris green; hot treatment only	2	2.00	153	67	27.36	437.76	8.8
C	Copper arsenite-fluoride; hot treatment only	2	2.25	162	72	28.32	453.12	9.1
D	Zinc chloride; preferably hot treatment	5	2.25	149	65	29.60	473.60	23.7
E	Zinc arsenite; cold treatment	2	2.25	52	11	32.54	520.64	10.4
F	Copper aceto-arsenite; Paris green; cold treatment	2	2.25	54	12	32.28	516.48	10.3

In the spring of 1925, fifty stubs of cedar, yellow pine, and chestnut were treated by open-tank and pressure processes with three of the copper-arsenic preservative solutions. These treatments correspond to treatments *B*, *C*, and *F* described below. The pine sticks were square, sawn timbers and the others round sections of poles. After a brief seasoning they were set in a fungus test pit in New Jersey where attack by insects and fungi is unusually severe. An inspection early in 1927 showed every piece in perfect condition both below and above the ground line. In the same period untreated chestnut stubs lost 1 inch (2.5 cm.) of their diameter due to rot and were also riddled by borers. Another set of stubs treated with sodium fluoride–dinitrophenol, with substantially the same exposure, showed a decrease in diameter of 0.5 inch (1.3 cm.) and were moderately infested with borers.

In July and August, 1926, some tests on wood treated by four of the arsenical preservatives were made to get an idea of the permanence of these preservatives when exposed to rains.

Several months previous, a quantity of southern yellow pine sticks (2 by 4 by 30 inches or 5 by 10 by 76 cm.) were treated with different preservatives for weathering tests. Some of this treated timber was available and small sticks, 15 cm. long and 1 sq. cm. in cross section, were cut from the larger pieces for the laboratory experiment described below. These sticks were cut so that at least one side was from the surface of the 2 by 4-inch (5 by 10-cm.) stick.

Four of the preservatives tested were the insoluble arsenites of zinc and copper which have been developed in the Western Union Engineering Laboratories. Some sticks treated with standard 5 per cent zinc chloride solution and some untreated wood were included for purposes of comparison. Table VII gives the data on the treated wood.

A remarkable feature of the two cold treatments, *E* and *F*, is that better penetrations were secured than with the standard 5 per cent zinc chloride preservative (treatment D), which was applied at a temperature nearly 100° F. (55° C.) warmer.

All the treatments were somewhat heavier than would be given under plant conditions. For example, a standard zinc chloride treatment on yellow pine containing 50 per cent sapwood would be 8 ounces per cubic foot (8 kg. per cubic meter) of anhydrous zinc chloride. The pieces from which the sticks were cut were almost 100 per cent sapwood and, with similar treatment, would take up about 16 ounces of zinc chloride per cubic foot (16 kg. per cubic meter). Since they actually contain 23.7 ounces per cubic foot (24 kg. per cubic meter), it is seen that the treatment was about 50 per cent heavier than what is considered to be standard practice. It would be reasonable to expect a life of 12 to 15 years for such timber, even on the Atlantic Seaboard. There are, of course, no standards for the other treatments. It is probable that they, also, are about 50 per cent heavier than necessary.

Six pairs of sticks, a pair for each treatment, were then boiled for an hour, each pair by itself in 800 cc. of distilled water. At the end of the hour the sticks were rinsed in distilled water and again boiled for an hour in fresh water. The treatment was again repeated, giving a total of 3 hours' boiling in three different quantities of distilled water. The untreated sticks were given the same boiling.

After standing in air overnight, the sticks, with the required glassware, etc., were sterilized in an autoclave at 15 pounds per square inch (1054 grams per square centimeter) steam pressure for 30 minutes. They were then transferred to 8-inch (20-cm.) sterilized test tubes containing about 10 cc. of standard agar-malt sirup nutrient gel. The gel was next inoculated under aseptic conditions with a pure culture of *Fomes annosus*.

The accompanying photographs of the cultures were taken 1, 15, and 27 days after inoculation. An inspection at the time the last set of photographs was taken showed the following:

A—Untreated. A dense healthy growth of fungus covering the sticks for a distance of 4 inches (10 cm.).

B—2 per cent copper arsenite. No growth on the sticks. These sticks fully resisted attack.

C—2 per cent copper arsenite-fluoride. The copper fluoride in these sticks did not resist the boiling temperature, but broke down into oxyfluoride with liberation of hydrofluoric acid. This acid had some solvent action on the copper arsenite; consequently these sticks entered the test minus most of their preservative. The wood showed a feeble growth of fungus to a height of 0.4 inch (1 cm.). No further progress was made after the final pictures were taken, and 2 weeks later the fungus on the wood was dead.

D—5 per cent zinc chloride. These sticks showed a healthy growth of fungus to a height of 1 inch (2.5 cm.). The growth was as dense as on the untreated sticks but was progressing only 25 per cent as fast.

E—2 per cent zinc arsenite. The resistance of these specimens was 100 per cent effective.

F—2 per cent copper aceto-arsenite. No growth whatever took place on these sticks. In fact the fungus growing in the nutrient jelly appeared to shrink from physical contact with the wood. This feature was equally noticeable in cultures *B* and *E*. The slight growth noticeable in these photographs is in the jelly. By inclining the test tubes, a clear zone about 2 mm. wide could be seen around each stick.

The growths on culture *A* are principally of interest in showing how rapidly fungi may grow in untreated wood. We are no longer interested in the fluoride preservative, culture *C*. It has been supplanted by others which are superior from every point of view. It should be said that it is a good preservative and that boiling is not a fair test for it.

Culture *D*, 5 per cent zinc chloride, definitely broke down, despite the fact that the treatment was unusually heavy. It would appear very conservative, because of this failure, to say that the boiling test was equivalent to 10 to 15 years' exposure to the weather.

Cultures *B*, *E*, and *F* successfully resisted this drastic test. The wood was continually in contact with an active culture of fungus in an artificial nutrient medium, a condition more severe than anything which would occur in wood exposed to natural conditions.

Treatment *E*, zinc arsenite, is adapted to either pressure cylinder or open-tank treatments. Treatments *B* and *F* involve copper and, for the present, appear best suited for butt-treating in open tanks.

Hydrogen-Ion Control in Industrial Processes[1]

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Acidity and alkalinity are now controlled by hydrogen-ion methods in most lines of research and industrial work. Many, however, hesitate to use it, as they feel that its application requires the services of a specially trained chemist. The subject is discussed here in such simple terms as to enable the non-technical man to apply the method to his particular industry.

In DEVELOPING control methods for industrial processes, it was found that acidity and alkalinity were extremely important factors. Their real importance was not fully realized, however, until the introduction of hydrogen-ion control. Acidity and alkalinity were previously determined and regulated by means of litmus and other test papers and by titration. Hydrogen-ion measurements have shown that these older methods often give very erroneous and misleading results, and have explained why many processes which were apparently carried out under the same conditions often did not give products of uniform quality.

Many manufacturers, however, still hesitate to use hydrogen-ion control as they feel that its application requires the services of a highly trained chemist. This is not the case. In fact, it is almost as simple to determine hydrogen-ion concentration as it is to measure temperature, and these determinations can be made practically as easily and accurately by a plant foreman as by a trained chemist.

Theory of Hydrogen-Ion Concentration and Derivation of pH Values

According to the theory of electrolytic dissociation, all liquids of which water is a constituent contain free H and OH ions. When the number of H ions exactly equals the number of OH ions the solution is said to be neutral. If the number of H ions exceeds that of the OH ions the solution is said to be acid, if there is an excess of OH ions it is alkaline.

Pure distilled water will conduct an electric current to a very slight degree, showing that a very small proportion of the water is dissociated into H and OH ions. By the mass law,

$$\frac{\text{Concn. of H ions} \times \text{concn. of OH ions}}{\text{Concn. of undissociated } H_2O} = \text{a constant} \qquad (1)$$

Since the relative amount of undissociated water is extremely large, it can be taken as a constant, and equation (1) therefore becomes

$$\text{Concn. of H ions} \times \text{concn. of OH ions} = \text{a constant} \qquad (2)$$

By electrical conductivity measurements, this constant has been found to be 1/100,000,000,000,000, or 10^{-14}, at 22° C. Since in pure distilled water the number of H ions is equal to the number of OH ions, each must have a concentration of 1/10,000,000, or 10^{-7}.

This method of expressing H-ion concentration is very inconvenient. Sorensen, therefore, suggested the use of the term "pH," the pH value being the logarithm of the reciprocal of the hydrogen-ion concentration. Thus

$$\text{pH} = \log \frac{1}{(H^+)} \qquad (3)$$

in which (H^+) represents the concentration of H ions in grams per liter.

Just as an acid solution is said to be normal when it contains 1 gram of ionizable hydrogen per liter, so a solution is said to be normal with respect to hydrogen ions when it con-

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[1] Received April 30, 1927. Presented before several local sections of the American Chemical Society.

[2] President and Chemical Director, LaMotte Chemical Products Company.

tains 1 gram of ionized hydrogen per liter. Since one $1/(H^+)$ is the reciprocal of the normality of H ions in a solution, the pH value can also be defined as the logarithm of the denominator expressing the normality of H ions, such as $N/10$, $N/100$, $N/1000$, etc.

This method of expressing H-ion concentration has now been generally adopted. In the case of pure distilled water, in which the H-ion concentration is 0.0000001 gram per liter or $N/10{,}000{,}000$, the pH value would therefore be the log of 1/0.0000001 or of 10,000,000, which is 7.0. This value 7.0 is therefore the neutral point on the pH scale.

It will readily be seen that pH values below 7.0 will denote acidity, the degree of acidity increasing as the numbers decrease. For example, if a small amount of hydrochloric acid is added to pure distilled water which has an H-ion concentration of 10^{-7}, or a pH value of 7.0, the total number of H ions in the solution will be greater than 10^{-7}, and the solution will therefore be acid. Suppose the H-ion concentration is found to be $N/1{,}000{,}000$. The pH value will be the log of 1,000,000, which is 6.0. Similarly, if the H-ion concentration is $N/100{,}000$, the pH value will be 5.0, etc. It should be remembered that, since we are dealing with logarithmic values, a solution having a pH value of 6.0 contains ten times as many H ions as one having a pH value of 7.0. Similarly, a solution of pH 5.0 contains one hundred times as many H ions as one of pH 7.0.

From equation (2) it is apparent that as the H-ion concentration increases the OH-ion concentration must decrease, and vice versa. Even in a strongly alkaline solution, however, there are some H ions, and for the sake of simplicity it is advisable to express both acidity and alkalinity in terms of pH values.

From the fact that neutral water has an H-ion concentration of $N/10{,}000{,}000$, an alkaline solution must contain a smaller number of H ions. Let us assume that by adding a small amount of sodium hydroxide to pure water we decrease the H-ion concentration to $N/100{,}000{,}000$. The pH value of this solution would be 8.0. Similarly, if the H-ion concentration is reduced to $N/1{,}000{,}000{,}000$, the pH value would be 9.0. This shows why all values higher than 7.0 indicate alkalinity, the degree of alkalinity increasing as the numbers increase. It should be remembered here also that a solution of pH 9.0 contains ten times as many OH ions as one of pH 8.0, etc.

The exact meaning of H-ion concentration and pH values, and the derivation of the latter, can be made clear by a few concrete examples. An $N/10$ solution of hydrochloric acid is one which contains 3.65 grams of HCl or 0.1 gram of ionizable hydrogen per liter. Electrical conductivity measurements have shown that at 18° C. 91.4 per cent of the HCl is dissociated. The remaining 8.6 per cent, of course, exists as molecules. If the HCl were completely ionized, the $N/10$ solution would contain 0.1 gram of H ions per liter. Since, however, only 91.4 per cent is ionized, it contains $0.1 \times 91.4/100 = 0.0914$ gram of H ions per liter. The normality of this solution with respect to H ions is $1/0.0914 = N/10.94$. The pH value of $N/10$ hydrochloric acid is therefore the logarithm of 10.94 or 1.04.

An $N/10$ solution of acetic acid also contains 0.1 gram of ionizable hydrogen per liter. At 18° C. it is, however, dissociated only to the extent of 1.36 per cent. Hence the hydrogen-ion concentration is $0.1 \times 1.36/100 = 0.00136$ gram per liter. This is equivalent to an $N/735$ solution of H ions. The pH value of $N/10$ acetic acid is therefore the log of 735, which is 2.86.

Since the hydrogen-ion concentration of $N/10$ HCl is 0.0914 gram per liter and that of $N/10$ acetic acid is 0.00136 gram per liter, the hydrochloric contains almost seventy times as many hydrogen ions as the acetic acid.

Table I will give the worker some idea of the relationship between the total acidity or alkalinity and pH value of a few common acids and bases. The pH values have been given for $N/10$ solutions and are rounded off to the nearest 0.1 pH, as this is sufficiently accurate for general work.

Table I—pH Values of Some Common Acids and Bases

ACIDS	pH	BASES	pH
HCl	1.0	$C_6H_5NH_2$	7.8
H_3PO_4	1.5	$NaHCO_3$	8.4
CH_3COOH	2.9	$Na_2B_4O_7$	9.2
H_2CO_3	3.8	NH_4OH	11.3
H_3BO_3	5.2	Na_2CO_3	11.6
C_6H_5OH	6.0	NaOH	13.1

Buffer Action

It is clear from the foregoing discussion that if the solutions encountered in chemical processes were only solutions of known pure acids and alkalies their pH values could be calculated from the titration values and ionization constants. This is seldom the case, however, as the solutions normally contain relatively indefinite quantities of other substances, and usually a number of unknown impurities. Most of these solutions have what is known as "buffer action," which means that considerable quantities of acid or alkali can be added to them without changing their pH value. This action can best be illustrated by an example. Pure water, as stated above, has a pH value of 7.0. If 1 cc. of 0.01 N HCl is added to a liter of pure water, the pH value will be changed to about 5.0. Let us now consider a solution containing a mixture of sodium acetate and acetic acid. In this solution the dissociation of the acetic acid is very small.

$$CH_3COOH \leftrightarrows (CH_3COO)^- + H^+$$

The dissociation of sodium acetate is, however, large.

$$CH_3COONa \leftrightarrows (CH_3COO)^- + Na^+$$

Now suppose we add a small quantity of HCl to this solution. It is immediately largely dissociated into H and Cl ions.

$$HCl \leftrightarrows H^+ + Cl^-$$

We therefore have in solution H, Cl, Na, and CH_3COO ions. Acetic acid ionizes to only a very slight degree. This means that CH_3COO and H ions cannot exist together in solution to a very large extent. Therefore the H ions from the HCl will immediately combine with CH_3COO ions to form undissociated molecules of acetic acid, and the H-ion concentration or pH value of the solution will be only very slightly changed, if at all. The HCl added would of course be shown by titration. If, on the other hand, NaOH is added to this mixture, it will react with the H ions to form Na ions and H_2O. More acetic acid will then dissociate into CH_3COO and H ions and the H-ion concentration will be practically the same as it was before. It will therefore be seen that sodium acetate is a buffer salt and that considerable quantities of acids or alkalies may be added to solutions containing buffer salts without changing the pH value. Since this is true, it is clear that buffered solutions can be diluted with distilled water, even though the water shows a very acid reaction, without affecting the pH value. In fact, some solutions can be diluted as much as 1000 to 1. This is often important in making determinations on very highly colored and turbid solutions.

In general, the salt of any weak acid or weak base is a buffer salt. There are, therefore, very few solutions which are free from buffer action. For example, the phosphate in raw sugar and culture media, carbonates in raw water, carbonates and silicates in clay work, alum and rosin in paper sizing, etc., have buffer action.

The figures in Table II showing determinations on liquors in a sugar refinery[3] will bring out the importance of making

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[3] Blowski and Holven, THIS JOURNAL, 17, 1263 (1925).

pH determinations rather than determining the total acidity or alkalinity by titration.

Table II—Comparison of Acidity and Alkalinity by Titration with pH Values

Acidity by Titration	pH	Alkalinity by Titration	pH
Per cent		*Per cent*	
0.001	6.5	0.001	8.3
0.010	6.4	0.003	7.3
0.005	5.3		
0.005	7.0		

In the first pair of figures the acidity of the second liquor is just ten times that of the first one, as determined by titration. The pH values of the two are, however, practically the same. In the second pair of figures both have an acidity by titration of 0.005 per cent, while the pH values show the acidity of the first to be almost one hundred times greater than the second. The third pair of figures shows even greater discrepancy. By titration the second solution is three times as alkaline as the first. By pH measurements, however, the first is ten times as alkaline as the second. Solutions from other processes show similar errors.

Unbuffered Solutions

It will now be realized that no special precautions are necessary in making pH measurements on buffered solutions, since the addition of considerable amounts of acid or alkali can be made without affecting their pH value.

Such is not the case with distilled water or with unbuffered solutions. The fact that distilled water is one of the most difficult materials to test for pH is frequently overlooked. It is absolutely devoid of any buffering action, and is thus very susceptible to change either before or during the test—for example, by the absorption of carbon dioxide, etc.

Pure distilled water has a pH value of 7.0 at 22° C. The reaction of ordinary distilled water is always acid, however, because of the absorption of carbon dioxide. Water that has taken up carbon dioxide from the air until equilibrium has been established will contain about 0.3 per cent of carbon dioxide by volume, and the calculated pH should be 5.7. In fact, this is the value usually found in distilled water which has been freely exposed to pure air. Water from an efficient automatic still, when stored in closed non-soluble glass vessels, will have a pH of 6.0 to 6.4. If this water is boiled for a short time in a Pyrex vessel, and the vessel then fitted with a soda-lime tube, it will usually have a pH of 6.6 to 6.8.

When making a solution or suspension of an unbuffered material in order to determine its pH value, the water used should be as nearly neutral as possible, as any acidity will affect the pH of the dissolved material. Water having a pH value of 6.6 to 6.8 is usually satisfactory for this work. The proportion of material to water should always be kept the same, so that different determinations will be comparable. It is equally true that the indicator solutions should have a neutral reaction, since any excess acid or alkali will likewise change the pH value of the material.

These precautions are particularly important when the pH value of the material is near 7.0. Around this point small variations in hydrogen-ion concentration, due to absorption of carbon dioxide, etc., have a marked effect on the pH value, this effect being much less marked below 6.0 or above 8.0.

In making a test on distilled water or unbuffered solutions, the indicator and the material being tested should always be mixed in the test tube by means of a stirring rod, with the minimum of exposure to air, and readings should be made at once. If this is done, reliable results will be secured with the colorimetric method. In fact, this is the only way in which such solutions can be tested for pH, since electrometric methods are very unreliable when applied to most unbuffered solutions.

The pH of solutions is also sometimes affected by temperature. Measurements should therefore ordinarily be made at room temperature. In any case, they should be made under uniform conditions.

Determinations

Indicators—There are two methods of making pH determinations, the electrometric and the colorimetric. This discussion will be confined to the colorimetric method. Colorimetric pH measurements are based on the principle that various indicators change in color when acted upon by solutions of different acidities or alkalinities. Litmus paper is probably the simplest and best known indicator. Its color change is from red to blue—that is, if litmus paper is dipped into an acid solution, it turns red. If it turns only slightly red, we say the solution is "slightly" acid. If it turns deep red, we say the solution is "strongly" acid. Similarly, if the paper turns blue, we say the solution is "slightly" or "strongly" alkaline. These are very indefinite terms and their meaning varies enormously, depending largely on the personal opinion of the worker. Thus, what is "slightly" acid to one worker might be considered as "strongly" acid by another, and vice versa.

In making pH measurements we simply substitute definite pH values for the indefinite terms "strongly" and "slightly" acid and alkaline. The important point is that these pH values can be recorded and can be duplicated at any time by the same or different workers.

Theoretically, litmus and other test papers can be used for determining the pH of a solution. In practical application, however, the error is too great, chiefly because the range is so wide (pH 4.6 to 8.4) that the color changes are not distinct. It is practically impossible to tell the difference in the colors produced by solutions having pH values which differ by 1.0 pH unit. In fact, it has been shown in actual practice that solutions which specially prepared litmus indicated to be alkaline were really acid, and vice versa, when accurate pH measurements were made on the same solutions.

Some other test papers are more sensitive than litmus, but it is doubtful whether differences of less than 0.6 pH can be detected by their use. Even this degree of accuracy is seldom obtainable, as it is very difficult to obtain two batches of test papers which will give the same readings. Granting that a uniform paper can be obtained, we have no standards by which to judge. Thus a shade which would be considered as corresponding to a pH value of 6.0 by one worker might be considered as 6.6 by another. Since variations as large as 0.2 pH may be of serious consequence, the need for an accurate method is apparent.

Table III—Indicators for pH Determinations

Indicator	pH Range	Color Change
Metacresol purple	1.2 to 2.8	Red-yellow
Bromphenol blue	3.0 to 4.6	Yellow-blue
Bromcresol green	4.0 to 5.6	Yellow-blue
Chlorphenol red	5.2 to 6.8	Yellow-red
Bromthymol blue	6.0 to 7.6	Yellow-blue
Phenol red	6.8 to 8.4	Yellow-red
Cresol red	7.2 to 8.8	Yellow-red
Thymol blue	8.0 to 9.6	Yellow-blue
Nitro yellow	10.0 to 11.6	Yellow-orange
Sulfo orange	11.0 to 12.6	Yellow-orange

As stated above, litmus is very insensitive partly because it covers a wide range. In order to make accurate pH determinations it is therefore necessary to employ indicators with short ranges, so that the color changes are more distinct. This means that we need a number of indicators to cover the pH range 1.2 to 12.6. A complete set of indicators, developed

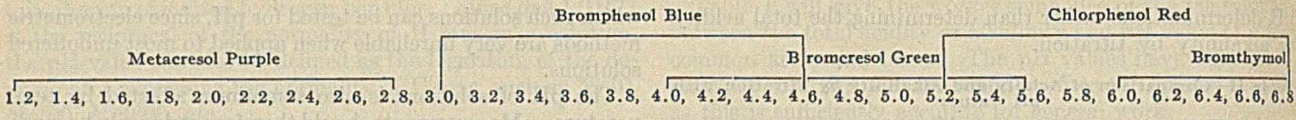


Figure 1—Range of Indicators

for just this purpose, with their respective pH ranges and color changes, is given in Table III. Figure 1 will make this even clearer. The color changes of these indicators are similar to that of litmus. For example, litmus is deep red in an acid solution (pH 4.6) and deep blue in an alkaline solution (pH 8.4). Similarly, chlorphenol red has a yellow color at pH 5.2 and a deep red color at pH 6.8; bromthymol blue is yellow at pH 6.0 and deep blue at pH 7.6, etc.

ROUGH TESTS—If the worker has no idea of the pH value of a given solution, it is necessary first to make a rough determination. To make the test, fill three or four graduated test tubes to the mark (10 cc.) with the solution to be tested. To the first one add 0.5 cc. of bromthymol blue indicator solution. This indicator is tried first as it has a pH range of 6.0 to 7.6, and therefore covers the neutral point pH 7.0. Hence it is possible by means of this one indicator to determine whether the solution being tested is neutral, acid, or alkaline. The color change of bromthymol blue is from yellow at 6.0 to a deep blue at 7.6. Therefore, if on adding this indicator solution a color intermediate between yellow and deep blue is obtained, the pH of the solution lies between 6.0 and 7.6 and it is either neutral or very slightly acid or alkaline. In this case no further rough tests are necessary.

If, however, a yellow color is obtained on adding the bromthymol blue indicator solution, the pH of the solution is at least 6.0 and possibly lower, since pH 6.0 is the acid end of the range of this indicator. Even if the solution had a pH of 5.0 or 4.0, it would still give a yellow color with bromthymol blue. If, then, a yellow color is obtained, 0.5 cc. of the bromcresol green indicator solution, which, as will be seen from Figure 1, covers a more acid part of the range (pH 4.0 to 5.6), should be added to the second test tube containing the solution of unknown pH. The color change for this indicator is from yellow at pH 4.0 to a deep blue at pH 5.6. If, therefore, a color intermediate between yellow and deep blue is obtained in this test, the pH of the solution lies between 4.0 and 5.6.

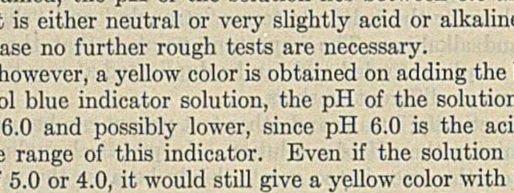


Figure 2—Bromthymol Blue Color Standards

These two indicators do not cover quite all the values between 4.0 and 7.6. Thus, if bromcresol green gives a deep blue color and bromthymol blue a yellow color, it is apparent that the pH of the solution lies around pH 5.6 to 6.0—that is, within the range of chlorphenol red (Table III). If a yellow color is obtained with bromcresol green, the test should be repeated using bromphenol blue, which covers a still more acid part of the range. If, on the other hand, on adding bromthymol blue indicator solution in the first test, a deep blue color is obtained, the solution is alkaline and has a pH value of at least 7.6 and possibly higher. The test should then be repeated using thymol blue, which covers a more alkaline part of the range.

This procedure must be followed in determining the range required for any specific work—that is, a rough test must be made on solutions from all steps of the process. Such tests have shown the range required in paper work to be pH 4.0 to 8.4, for water purification pH 5.2 to 8.4, etc.

ACCURATE MEASUREMENTS—Let us assume that in the first rough test—that is, the one in which bromthymol blue indicator solution was added to the solution in the test tube—a color intermediate between yellow and deep blue was obtained. This would show that the pH of the solution lies between 6.0 and 7.6. It is now a question of determining the exact pH value. For this purpose a set of bromthymol blue color standards and some form of comparator are required. A set of bromthymol blue color Standards consists of nine standard tubes and one tube of distilled water, as shown in Figure 2.

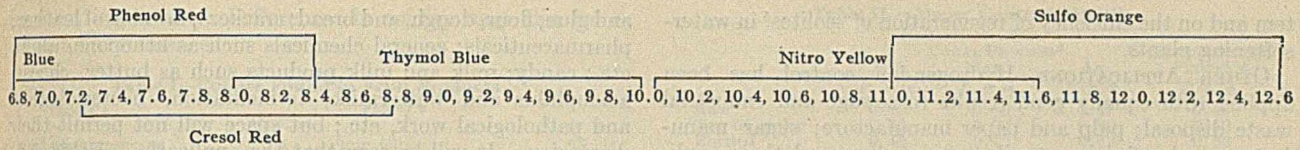
The nine tubes contain 10 cc. of solutions of definite pH value—that is, 6.0, 6.2, 6.4, 6.6, 6.8, 7.0, 7.2, 7.4, and 7.6—to each of which 0.5 cc. of bromthymol blue indicator solution has been added. It is seen that these standards are made up in exactly the same manner in which the test was made, except that solutions of definite pH values were used. The tube marked pH 6.0 will have a yellow color and that marked pH 7.6 a deep blue color. The intermediate tubes will have colors intermediate between yellow and blue. All that is now necessary is to match the test sample with the standards.

Since few solutions which are encountered in chemical work are both clear and colorless, the effect of color and turbidity of the sample must be eliminated in making comparisons with the standards. This is done by means of a comparator arrangement such as that illustrated in Figure 3.

Fill three test tubes to the mark (10 cc.) with the solution to be tested, and place them in the three holes in the block marked *B*, *A*, and *C*. To the middle tube add 0.5 cc. of bromthymol blue indicator solution by means of a graduated pipet and nipple, and shake to insure thorough mixing. Place an ampoule of distilled water in the hole marked *D* and two of the bromthymol blue color standards, differing by only 0.2 pH—for example, 6.8 and 7.0—in the two holes *E* and *F*. The comparator block represented by Figure 3 contains three slots extending through the block from *E* to *B*, *D* to *A*, and *F* to *C*, so that the tubes can be compared in pairs. Look through the three pairs of tubes, holding them toward the light, and change the color standards if necessary, until the central pair of tubes exactly matches one of the other pairs, or until the color through the central pair lies between the colors of the pairs on either side. Always make sure that the standards placed on either side of the ampoule of distilled water differ by only 0.2 pH. If an exact match is obtained, the pH of the solution is read off directly from the standard with which the match is obtained. If, however, the color of the central pair of tubes lies between the colors of the pairs on either side, the pH value is taken as the average of the two.

If it had been found, by the first rough test, that the pH of the solution lay between pH 5.2 and 6.8, the determination would of course be made in an exactly similar manner, except that chlorphenol red indicator solution would be added to the sample and the comparison made with the chlorphenol red color standards.

The reason for this arrangement of tubes is to eliminate



for Hydrogen-Ion Control

any effect of color or turbidity in the sample which is being tested. For example, suppose that we are testing a colored solution. We shall designate this colored solution by *G*, water by *W*, and the indicator solution by *I*. Referring to Figure 3, *B*, *A*, and *C* represent the three test tubes which are filled with the solution which is being tested. *D* represents the ampoule of distilled water, and *E* and *F* the color standards.

To make this clear, the color standards may be considered as made up of water and indicator solution. They do, of course, contain solutions of salts to give them definite pH value, but as these solutions of salts are clear and colorless they may be considered as made up of only these two materials.

It will be seen from Figure 3 that each pair of tubes (*B* and *E*, *A* and *D*, *C* and *F*) contains the colored solution *G*, indicator solution *I*, and water *W*, the only difference being that the indicator solution has been added to the colored solution in the central test tube, instead of to the distilled water tube which is placed behind it. The final combination, however, is the same in all pairs. It is therefore apparent that, when the proper color standards are in place, an exact match must be obtained, since the observer is looking through exactly the same materials in each pair of tubes. The conditions would be similar if the solution which is being tested were turbid instead of colored. Special comparators, designed to facilitate the making of measurements of this kind, are now on the market.

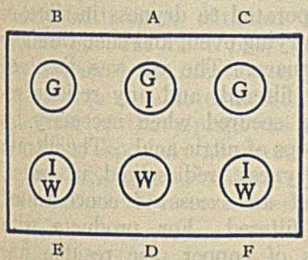


Figure 3—Comparator

As previously shown, since the pH ranges of practically all the indicators overlap, it is usually possible to make determinations on a given sample with two different indicators and thus check the results obtained.

The worker should be warned against possible errors due to matching against the color standard on either end of any given set. Thus, a test sample may match the bromthymol blue standard pH 7.6, and yet have a much higher pH value, as pH 7.6 is the end of the range of bromthymol blue. In such a case the test should be repeated using phenol red, etc.

Some solutions are so highly colored or turbid that sufficient light will not pass through them to make a colorimetric determination possible. This difficulty can often be overcome by dilution or by filtering through a good grade of wood charcoal. If the charcoal has been first washed with alkali, then with acid, and finally with distilled water, the pH of the solution will not be changed to any great degree, especially if it is highly buffered.

Applications

It is impossible to discuss all the applications of hydrogen-ion control to research and industrial work, or to discuss any one application in detail. All that will be attempted is to give the outstanding points as applied to water purification and to list some of the other more important applications.

WATER PURIFICATION—Water purification consists primarily in removing suspended matter, color, and bacteria. This operation is known as coagulation and is usually accomplished by the addition of alum. The alum combines with the natural alkalinity of the water to form aluminum hydroxide or other complex aluminum salts, which settle out and carry the color, suspended matter, and bacteria down to the bottom of the settling basin.

Coagulation takes place most completely and rapidly at a definite pH value, this value being different for different waters, owing to variation in color, turbidity, natural alkalinity, the season, temperature of the water, source of supply, etc. Catlett[4] found that the optimum pH for waters in North Carolina varied from 4.3 for certain highly colored waters, to 7.6 for some turbid waters which were free from color. It is therefore necessary to determine the optimum for each individual water and this can best be done by means of the "jar test."[4]

In making jar tests, solutions of definite strength of alum, soda ash, and lime are made up, for example, so that 1 cc. contains 0.1 grain of alum or alkali. One gallon of the water to be tested is then placed in each of several jars of uniform size and shape. If the water contains sufficient natural alkalinity to give a good floc, it is only necessary to add varying quantities of the alum solution to the different jars and note which gives the quickest floc. The pH of the water in each jar is determined, and that of the one giving the best floc is taken as the optimum pH value for coagulation of the water in question.

If the water does not contain sufficient alkalinity to give a floc, a definite amount of alum should be added to each jar and the amount of alkali varied. After noting the one which gives the best floc, and making the necessary pH determinations, another set of tests should be made, increasing or decreasing the amount of alum as required. This is advisable since the same pH value may be obtained by the use of smaller amounts of chemicals.

By this procedure the optimum pH value for a given water is determined. This means that the smallest possible amounts of alum and alkali necessary to give the best and quickest floc are used at all times, so that a good floc is obtained but no chemicals wasted. Hydrogen-ion control has resulted in reducing the chemicals to less than one-half that ordinarily used in a large number of purification plants, but, what is probably even more important, the operator has been able to deliver to the consumer a water of uniformly good quality.

Poor coagulation may be caused by an over as well as an under dose of coagulant. Coagulation at the optimum means a better filter effluent, as it eliminates practically all solvent action on the floc and the appearance of aluminum in the effluent. It also insures a higher bacterial efficiency as the bacteria are removed by the floc, increases the rate of filtration, and makes possible a decrease in the size of the coagulating basin.

When alum or acid are used in any purification process, the number of hydrogen ions is increased, which tends to increase corrosion and produce red water. In many cases it is therefore necessary to decrease the number of H-ions—that is, to increase the pH—by treating the water with lime, soda, or some other alkali either before or after filtration. By pH control the reaction of the water can be exactly regulated to the point where the smallest amount of corrosion will take place with the addition of the least amount of alkali. The pH also has a very marked effect on the formation and preservation of a protective coating on the distribution sys-

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[4] *J. Am. Water Works Assocn.*, **11**, 887 (1924).

tem and on the efficiency of regeneration of zeolites[5] in water-softening plants.

Other Applications—Hydrogen-ion control has been applied with equally good results to sewage and industrial waste disposal; pulp and paper manufacture; sugar manufacture and refining; manufacture of dyes and their application to fabrics; manufacture of pigments; nickel and acid zinc plating; ceramics; canning of food products; gelatin and glue; flour, dough, and bread; crackers; tanning of leather; pharmaceuticals; general chemicals such as lithopone, alum, etc.; candy; milk and milk products such as butter, cheese, acidophilus and buttermilk; fermentation, bacteriological and pathological work, etc.; but space will not permit their discussion. It will be seen that the application of this control method is practically universal, as it must be, since acidity and alkalinity are important to almost every chemist and manufacturer.

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[5] Sweeney and Riley, This Journal, **18**, 1214 (1926).

Copper as an Industrial Contaminant in Foodstuffs[1]

By C. G. King and G. Etzel

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Important objections to an appreciable increase in the copper content of foodstuffs may be considered under the following headings: (1) the direct poisoning effect upon the body,[2] (2) a tendency to cause or accelerate the development of disagreeable flavors,[3] (3) an acceleration of the destruction of vitamin C,[4] and (4) the production of "off" color.[5] Factors connected with (2) and (4) are generally recognized in plant practice, because their relationship to the market value of products is fairly obvious. However, (1) and (3) are not so obvious and are liable to be given less consideration than they deserve.

F. B. Mallory, who has furnished the most careful evidence relative to cumulative copper poisoning, estimates that more than 5 to 10 mg. per day may produce toxic results. This is a much lower limit than that previously estimated by other investigators whose observations were not so complete.[6] Hess[4] has shown that small amounts of copper (2.5 p. p. m.) may accelerate the destruction of vitamin C in milk. If the same phenomenon occurs in fruits and vegetables it would be an important factor to consider in their preparation, since it is difficult to conserve their vitamin C content.

Experimental

The present investigation deals with the copper content of three types of foods commonly prepared in copper or brass equipment: (1) four groups of acid fruit products representing different trade practices, (2) milk from nine different plants, and (3) carbonated beverages from two plants.

The xanthate method of determining copper[7] was used, chiefly because of its sensitivity, and experience showed it to be suitable for this purpose. It is sensitive to 0.005 mg. in 50 cc. and gives accurate results when adequate precautions are observed.

Precautions—(1) Contrary to statements in the literature,[7] nickel gives a color intensity and shade very similar to copper. Where nickel is present in significant amounts, another method must be used or the nickel must be removed before determining copper.

(2) The use of brass burners for ignition may introduce appreciable quantities of copper; hence it is recommended that all drying and ignitions be carried out in electric ovens or muffles.

(3) High concentrations of other salts may affect the color intensity and produce turbidity.

(4) Fresh xanthate solution should be made up every few days and the dry salt ($KOEtCS_2$) should be prepared or recrystallized every few weeks. Otherwise a faint cloudiness interferes.

(5) All water used, even for rinsing apparatus, should be especially distilled. That from the usual copper still with blocked tin condenser and piping gives a distinct color with the reagent.

Procedure—A uniform sample was removed from the glass container, weighed, evaporated to dryness in silica or porcelain dishes in an electric drying oven, and then carefully ashed in an electric muffle furnace. The ash was dissolved in hydrochloric acid, diluted, filtered, and any residue reashed and complete oxidation secured when necessary by the addition of one or more drops of nitric acid. The filtrate was evaporated nearly to dryness, redissolved in water, made alkaline by addition of an excess of concentrated ammonium hydroxide, and filtered. For products with comparatively large amounts of copper, the residue was redissolved in hydrochloric acid and again precipitated and the filtrate combined with the first. The excess ammonia was evaporated over an iron hot-plate, the solution made neutral or very faintly acid with dilute acetic acid, and either used directly for developing the color (for milk and beverages) or made up to volume and an aliquot taken (for fruit products). Color comparisons were made in 50-cc. Nessler tubes after the addition of 10 cc. of 0.1 per cent xanthate solution. Standards were prepared at the same time having 0.5, 1.0, 1.5 to 12.0 cc. of fresh copper sulfate solution, 1 cc. of which contained 0.01 mg. of copper.

Results

Each value given in the tables represents at least two determinations on each of two samples taken. Only one significant figure is given in most cases because of the variations found in different samples from the same source.

Fruit Products—The differences shown in Table I are due mainly to variations in care and type of equipment, rather than to such factors as time and temperature of heating or composition of the raw materials. Contrasts in sanitary practice were as striking as contrasts in copper content. The chief factors involved seemed to be (1) protection of copper equipment by tin or other metal, (2) thoroughly cleaning all copper surfaces between batches, (3) keeping exposure to the air at a minimum, and (4) allowing only the minimum of time of contact with copper beyond that actually needed for cooking. A separate study of each factor was not made, but it appeared that (1) and (2) were

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[1] Received April 27, 1927.

[2] Mallory, Mellon Lecture, School of Medicine, University of Pittsburgh, 1925; *Am. J. Path.*, **1**, 117 (1925); *Arch. Internal Med.*, **37**, 336 (1926); *J. Am. Med. Assocn.*, **86**, 1552 (1926).

[3] Emery, *U. S. Dept. Agr., Bur. Animal Ind., Ann. Report*, **1909**, p. 265; Emery and Henley, This Journal, **14**, 937 (1922); Supplee and Bellis, *J. Dairy Sci.*, **5**, 455 (1922); Rice, *Ibid.*, **6**, 262 (1923); **9**, 459 (1926).

[4] Hess, This Journal, **13**, 1115 (1921); *J. Am. Med. Assocn.*, **82**, 952 (1924).

[5] *Natl. Canners' Assocn.*, *Bull.* **6** (1915).

[6] Drummond, *J. State Med.*, **32**, 382 (1924); Rost and Weitzel, *Arb. Reichsgesundh.*, **51**, 494 (1919); Panton, *Pharm. J.*, **110**, 393 (1923); Lehman, *J. Chem. Soc.* (*London*), **70**, 486 (1896).

[7] Supplee and Bellis, *J. Dairy Sci.*, **5**, 455 (1922); Scott, "Standard Methods of Chemical Analysis," 4th ed., p. 197.

the most important. Differences in acidity may also have had a minor influence.

Table I—Copper Found in Fruit Products

PLANT 1	P. p. m.	PLANT 3	P. p. m.
Strawberry preserves	4	Plum jelly	55
Blackberry preserves	4	Strawberry jelly	60
Cherry preserves	3	Raspberry jelly	80
Apple butter	3	Raspberry preserves	45
Chile sauce	7	Apple butter	110
Ketchup	8	Chile sauce	18
PLANT 2		PLANT 4	
Currant jelly	7	Raspberry jelly	2
Raspberry jelly	5	Raspberry preserves	7
Raspberry preserves	4	Blackberry preserves	4
Peach preserves	6	Cherry preserves	4
Strawberry preserves	10	Strawberry preserves	9
Blackberry preserves	3	Apricot preserves	11
Apple butter	24	Plum preserves	6
Grape jam	4	Peach preserves	4
Chile sauce	8	Pineapple preserves	3
Ketchup	12		

TESTS DURING PREPARATION IN COPPER EQUIPMENT

	Plant A P. p. m.	Plant B P. p. m.
Apple cider concentrate (*a*)	85	25
Apple pulp (*b*)	5	3
Finished apple butter (1*a*:10*b*)	30	12
Tomato pulp	6	4
Same after cooking approx. 1.5 hours	17	6

Eating a hundred grams per day of such products as those from Plant 3 would alone cause one to exceed the limit of copper previously suggested, without considering that which would normally be supplied in natural foods.[8] Incidentally, this brand was the cheapest of the group and that of Plant 1 the most expensive.

Milk—The results of the tests on milk (Table II) correspond closely with those obtained by Supplee and Bellis. The smaller amount of copper getting into the milk during Electropure pasteurization is probably due to the shorter exposure to metallic equipment while hot, as the extent and condition of the piping was similar. The copper content of milk is especially important in its effect upon flavor.

Table II—Copper Content of Milk

Pasteurized Milk

	Usual Process[a] Min. P. p. m.	Usual Process[a] Max. P. p. m.	Usual Process[a] Av. P. p. m.	Electropure Process[b] P. p. m.
Raw	0.40	0.60	0.47	0.45
Top of cooler	0.45	0.70	0.60	0.50
Bottled	0.48	0.72	0.62	0.52

Raw Milk

Average of five samples delivered by farmers to receiving station:
Raw..........0.43 p. p. m.
Same after screening..........0.45 p. p. m.
Average of three small batches screened after copper screens had stood exposed to air for about 5 minutes between loads..........0.97 p. p. m.

Condensed Milk

Average of three samples of skimmed milk, condensed to 36 per cent total solids in copper vacuum pans..........3.7 p. p. m.

[a] Average of duplicate tests at five plants, pasteurizing 30 minutes at 142° F. in tin-lined vats and using tin-lined copper piping.

[b] Average of two plants, heating to 162° F. between carbon electrodes.

Carbonated Beverages—The tests on carbonated beverages (Table III) show that normally very little copper is dissolved. In general practice the first few bottles of each run are discarded to avoid mixing of sirups, so that those which contain appreciable amounts of dissolved metal are automatically discarded. Since such beverages are always prepared cold, with little access of air, and are exposed to the metal for only a short time, little contamination with copper would be expected in normal plant practice.

Table III—Copper Found in Carbonated Beverages Produced in Brass Equipment

	P. p. m.
Lemon soda	0.5
Cream soda	0.3
Cherry soda	0.5
Orange soda	0.4
Grape soda	0.5
Coca Cola	0.6
Root beer	0.5

	Plant I P. p. m.	Plant II P. p. m.
First bottle of lemon soda at beginning of run	0.8	0.9
Fifth bottle	0.6	0.7
After 20 minutes' continuous run	0.5	0.6

Acknowledgment

The authors wish to acknowledge the assistance given by P. A. Zook and W. H. Busch in supplying some of the materials for analysis.

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[8] McHargue, *J. Agr. Research*, **30**, 193 (1925); Guermont, *Compt. rend.*, **171**, 196 (1920); Maquenne and Demoussy, *Ibid.*, **170**, 87 (1920).

Adhesives and Adhesion[1]

Mechanical Properties of Films of Adhesives

By J. W. McBain and W. B. Lee

University of Bristol, England, and Stanford University, Calif.

Typical and significant data are presented for the mechanical properties of a number of adhesives and adhesives with added substances. The observations emphasize the essential importance of "deformability" of an adhesive. Both this and tensile strength depend upon such factors as degree of humidity. The brittleness of an adhesive film may be greatly increased or entirely eliminated by appropriate additions. The strongest adhesive film here measured is isinglass with a tensile strength of 8 tons to the square inch in an atmosphere of 0 per cent humidity; the weakest are the gums and sodium silicates with a tensile strength of only a few hundred pounds per square inch.

PREVIOUS papers have demonstrated the significance of the determination of tensile strength of adhesives and have provided a ready routine method for this purpose.[2 to 5] The present paper indicates the importance of the study of other mechanical properties of films of adhesives, such as elasticity, brittleness, flexibility, ductility (in general "deformability"), relaxation, and other stress-strain relations, likewise taking into account the influence upon the results of such factors as humidity and rate of loading. Some of these factors can be estimated without much elaboration during the ordinary tensile strength tests of the films.

Although most of the tests have been carried out upon one particular gelatin, obtained commercially in the form of thin films and used by lithographic workers for tracing, which thus represents a moderately good grade of gelatin glue, a number of other adhesives have been added to the list for which numerical data are now available. These are starch ester, gum arabic, gum acacias, celluloid, nitrocellulose, gelatin glues containing various admixtures, and products derived from the swim-bladder of hake and sturgeon,

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[1] Received May 9, 1927. Investigation undertaken for the Adhesives Research Committee of the Department of Scientific and Industrial Research, Great Britain, and published by permission of this Department.

[2] McBain and Hopkins, *J. Phys. Chem.*, **29**, 197 (1925).

[3] *Ibid.*, **30**, 114 (1926).

[4] Second Report of Adhesives Research Committee, **1926**, p. 34.

[5] McBain and Lee, *J. Soc. Chem. Ind.* (1927); cf. *Proc. Roy. Soc.* (*London*), **A113**, 605 (1927).

including the best refined isinglass. Table I shows typical results for all these adhesives. It will be shown in detail for the case of gelatin that the results are greatly dependent upon the degree of humidity.

Table I—Tensile Strength of Films of Typical Adhesives

(Under arbitrary conditions, usually 55 per cent relative humidity and room temperature)

ADHESIVE	TENSILE STRENGTH Lbs./sq. in.[a]	REMARKS
Isinglass	13,000[b]	Tough
High-grade gelatin	12,000	Tough
High-grade gelatin glue A[c]	12,000	Tough
Glue A + peptone (5:1)	10,500	Brittle
Partially hydrolyzed A	10,000	Brittle
Glue A + glucose (5:1)	9900	Flexible and ductile
Glue A + glycine (5:1)	9500	Brittle
Purest gelatin	9500	Tough
Glue A + glycerol (20:1)	8500	Flexible
Celluloid	8500	Ductile
Nitrocellulose	8000	Flexible
Starch	7000	Ductile
Starch ester	5000[d]	Flexible
Gum acacia + glycerol	(1000)	Ductile
Silicate of soda[e] J or 3	600	Very brittle
Silicate of soda A or 4	500	Very brittle
Silicate of soda C or 2	300	Very brittle
Silicate of soda K or 1	150	Less brittle
Gum arabic	...	Very brittle
Gum acacia	...	Very brittle

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

[b] This value is increased to 21,000 lbs./sq. in. at 0 per cent humidity.

[c] This is the same as "Glue A," (see footnote 2, p. 193), "Adhesive H" (see footnotes 3, p. 119, and 4, p. 50), and Cannon's I. L. Propeller (cake) glue (see footnote 4, p. 102).

[d] Temperature, 16° C.; relative humidity, 58 per cent.

[e] For particulars of composition, etc., see footnotes 2 and 4, p. 56.

Three points are brought out in Table I: first, the high tensile strength of so many of the adhesive materials, far transcending the strength of ordinary glued joints; second, the information given in the last column which is emphatically of as great practical importance as the tensile strength. Lack of "deformability" largely impairs the value of an adhesive, which therefore cannot adapt itself to the changes of shape and volume incident to setting and drying when making the joint, or caused by subsequent changes such as varying humidity or mechanical bending of the joint itself. The extreme case is exhibited by such adhesives as gum arabic, which in a pure dry condition fly violently to pieces. Since it does not very much matter whether the adaptation takes place by flow or elastic yield we have in a previous communication[5] coined the term "deformability" to express this almost essential property of an adhesive.

Note—Browne and Truax [Colloid Symposium Monograph, Vol. IV, 263 (1927)] emphasize that during drying of a wooden joint glue is subjected to severe stresses which elastic jellies are peculiarly fitted to withstand, and they define the word "glue" so as to include suitable "emulsoid sols" which form elastic jellies. We do not agree with all their data and conclusions. It is a *non-sequitur* to argue, as they do, that because water wets woods any hydrophilic colloid must do likewise in the absence of water. Again, they have overlooked the fact that the interstices and mechanical embedding to which we have referred are on an ultramicroscopic scale and therefore subject to direct microscopic test; for example, we stated that gelatin passes freely through smooth continuous sheets of viscose.

The third point illustrated by Table I is that the silicates possess only a small percentage of the strength of the other common adhesives. In addition they are very brittle, which further detracts from their value as adhesives except for special purposes such as use on glass surfaces.

Influence of Humidity on Tensile Strength

Several workers have drawn attention to the importance of controlling the degree of humidity in testing adhesives, but no comprehensive study of this factor has been made.

Note—After this paper was submitted attention was called to the interesting paper by Bateman and Town [THIS JOURNAL, **15**, 374 (1923)] containing a series of measurements on the tensile strength of hide and veneer glues at various degrees of humidity. The advantage of using our very thin films is apparent from an inspection of their data and from their statement that the strength they observed was probably not true tensile strength but that reduced by stresses set up by drying. For example, they failed to obtain measurements with specimens dried at less than 30 per cent relative humidity. Although the general trend of their results resembles ours, the form of their curve is different and the extreme values for tensile strength range from only a few hundred pounds up to nearly 20,000 pounds per square inch; the approximate tensile strengths they obtained, for example at 85 per cent humidity, for the two glues (hide and veneer) were 700 and 1700 pounds per square inch as compared with our 9000 pounds per square inch for lithographic gelatin.

It is easy to do this when using McBain and Hopkins' method of testing strength of adhesives in the form of thin films. This is illustrated by Table II and Figure 1, which refer to a commercial sample of lithographer's sheet gelatin 0.004 to 0.005 inch (0.10 to 0.13 mm.) thick. The test pieces, 4 inches (10 cm.) long and 0.5 inch (1.3 cm.) wide, were stored at various humidities in desiccators over various dilutions of sulfuric acid whose vapor pressures are obtained from reference tables. The determinations were completed within 3 or 4 minutes after taking the samples from the desiccators, a method easily adaptable to "glue-house" technic. The rate of loading was high—approximately 80 to 90 pounds per square inch per second.

Table II—Tensile Strength of Lithographic Gelatin at Various Humidities (Sample C)

H_2SO_4[a] Per cent	HUMIDITY Per cent	TIME STORED Days	TENSILE STRENGTH Lbs./sq. in.[b]
Concd.	0 (approx)	3	17,000 (15,920)
Concd.	0 (approx.)	1	15,200; 15,000; 14,400
85.6	Above 5	11	16,200
85.6	Above 5	7	16,000; 15,000; 14,600; 14,500
59.0	18.5	1	14,600; 14,200; 13,800; 13,700; 13,400
35.1	65	3	12,400; 12,300; 12,200 (11,570)
20.8	87	3	9200; 8700; 8500; 8400; 8200
15.2	93	3	6600; 6600; 6200; 6100
Water	100	7	Not above 800

[a] By analysis.

[b] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

The results are very striking. The tensile strength of the gelatin when dry rises to 8 tons to the square inch and practically disappears at 100 per cent humidity. At 50 per cent humidity the extension up to fracture was only 3 per cent. These strips resemble paper in that they are flexible in bending and rupture in tension with only a small elongation. When stored over water the film flowed under small loads. The results accord with the micellar explanation developed by McBain.[6]

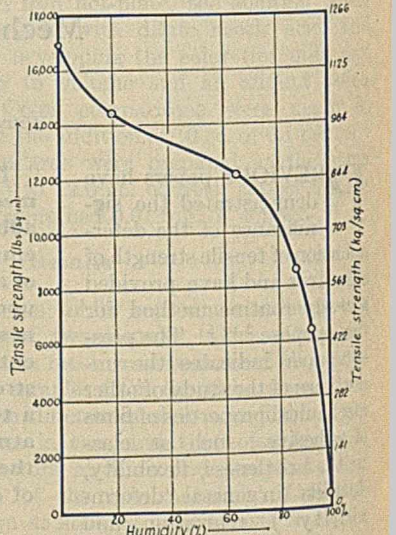

Figure 1—Tensile Strength of Lithographic Gelatin at Various Humidities—Temperature 16° ± 1° C.

Influence of Rate of Loading on Tensile Strength Observed

Next to degree of humidity it is important to keep the rate of loading constant from the beginning of the test. This is easily done when using a Schopper paper tester, and still more when employing the most recent development of the Schopper machine with its complete equipment of recording drums. Alt[7] has given a linear formula connecting breaking load with rate of loading: $P_2 = P_1 + k(v_2 - v_1)$, where P_2 and P_1 denote two breaking loads and v_2 and v_1 the

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[6] *J. Phys. Chem.*, **31**, 564 (1927); **30**, 239 (1926).

[7] "Einfluss der Zerreissgeschwindigkeiten bei der Prüfung von Textilstoffen," *Textileforschung*, **1** (1919), *Mai Heft*, **2**, 26.

corresponding rates of loading, *k* being a constant for the material. However, for our gelatin there is no such linear connection between increase in breaking strength and increase in rate of loading; it is much truer to state that a fourfold increase in the rate of loading increases the breaking strength by about 15 per cent.

Effect of Added Substances upon Mechanical Properties of Gelatin and Glue

The properties of gelatin and animal glues may be greatly modified, often to advantage, by the use of admixed substances. Even the best commercial gelatin glue is brittle when sufficiently dried, whereas it is much weaker, but quite flexible, in a damp atmosphere. At a constant humidity the brittleness may be increased or entirely eliminated by admixtures. The data in Table III refer to films prepared from a solution containing the indicated amount of the admixture to 10 grams of air-dried glue A and 100 cc. of water.

Table III—Tensile Strength and Brittleness of High-Grade Gelatin Glue with Added Substances

(Temperature of storage and measurement, 14° to 17° C.)

SUBSTANCE ADDED TO 10 GRAMS GLUE		TENSILE STRENGTH OF FILM	CHARACTERISTICS OF FILM
	Grams	*Lbs./sq. in.*[a]	
		HUMIDITY 55 PER CENT (APPROX.)	
None		12,000; 11,950	Flexible, tough
Peptone	1	10,650	Brittle[b]
	2	10,500; 10,500	Brittle[b]
	5	8850; 8600; 8500; 8300	Very brittle
	8	(Probably 5000–6000)	Remarkably brittle, film originally opaque
Glucose	2	9950; 9350; 9300	Flexible
	4	6850; 6750	Flexible
	5	6450; 6200; 6050; 5950	Flexible and plastic
	7.5	4300; 4000; 3950	Very flexible
	9	(1650; 1600; 1400; 1350) (1100, slower rate of loading)	Remarkably flexible
Glycine	1	9900; 8750; 8500	Brittle[b]
	2	9500; 9500; 8900	Brittle[b]
	8	1600 (order only)	Remarkably brittle, film originally opaque
Glycerol	0.5	8500; 8350; 7850; 7550	Flexible; definite but faint opalescence under stress
		HUMIDITY 0 TO 5 PER CENT	
None		22,000, 2100	Very brittle
Glycerol	3 cc.	14,600; 14,500; 13,700; 13,350	Flexible
Urea	3	15,000	Brittle

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

[b] Milky markings appeared near breaking point.

GLYCEROL—Films containing glycerol are still very strong but are flexible unless dried over concentrated sulfuric acid. A general, not striated, opalescence appears in these films when highly stressed.

GLUCOSE—The effect of adding glucose to gelatin or gelatin glue has been described in another communication.[5] Briefly, it consists in making the gelatin highly flexible and ductile although decreasing the breaking strength.

PEPTONE—Peptone distinctly impairs the breaking strength of gelatin, but its outstanding effect is the brittleness which is imparted to the film of glue. The samples of glue which contained almost an equal weight of peptone were so extremely brittle that they had to be soaked in water before they could be cut even approximately to the standard of test film. Even so, upon drying these test pieces were highly distorted.

When a film is strained to its breaking strength a general opalescence or cloudiness regularly appears, as in the films containing glycerol. A second phenomenon is the formation of permanent milky lines producing a hornlike opacity; these have likewise been observed with glue, isinglass, and "lithographic" gelatin, and with glue containing glycine. Frequently these milky lines or bands are at a characteristic angle to the axis of pull. Both phenomena differ from the clear striae or lines that appear upon the surface of a smooth metal such as copper when stretched enough to take permanent set. The latter are known as Lüder's or Hartmann's lines for metals, but we have observed them regularly with cellulose (characteristic angle for celluloid 90 degrees to the axis of pull). Sir Herbert Jackson informs us that they are observed with glass. The overstrained celluloid is rendered permanently doubly refracting. These several appearances deserve further study on account of the clue they give to heterogeneity existing on a microscopic scale.

GLYCINE—Peptones and glycine are important degradation products of glue. Dakin[8] obtained 25.5 per cent of glycine from gelatin. McBain and Hopkins[2] showed that, whereas glue heated at 90° or 100° C. suffered appreciable loss of strength, the greatest effect was the brittleness which developed and soon rendered the glue useless. The data in Table III show the same effect of glycine. The effect of heating 10 per cent solution of glue for the much shorter period of 2 hours at 100° C. was tested after mixing it with an equal amount of 10 per cent solution of original glue. This film was still moderately flexible and showed a tensile strength of 11,000 pounds per square inch as compared with a film of untreated glue which gave 12,000 pounds per square inch.

Acacia Gums

Films made from Kordofan and Senegal gum arabic, on drying, spontaneously fly into splinters from internal strain. Even when the films contained 1 part of glycerol to 5 parts of gum, they were still so brittle in an atmosphere of about 30 per cent humidity that they fractured either spontaneously or on touching them gently. At about 80 per cent humidity they were flexible and slightly sticky with a tensile strength not exceeding 1000 pounds per square inch. They stretched to a neck before breaking, after which the films recovered like rubber.

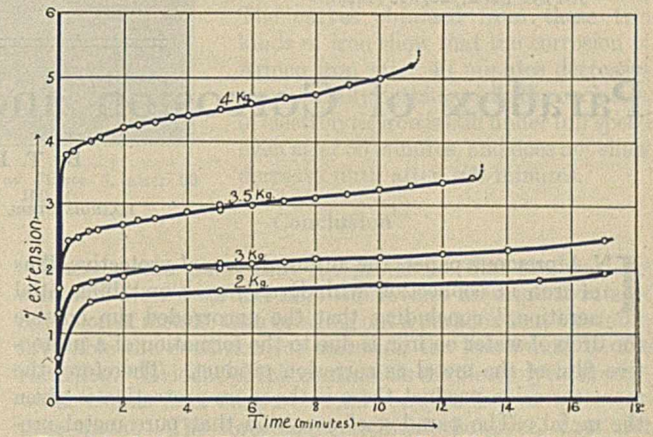

Figure 2—Lithographic Gelatin (Sample B); Effect of Time Factor at Given Load—Temperature, 18° C.; Relative Humidity, 73 Per Cent

Tests of Bombay Leaf, Swim Bladder of Sturgeon, and Refined Isinglass

Ten grams of sawn-up pieces of Bombay Leaf (swim bladder of hake) were soaked overnight in 100 cc. of water, but even at 60° to 70° C. considerable residue remained. Films prepared from the supernatant liquid are quite as strong as best gelatin or glue.

A similarly prepared extract from the swim bladder of the sturgeon left only a small residue and the films were as strong as those from Bombay Leaf. The residue, when brought into solution at 100° C. gave still stronger films. A second pair of experiments exhibited a similar influence of temperature of extraction. Films from refined isinglass tend to stick to ferrotype plate, and much more so to celluloid. Table IV shows that these films are stronger than those of any other adhesive. The lower strength of films made from the first extract may probably be ascribed to the higher proportion of amino acids in that extract.

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[8] *J. Biol. Chem.*, **44**, 524 (1920).

Table IV—Tensile Strength of Films of Bombay Leaf, Swim Bladder of Sturgeon, and Refined Isinglass

SUBSTANCE[b]	TENSILE STRENGTH	RELATIVE HUMIDITY	REMARKS
	Lbs./sq. in.[a]	*Per cent*	
Bombay Leaf	21,500; 12,400; 12,000	54	
Swim bladder of sturgeon:			
Expt. 1: 1st extract	12,700; 12,550; 11,500	59	Extracted at 60–70° C.
2nd extract	15,600; 14,100	59	Residue from 1st extract[c]
Expt. 2: 1st extract	9400; 9000	57	Extracted at 55–65° C.
Expt. 3: 1st extract	12,700	57	Extracted at 100° C.
Refined isinglass	13,750; 13,550	59	
	12,550; 11,200; (9500) (9200)	59	Films difficult to remove from plate
	21,650; 20,600	0	Moderately brittle

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

[b] 10 grams of substance taken to 100 cc. of water.

[c] Heated with 100 cc. water in a beaker immersed in boiling water and allowed to gel; reheated at 100° for 5 minutes.

Nitrocellulose Adhesives

Films were prepared by dissolving specimens of nitrocotton similar to those described by McBain, Harvey, and Smith[9] in a number of pure solvents. The results emphasize the necessity for allowing a sufficient time for drying. Films from ethyl lactate dry very slowly and those from furfural still more slowly. Numerical results (Table V) were obtained when using amyl acetate and diethyl carbonate as solvents, the latter appearing to yield stronger films under comparable conditions. As is seen in the second line of Table V, the effect of the time of drying offsets any effect of the degradation of the nitrocotton which results when the original solution is maintained at 55° C. for 14 days.

Table V—Tensile Strength of Films of Nitrocellulose

SOLVENT	TIME OF DRYING	TENSILE STRENGTH	REMARKS
	Days	*Lbs./sq. in.*[a]	
Amyl acetate	7	7500; 7000; 7000	4.8% nitrocellulose
Amyl acetate	13[b]	11,000; 10,800; 9900	Films thinner than usual
Diethyl carbonate	6	9300; 8000; 8000	2.3% nitrocellulose

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

[b] Same solution as in first line but heated at 55° C. for 14 days before used for making film.

Films prepared from a well-known commercial nitrocellulose cement showed a tensile strength of 6400 pounds per square inch independent of the thickness of the film. In these tests the films were dried naturally in the air until all smell of solvent had disappeared.

Films of celluloid showed a tensile strength of about 8500 pounds per square inch independent of the thickness of the film. The results with a single specimen are reproducible within ±1 per cent. The celluloid is ductile, the cross-section area diminishing by nearly one-quarter before fracture.

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[9] *J. Phys. Chem.*, **30**, 312 (1926).

Paradox of Corrosion and Protective Film Theory[1]

By T. Fujihara

ILLINOIS STEEL CO., GARY, IND.

IN A previous paper[2] the author discussed protective films of iron in connection with Evan's work on "differential aeration," concluding that the uncorroded rim outside the drop of water on iron is due to the formation of a protective film of the metal as corrosion product. Therefore, the more corrosion product there is the more protection is given the metal. The paradox of corrosion that pure metal protects less than impure metal may be explained by the following experiment.

Experimental Procedure

The purpose of the experiment was to determine whether electrolytic iron or Armco iron produces the more protective film when subjected to the corrosion of water. Specimens of iron were prepared exactly as in ordinary metallographic investigations. The polished metal surface was set under a microscope with vertical type and a few drops of corrosive liquid were placed on the surface by means of a pipet, the drop of liquid being made as flat as possible to eliminate excessive refraction of light, especially near the edge of the drop.

Electrolytic iron melted *in vacuo* was tested first. After subjecting the polished surface of the specimen to corrosion of freshly distilled water in the manner described, it was examined under a microscope having a magnification of 100 diameters. There was no marked corrosion after one hour, but a few spots on the surface of metal started to produce redundant corrosion rings. One of these spots was photographed for investigation at intervals of 20 minutes. (Figures 1 to 4) The experiment was then repeated using Armco iron. A number of corrosion spots appeared after 30 minutes. One of these spots surrounded by the characteristic corrosion

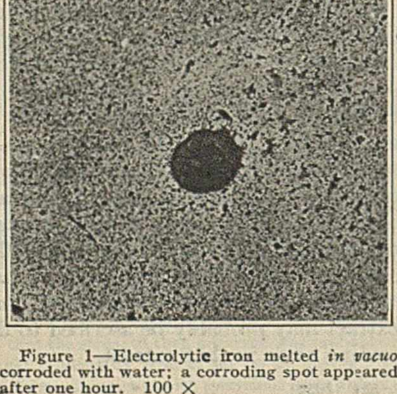
Figure 1—Electrolytic iron melted *in vacuo* corroded with water; a corroding spot appeared after one hour. 100 ×

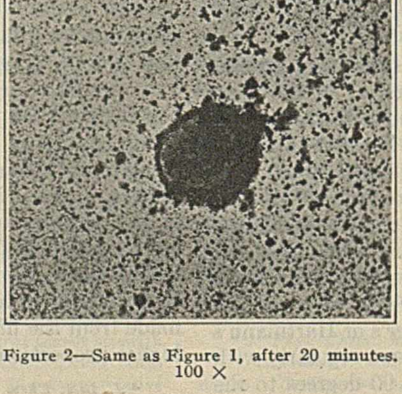
Figure 2—Same as Figure 1, after 20 minutes. 100 ×

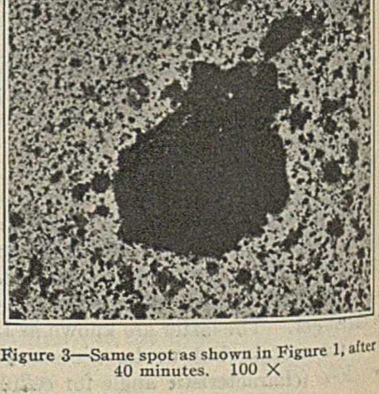
Figure 3—Same spot as shown in Figure 1, after 40 minutes. 100 ×

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[1] Received March 9, 1927. From a thesis on "Corrosion of Iron" presented to the faculty of Harvard University as part of the requirement for the degree of doctor of science.

[2] *Trans. Am. Electrochem. Soc.*, **49**, 327 (1926).

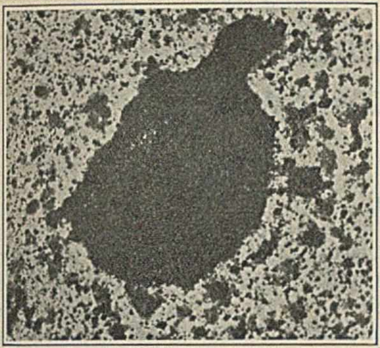
Figure 4—Same spot as Figure 1, after 60 minutes. 100 ×

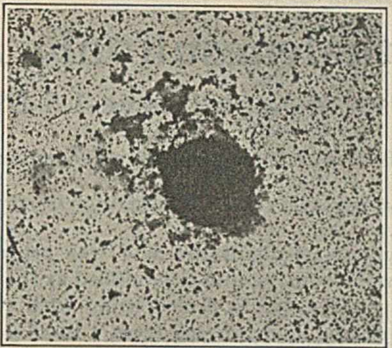
Figure 5—Armco iron corroded with water; corroding spot appeared after half an hour. 100 ×

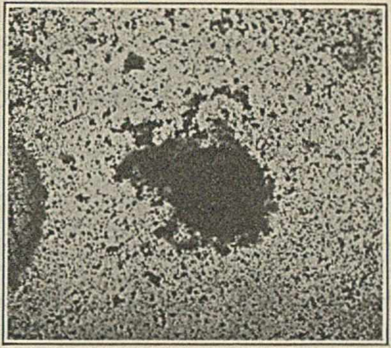
Figure 6—Same spot as Figure 5, after 20 minutes. 100 ×

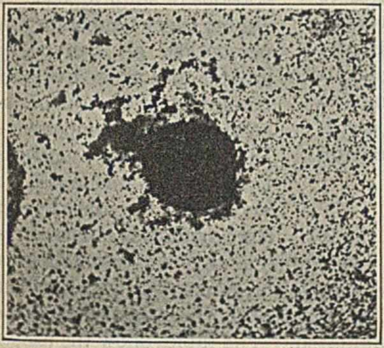
Figure 7—Same spot as Figure 5, after 40 minutes. 100 ×

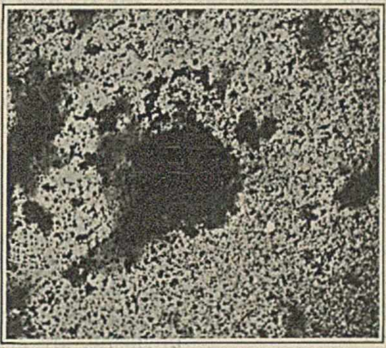
Figure 8—Same spot as Figure 5, after 60 minutes. 100 ×

ring was photographed at intervals of 20 minutes, as with the electrolytic iron. (Figures 5 to 8)

Results

Armco iron corroded much faster than electrolytic iron in the beginning. However, a corrosion spot appearing on Armco iron after a certain period of time enlarged much more slowly than a similar spot on electrolytic iron. The rate of corrosion of these two kinds of iron after a certain period—that is, one hour in the case of electrolytic iron and a half hour in that of Armco iron—is shown in Figure 9. The curve is similar to that obtained by a purely chemical process, such as the oxygen drop method of Speller and co-workers.[3] On the same principle, the curve obtained by the author using a so-called corrosion cell filled with Armco iron is shown in Figure 10.

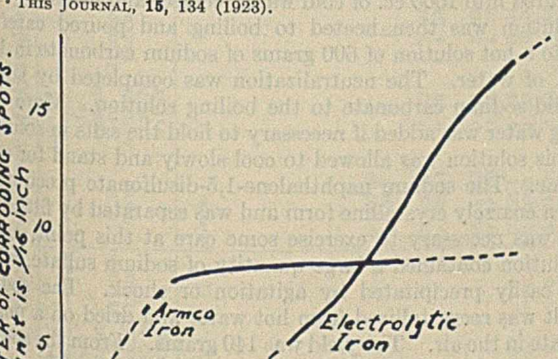

Figure 9—Effect of Film Protection upon Rate of Corrosion of Armco Iron and Electrolytic Iron Melted *in Vacuo*

The rate of corrosion decreases with time, owing to gradual increase of protective film formed as corrosion product. The curves obtained from these two kinds of iron show that the corrosion of Armco iron after 40 minutes decreases to practically nothing while the corrosion of electrolytic iron is still under full speed even after 60 minutes, and does not show decrease until after 100 minutes.

Conclusion

These results show that the protective film produced by corrosion after a certain time will reverse an original rate of corrosion of metals, thus bringing out a paradox that the more favorable the condition for corrosion the less would be the corrosion. Evidently, this contradicts the electrolytic theory, which claims that the pure metal corrodes less than the impure metal. The foregoing statement, however, does not mean that the total corrosion of Armco iron is less than that of electrolytic iron. Experiment proved that Armco iron was protected by corrosion products better than electrolytic iron after a certain period of time in which both had begun to corrode.

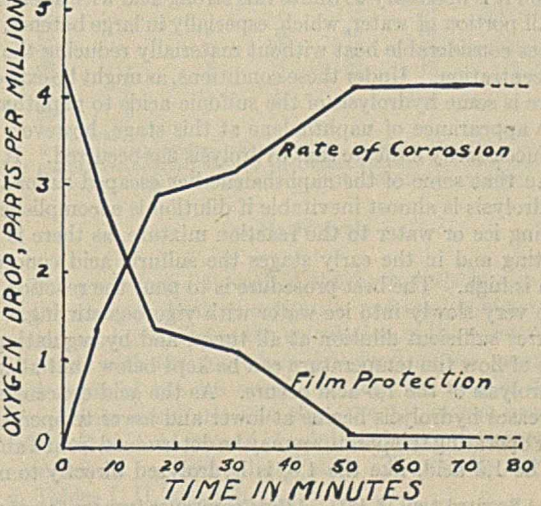

Figure 10—Relationship between Rate of Corrosion and Film Protection. Determined by Oxygen Drop Method Using a Corrosion Cell Filled with Armco Iron Plates

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[3] This Journal, 15, 134 (1923).

Naphthalenesulfonic Acids[1]

VIII—Hydrolysis of Naphthalene-1,5-Disulfonic Acid

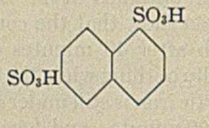
By D. F. J. Lynch and John T. Scanlan

Color Laboratory, Bureau of Chemistry, Washington, D. C.

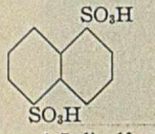
Naphthalene-1,5-disulfonic acid was prepared, isolated from its isomers, and crystallized as the free acid. This acid was heated in sealed tubes with concentrations of sulfuric acid ranging from 1 to 85 per cent at temperatures ranging from 100° to 220° C. in exactly the same way as was the 1,6 acid.[2] The results are similarly tabulated for comparison.

The general rule deduced for the 1,6 acid applies to the 1,5 acid. When the 1,5 acid is heated with low concentrations of sulfuric acid it is hydrolyzed directly to naphthalene. In the higher concentrations of sulfuric acid it is converted by hydrolysis and resulfonation of the naphthalene formed into those isomeric disulfonic acids which would be obtained by the sulfonation of naphthalene under identical conditions.

BY THE usual commercial method naphthalene-1,5-disulfonic acid and naphthalene-1,6-disulfonic acid are prepared simultaneously and separated later. For this reason it was thought advisable to follow a recently published paper on the hydrolysis of the 1,6 acid[2] with a study of the hydrolysis of the 1,5 acid. A comparison of the structural formulas of the two isomers



Naphthalene-1,6-disulfonic acid



Naphthalene-1,5-disulfonic acid

shows that the 1,6 acid has one sulfo group in the alpha position and one in the beta position, whereas in the 1,5 isomer both sulfo groups are in the alpha position. The 1,5 acid is therefore less stable than the 1,6 acid, and its formation is favored by lower temperatures in the sulfonation reaction. Therefore these two acids are formed at the same time when naphthalene is disulfonated at temperatures below that at which the 2,7 isomer is produced and the relative proportions of the 1,5 and 1,6 acids vary with the temperature within certain limits.

In the ordinary commercial process for the production of the 1,5 acid, which is fundamentally the same as the method of preparation given in this paper, strong fuming sulfuric acid is used at a comparatively low temperature, and almost equal parts of the 1,5 and 1,6 acids are produced. To effect a separation it is necessary to dilute this strong acid with a relatively small portion of water, which, especially in large batches, generates considerable heat without materially reducing the acid concentration. Under these conditions, as might be expected, there is some hydrolysis of the sulfonic acids to naphthalene. The appearance of naphthalene at this stage, however, does not necessarily indicate that hydrolysis has occurred. It may mean that some of the naphthalene has escaped sulfonation. Hydrolysis is almost inevitable if dilution is accomplished by adding ice or water to the reaction mixture, as there is local heating and in the early stages the sulfuric acid concentration is high. The best procedure is to pour the reaction mixture very slowly into ice water with vigorous stirring. This insures sufficient dilution at all times, and by regulating the rate of flow the temperature can be kept below that at which hydrolysis of the 1,5 acid occurs. As the acid concentration increases hydrolysis begins at lower and lower temperatures. Safe operating temperatures may be determined from Table II.

The 1,5 acid, like the 1,6, is hydrolyzed directly to naphthalene without the intermediate formation of either of the monosulfonic acids. The less stable 1,5 acid begins to hydrolyze at lower temperatures than the 1,6 acid, especially in the lower concentrations of sulfuric acid. At almost every temperature the percentage of hydrolysis is greater and where hydrolysis is complete it is accomplished at much lower temperatures. In the higher acid concentrations the 1,5 acid is also converted into the other isomers, the 1,6, the 2,6, and the 2,7. Here again it is observed that the 1,5 acid is slightly less stable, as this conversion occurs at lower temperatures and in lower concentrations of sulfuric acid. These results, together with the quantitative measurements, are here tabulated. The tables show the temperature at which hydrolysis begins in each concentration of sulfuric acid employed and the temperature at which charring, indicated by the presence of sulfur dioxide, takes place. The percentages of hydrolysis are those which obtain when the reaction takes place in a closed system.

Preparation of Material

The naphthalene was sulfonated by adding 165 grams slowly with stirring, to 30 per cent oleum, obtained by pouring 500 grams of melted 50 per cent fuming sulfuric acid into 190 grams (103 cc.) of concentrated sulfuric acid (sp. gr. 1.84). During the addition of the naphthalene the temperature was kept below 60° C. When the temperature no longer showed a tendency to rise, the reaction mixture was heated on the steam bath for 18 hours. Thus far the method is the same as that given by Ewer and Pick.[3] The reaction mixture was poured into 1600 cc. of cold water, cooled, and filtered. This solution was then heated to boiling and poured carefully into a hot solution of 600 grams of sodium carbonate in 1500 cc. of water. The neutralization was completed by adding solid sodium carbonate to the boiling solution. More boiling water was added if necessary to hold the salts in solution. This solution was allowed to cool slowly and stand for some time. The sodium naphthalene-1,5-disulfonate precipitated in a coarsely crystalline form and was separated by filtration. It was necessary to exercise some care at this point, as the solution contained a large quantity of sodium sulfate, which is easily precipitated by agitation or shock. The sodium salt was recrystallized from hot water and dried on a porous plate in the air. The yield was 140 grams. From the sodium salt, $(NaSO_3)_2C_{10}H_6.2H_2O$, the barium salt was prepared by double decomposition with barium chloride and washed thoroughly with several successive portions of hot water, in which it is very insoluble. A weighed portion of this purified barium salt, $Ba(SO_3)_2C_{10}H_6.H_2O$, was treated with an equimolecular quantity of sulfuric acid and the precipitated barium

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[1] Received April 18, 1927. 133rd Contribution from the Color Laboratory, Bureau of Chemistry.

[2] This Journal, 19, 417 (1927).

[3] German Patent Application E 2619 (1889).

Table I—Effect of Hydrolysis on Naphthalene-1,5-Disulfonic Acid in the Presence of Sulfuric Acid at Various Temperatures

Strength of H_2SO_4	100° C.			120° C.			140° C.			160° C.			180° C.			200° C.			220° C.		
	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed	1,5 Acid	Increase in Acidity (0.25 N NaOH)	Hydrolyzed
%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%	*Gram*	*Cc.*	%
1	...	...	...	...	...	...	...	...	...	0.50	0.26	1.87	0.50	1.82	13.11	0.50	7.42	53.47	0.50	13.71	98.79
											0.22	1.58		1.21	8.72		7.12	51.30		13.81	99.51
5	...	...	...	...	...	...	...	...	...	0.50	0.45	3.24	0.50	2.43	17.51	0.50	9.71	69.97	0.50	13.74	99.01
											0.35	2.52		1.82	13.11		9.18	66.15		13.91	100.23
9	...	...	...	...	...	...	...	...	...	0.50	0.68	4.90	0.50	3.22	23.20	0.50	10.59	71.55	0.50	13.75	99.08
											0.52	3.75		2.94	21.18		10.81	73.00		13.67	98.50
22	...	...	...	...	...	...	0.50	0	0	0.50	0.81	5.84	0.50	8.74	62.98	0.50	13.71	98.79	...	...	...
								0	0		0.67	4.83		8.52	61.39		13.96	100.59			
42	...	...	...	0.50759	0	0	0.50742	0.14	0.99	0.56402	6.92	44.21	0.45475	12.69	100.53	...	...	...	...	...	...
				0.5043	0	0	0.50094	0.41	2.95	0.50118	6.25	44.93	0.60486	16.47	98.10						
							0.63649	0.15	0.85												
64	...	...	...	0.50087	0.20	1.44	0.49093	5.13	37.65	0.51616	5.98	41.74	0.47196	3.58	27.33	0.5248	7.23	49.64	...	...	...
				0.50534	0.59	4.21	0.49485	5.41	39.39	0.50030	6.01	43.28	0.51015	4.09	28.88	0.46083	7.26	56.77[a]			
							0.48349	4.94	36.81												
69	...	...	...	0.49533	0.32	2.33	0.51911	4.99	34.63	0.49678	3.64	26.40	0.51896	2.38	16.52	...	...	...	...	...	...
				0.49165	0.65	4.76	0.61423	5.52	32.38	0.57364	4.70	29.52	0.48164	1.94	14.51						
73	0.5826	0	0	0.4971	1.11	8.04	0.51551	3.57	24.95	0.52776	1.62	11.06	0.54473	0.78	5.16	...	...	...	...	...	...
	0.49878	0	0	0.5003	1.33	9.58	0.48572	3.01	22.33	0.73872	2.22	10.83	0.49301	0.53	3.87[a]						
77	0.4987	0	0	0.49701	2.53	18.34	0.52623	0	0	0.50325	0	0	...	...	...	...	...	...	...	...	...
	0.50006	0	0	0.49581	2.37	17.22	0.41535	0	0	0.46811	0	0									
85	0.43049	0	0	0.5003	0	0	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
	0.57323	0	0	0.5015	0	0															

[a] Charred.

sulfate filtered off and washed with cold water. The combined filtrate and washings were evaporated to a small volume and the sulfonic acid was precipitated by the addition of concentrated hydrochloric acid. The crystalline product was filtered off and dried in a vacuum over 50 per cent potassium hydroxide to remove all traces of hydrochloric acid. The free acid has the formula $C_{10}H_6(SO_3H)_2.4H_2O$. This hydrate is stable under ordinary conditions. It does not give up water at room temperature in a vacuum and does not absorb moisture when exposed to the air. For this reason the free 1,5 acid is much easier to handle than the 1,6 isomer.

The formulas for the salts of the 1,5 acid and the method of isolating the crystalline, free acid were taken from a paper by Fierz-David and Hasler.[4] Analysis, by titration with standard alkali, of the free acid prepared in this way gave the following results:

1,5 Acid	0.2626 N NaOH	Anhydrous 1,5 Acid
Grams	*Cc.*	*Per cent*
0.7738	16.36	79.98
0.7754	16.41	80.04
0.7769	16.44	80.03
0.7715	16.33	80.06
0.7746	16.41	80.13
0.7743	16.40	80.11
Average		80.06
Calculated for $C_{10}H_6(SO_3H)_2.4H_2O$		79.96

This is a reasonable guarantee of purity, as the presence of either of the two monosulfonic acids would materially affect the percentage of anhydrous acid, and both of the other two disulfonic acids, the 1,6 and the 2,7 which might be formed at this temperature, form barium salts that are readily soluble in hot water and would have been eliminated in the process of purification. The fact that the material shows no tendency to give up its water of hydration also indicates the absence of the 1,6 acid. The only remaining sulfonic acid—the 2,6 acid—cannot be formed at the temperature employed. Owing to the stability of the 1,5 tetrahydrate, it was deemed unnecessary to assay the samples before use. It was assumed in all the work that the material was the pure naphthalene-1,5-disulfonic acid tetrahydrate, and the calculations were based on this assumption.

Table II—Average Hydrolysis of Naphthalene-1,5-Disulfonic Acid in Closed System

(Figures in per cent)

H_2SO_4 Strength	100° C.	120° C.	140° C.	160° C.	180° C.	200° C.	220° C.
1	..	..	..	2	11	52	99
5	..	..	..	3	15	68	100
9	..	..	..	4	22	72	99
22	..	..	0	5	62	100	..
42	..	0	2	45	99	..	..
64	..	3	38	42	28	53[a]	..
69	..	4	34	28	16	..	..
73	0	9	24	11	5[a]	..	..
77	0	18	[b]	[b]	..	..	..
85	0	[b]	..	..	..	..	..

[a] Charred.

[b] Titration showed no change in the quantity of sulfonic acid present but qualitative analysis showed that other isomers had been formed by resulfonation. Table III gives results of the qualitative analysis.

Hydrolysis

The procedure followed in the hydrolysis of the 1,5 acid in the analysis, both quantitative and qualitative, of the reaction products, and in the calculation of the percentages was identical with the procedure described in the paper on the hydrolysis of the 1,6 acid.[2] As the 1,5 acid is somewhat less soluble in sulfuric acid than the 1,6, it was necessary to use the solid acid instead of solutions where the concentration exceeded 22 per cent sulfuric acid. The results are recorded in Tables I, II, and III.

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[4] *Helv. Chim. Acta*, **6**, 1133 (1923).

Discussion of Results

The results seem to support the theory advanced to explain the behavior of the 1,6 acid—namely, that the conversion of any of the naphthalenesulfonic acids to others involves hydrolysis and subsequent resulfonation. Like the 1,6 acid the 1,5 acid undergoes hydrolysis directly to naphthalene in the lower concentrations of sulfuric acid and it is converted into the other isomers in the higher concentrations. At any temperature where the 1,6 acid is converted into isomeric acids the 1,5 acid is converted into the same isomers, the 2,6 and 2,7 acids. In the case of the 1,5 acid, however, the conversion also takes place under conditions which do not produce such a change in the 1,6 acid—that is, at lower temperatures and in less concentrated sulfuric acid. This, of course, indicates that the 1,5 acid is less stable and is either more readily hydrolyzed or more susceptible to intramolecular rearrangement. If it is a case of intramolecular rearrangement and we find it possible for the 1,5 acid to rearrange its sulfo groups into the 1 and 6 positions, we would expect that where the 1,6 acid is stable and the 1,5 acid unstable the latter would be transformed into the former. Table III shows that at 140° C. in 73 per cent sulfuric acid the 1,5 acid is converted into the 1,6 acid and a trace of the 2,7 acid. Under identical conditions the 1,6 acid was partially hydrolyzed, but no other isomers were obtained. At 140° C. in 77 per cent sulfuric acid, however, where the 1,6 acid showed similar stability, the 1,5 acid has been completely replaced by the 2,7 acid. Thus we see that, although the 1,5 acid can be converted into the 1,6, it is not always so converted under conditions in which the 1,6 acid is stable. Hence the reaction is apparently not a rearrangement. The most probable explanation is resulfonation of the naphthalene produced by hydrolysis. The factor which determines the products in that case is the course of the reaction between naphthalene and sulfuric acid under the existing conditions. This is satisfied in every case, for wherever the initial acid is sufficiently hydrolyzed new isomers appear and they are always the ones that would be produced by the sulfonation of naphthalene under identical conditions.

Table III—Products[a] Obtained by Heating Naphthalene-1,5-Disulfonic Acid with Various Concentrations of Sulfuric Acid at Different Temperatures

H_2SO_4 Strength %	100° C.	120° C.	140° C.	160° C.	180° C.	200° C.	220° C.
1	...	...	...	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	$C_{10}H_8$
5	...	...	...	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	$C_{10}H_8$
9	...	...	...	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	$C_{10}H_8$
22	...	...	1,5	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	$C_{10}H_8$	...
42	...	1,5	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	...	...
64	...	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$ SO_2	...
69	...	1,5 $C_{10}H_8$	1,5 $C_{10}H_8$	2,6 2,7 $C_{10}H_8$	2,6 2,7 SO_2[b] $C_{10}H_8$	...	...
73	1,5	1,5 $C_{10}H_8$	1,6 2,7[b] $C_{10}H_8$	2,6 2,7 $C_{10}H_8$	2,6 2,7 SO_2[b] $C_{10}H_8$	...	...
77	1,5	1,5 $C_{10}H_8$	2,7	2,6 2,7	...	...	...
85	1,5	1,5 2,7	...	...	...	...	...

[a] 1,5 is naphthalene-1,5-disulfonic acid; 1,6 is naphthalene-1,6-disulfonic acid; 2,6 is naphthalene-2,6-disulfonic acid; 2,7 is naphthalene-2,7-disulfonic acid; and $C_{10}H_8$ is naphthalene.

[b] Trace.

Fate of Grease in Sludge Digestion[1]

By S. L. Neave with A. M. Buswell

State Water Survey, University of Illinois, Urbana, Ill.

THE scarcity of literature on the bacterial degradation of fats and soaps indicates a need for further investigation. O'Shaughnessy[2] pointed out that a little over one-third of the fatty matter is lost during digestion of sewage sludge, while the laboratory experiments of Bach and Sierp,[3] on the anaerobic digestion of various foodstuffs, showed as high as 50 per cent decomposition of the fats. In a recent paper the present writers[4] have shown that the percentage of "grease" (using this term loosely to include oils, fats, and soaps extractable by petroleum ether) is the same in freshly settled sewage solids and in the digested sludge; consequently, since about 30 per cent of the solid matter is liquefied during digestion, a corresponding decrease in grease must occur. Fat-splitting bacteria have been reported in the Imhoff tank flora by Hotchkiss and Murray,[5] though Rudolfs[6] reports no decomposition of grease during sludge digestion.

Some of the tests in this laboratory have indicated that, whereas sodium and potassium soaps, which would predominate in a soft-water region, strongly resist bacterial action, the calcium soaps of our hard-water sewage are readily decomposed. This point is receiving further study to see whether the predominant cation may not explain the reported variability in grease digestion. The present paper reports experimental evidence that grease not only can digest, but also may serve as an important source of methane.

Experimental Procedure

Sewage solids were obtained from a settling tank operating on a purely domestic sewage from a combined system. A thoroughly mixed sample of the solids was divided into thirteen 1-liter portions, one portion being used for the initial analysis and the other twelve being placed in bottles fitted for gas collection. No initial seeding was used. Each week one bottle was removed and the contents analyzed. After 3 weeks, when gas evolution had nearly ceased, three of the remaining bottles received 5 grams of lime each to bring the pH from 5.0 back to 6.8, and then digestion was allowed to proceed for comparison with the untreated ones.

Analytical Method—The solids were drained on a Büchner funnel using suction, and the resultant cake, containing about 72 per cent water, was dried to constant weight at 100° C. On the filtrate were determined pH, free amino nitrogen, total amino nitrogen after hydrolysis with 33 per cent sulfuric acid, ammonia, urea, total nitrogen by Kjeldahl digestion, volatile fatty acids by steam distillation, and lactic acid by vacuum distillation. On the dry cake were determined total dry weight, ash, grease (including soaps), cellulose, and total nitrogen; also a 5-gram sample was hydrolyzed with 33 per cent sulfuric acid and the nitrogenous com-

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[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *J. Soc. Chem. Ind.*, **33**, 3 (1914).

[3] *Centr. Bakt. Parasitenk., II Abt.*, **62**, 24 (1924).

[4] This Journal, **19**, 233 (1927).

[5] *Am. J. Pub. Health*, **13**, 562 (1923).

[6] *N. J. Agr. Expt. Sta., Bull.* **427**, 64 (1926).

ponents were determined as humin-N, amid-N, amine-N, purine bases, and total nitrogen by Kjeldahl digestion. Some of these data relate to an independent study of the nitrogen cycle and are omitted in the present discussion.

Results

Table I summarizes the analytical results on the initial solids and on the digesting sludges at weekly intervals. Results for the eighth week are averages of two bottles, the duplication being thought desirable to check both analytical accuracy and uniformity in the digestion processes; the deviation was too slight to justify tabulating both. Figure 1 shows the decrease in total weight of solids in the bottles and Figure 2 the decrease in organic content of the solids. The curves indicate that lime increases the rate, rather than the extent, of digestion, though this drop in organic matter (Figure 2) may be due only to increased solubility in the more alkaline liquor, as noted before.[4] This variation in solubility with pH is receiving further study, so that the apparent digestive processes may be corrected for it.

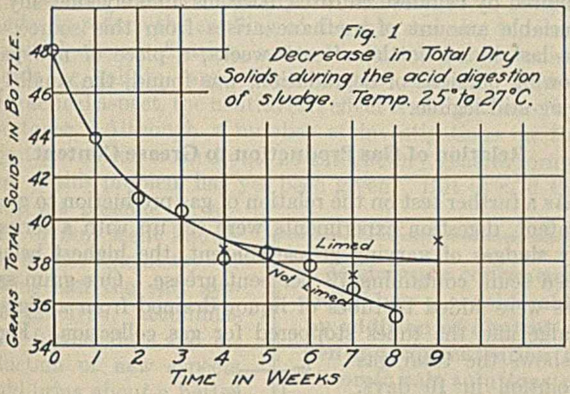
Fig. 1 Decrease in Total Dry Solids during the acid digestion of sludge. Temp. 25° to 27°C.

The proteolytic flora is largely suppressed in this acid digestion and more than 80 per cent of the loss in organic matter can be accounted for as grease digested. The degradation of grease (Figure 3) seems to be more complete in the limed series, though here again it may be only a solubility effect. The second peak in gas evolution following liming (Figure 5) cannot be taken as a criterion of increased liquefaction, because the gas originates from substances already in abundance in solution. Also, the peak in the lower fatty acid production following the addition of lime (Figure 4) may indicate merely the formation of soluble or peptized calcium salts of these acids.

Observations to date indicate that a pH of 5.0 is too acid for the most rapid digestion of grease, though the writers are now building up an acid-digesting flora, by a procedure analogous to that followed in obtaining the usual alkaline flora, to see whether this method of removing the bulk of the acid-producing components may be an economical step prior to a final alkaline period to remove obnoxious nitrogen compounds. Another series of experiments is directed toward methods for controlling the acidity. In addition to liming and to utilizing the buffer value of a large excess of alkaline sludge, slight aeration seems to offer interesting possibilities. To the writers' knowledge this has not been attempted in sludge digestion, though the industrial processes for cellulose fermentation make use of restricted aeration, and in the activated sludge process the sludge neither becomes acid nor has the greasy nature of settled sewage solids. Oxygen increases the pH by converting acetic acid into carbon dioxide and water, and thus oxygen may be considered as a base. For example, one of the liquors, having a pH value of 5.2, received roughly 0.02 cubic foot of air per gallon (145 cc. per liter) per hour and in 18 hours had reached a pH of 7.2. This change, like the acidity of a digesting sludge, is slightly dependent upon carbon dioxide, but an actual decrease in volatile fatty acids from 211 mg. to 80 mg. per liter was observed.

The origin of methane in digestion-tank gases has never been conclusively determined. Since paper pulp is a known component of sewage solids, and since cellulose fermentation can give methane, it has been assumed that sewage-tank methane also arises from cellulose. The writers' experiments do not support this assumption. Accurate gas measurements were obtained only on the limed series, though the gas had the same composition in both series. In the 9 weeks the limed bottle had evolved 2860 cc. of gas of the following composition: CH_4 75.8, CO_2 16.9, H_2 3.6, N_2 3.7 per cent. This volume is equivalent to 80 cc. per gram of organic matter or 275 cc. per gram of organic matter digested. Acetic acid has been shown by Groenewege[7] and others to be a precursor of methane in cellulose fermentation, and the "acetate sludge" of Bach and Sierp[8] points to a similar mechanism in sludge digestion. Groenewege[9] has further shown that calcium for-

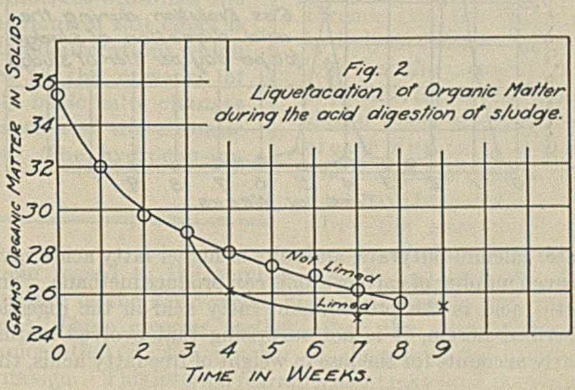
Fig. 2 Liquefacation of Organic Matter during the acid digestion of sludge.

Table I—Acid Digestion Data

Time	Total Solids	Ash	Organic Solids	Grease	pH of Liquor	Lower Fatty Acids in Liquor	Total Solids	Nitrogen Liquor	Cellulose
Weeks	*Grams*	*Grams*	*Grams*	*Grams*		*Grams*	*Grams*	*Grams*	*Grams*
0	47.9	12.5	35.4	12.4	6.9	0.2	1.39	0.07	6
1	43.8	11.8	32.0	6.8	5.4	1.4	1.23	0.12	6
2	41.0	11.3	29.7	5.3	5.0	1.9	0.99	0.15	5
3	40.4	11.5	28.9	4.9	5.0	2.8	0.93	0.28	6
4	38.1	10.2	27.9	4.0	5.0	3.8	0.87	0.37	...
4[a]	38.6	12.5	26.1	3.6	6.0	5.2	0.89	0.41	...
5	38.4	11.1	27.3	5.1	5.0	3.6	0.82	0.33	...
6	37.8	11.0	26.8	4.6	5.0	3.7	0.72	0.61	...
7	36.7	10.6	26.1	4.6	5.0	4.1	0.80	0.37	
7[a]	37.4	12.6	24.8	2.7	6.4	3.2	0.56	0.58	5.5
8	35.4	9.9	25.5	3.8	5.0	4.2	0.72	0.47	6.0
9[a]	39.0	13.7	25.3	2.7	6.4	2.7	0.51	0.70	5.5

[a] Limed.

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[7] *Mededeel. Alg. Proefsta. Landb. Dept. Landb., Nijv. Handel,* **13,** 1 (1923).

[8] *Centr. Bakt. Parasitenk., II Abt.,* **60,** 318 (1923).

[9] *Mededeel. Burgerlijk. Geneeskund. Dienst Nederland-Indië,* **1920,** No. 1, p. 75.

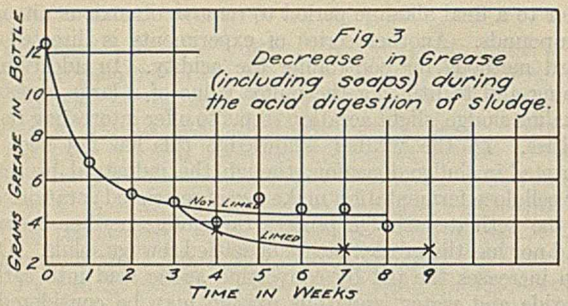

Fig. 3
Decrease in Grease (including soaps) during the acid digestion of sludge.

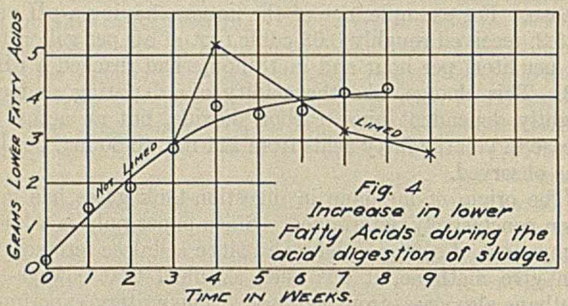

Fig. 4
Increase in lower Fatty Acids during the acid digestion of sludge.

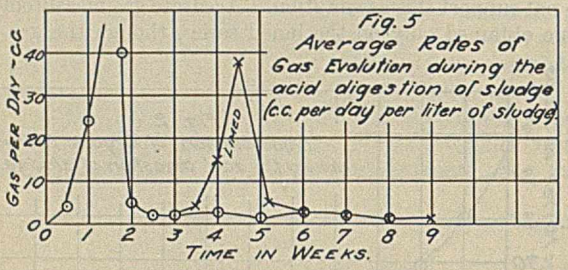

Fig. 5
Average Rates of Gas Evolution during the acid digestion of sludge (c.c. per day per liter of sludge)

mate, calcium butyrate, and salts of higher fatty acids having an even number of carbon atoms can produce methane. Since acetic acid is the predominant fatty acid in the digestions described herein, it is not surprising that evolved methane nearly accounts for the loss in weight of free fatty acids, thus:

	Grams
Loss in grease containing 12.5 per cent Ca (as soaps) = 9.7 or on an ash-free basis	8.5
Free fatty acids remaining in liquor	2.7
Loss in free fatty acids	5.8
Acetic acid equivalent of the methane evolved	5.3

If methane arises chiefly from de-carboxylation of acetic acid, thus:

$$CH_3COOH = CH_4 + CO_2$$

we would expect to find a 1:1 molecular ratio of CH_4:CO_2. Actually, without obtaining that portion of the carbon dioxide which was combined with ammonia and calcium, but correcting for that in simple solution, the ratio was 1:0.4. A different experimental technic would be desirable to establish this ratio.

It should be noted that fatty acids, hence acetic acid and methane, can arise not only from cellulose, starch, etc., and from grease, but also by de-amination of the amino acids. Theoretically, therefore, methane may arise from carbohydrates, fats, or proteins, or from all three. In acid digestions the protein degradation is slight; indeed, that is why the resultant sludge is not well digested. The lower carbohydrates, being soluble, are not present to any appreciable extent in the sludge, though traces of starch, pentosans, and glycoproteins may be found. It is probable that the small amount of hydrogen evolved early in digestion is a fair indication of the quantity of available carbohydrates, since they usually ferment anaerobically to carbon dioxide and hydrogen. The writers' laboratory tests, though not yet completed, have so far failed to show methane in the gases from the following when seeded with sludge liquor: inulin, starch, dextrin, raffinose, maltose, sucrose, lactose, salicin, glucose, fructose, dulcitol, mannitol, adonitol, and glycerol—all of which, however, give hydrogen. The analyses for cellulose (Table I), using the common Schweitzer's reagent extraction of grease-free samples, show that no large decrease in amount has occurred. This, of course, does not cover the alkaline range, but even there, if we consider the relatively brief period in the digestion tank as compared with the months commonly required by cellulose cultures, it seems unlikely that any appreciable amount of methane arises from this source. In the last limed bottle, after 9 weeks, a piece of newspaper showing no signs of degradation, was found, the small type being still legible.

Relation of Gas Production to Grease Content

As a further test on the relation of gas production to grease content, digestion experiments were set up with a series of dry sludges of varying grease content, the highest being a dried scum containing 73 per cent grease. One-gram samples were added to tubes of liquor drained from a digested sludge and the tubes stoppered for gas collection. Figure 6 shows the total gas evolution in 10 days, the relative volumes being roughly proportional to the percentage of grease. The mechanism of the fatty acid degradation is now under study; it seems to be primarily a hydrolysis on the beta carbon atom resembling the familiar beta oxidation of fats.

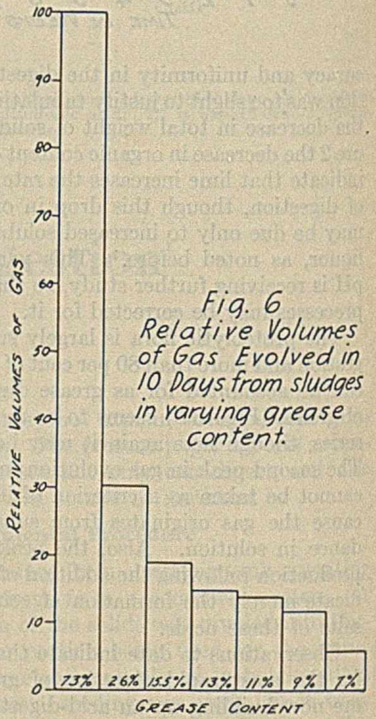

Fig. 6
Relative Volumes of Gas Evolved in 10 Days from sludges in varying grease content.

Summary

1—In the acid type of sludge digestion, a rapid destruction of grease and calcium soaps occurs with the production of lower fatty acids.

2—Some of the lower fatty acid ferments further to give methane.

3—Proteolysis is hindered by the low pH and, as a result, the sludge is not well digested.

4—The rate of fermentation, as measured by gas production, is roughly proportional to the grease content of the solids, a scum high in grease being the most vigorous gas producer.

5—Cellulose is believed to undergo little, if any, digestion during the ordinary sludge-digestion period.

German "Oil from Coal" Assured

Trade Commissioner William T. Daugherty, of Berlin, states that Generalkonsul Bruckmann, head of the A. G. für Industrie und Technik, which last year traded its control of Bergius coal hydrogenation patents to the German Dye Trust, recently advised the company's stockholders that beginning next year the I. G. would produce enough oil from coal to meet one-half of the local demand.

The Neutral Salt Effect in Chrome Tanning

I—Action of Neutral Chlorides upon the Tanning Property of Chromic Chlorides[1]

By K. H. Gustavson

Widen-Lord Tanning Co., Danvers, Mass.

Moderately concentrated solutions of chromic chlorides show a considerable increase in tanning property by addition of neutral chlorides, although the hydrogen-ion concentration is increased. In concentrated chromic salt solutions neutral chlorides diminish the chrome fixation. This particular neutral salt effect is governed chiefly by the constitutional alterations which the chromic chloride undergoes in the presence of neutral chlorides. For extremely basic salts changes affecting the degree of agglomeration of the chromic complex also are of importance. The hydrogen-ion factor fails to solve this problem.

IN CHROME-TANNING leather by the one-bath method the acidities of the solutions of basic sulfates or chlorides of chromium usually employed lie between 2.5 to 3.5 pH. In order to reduce the swelling of the skin and also to retard the initial chrome fixation, neutral salts, as a rule sodium chloride or sulfate, are added to the solution. Besides this practical aspect, the neutral salt effect is also of theoretical importance. Although a number of investigations on this subject have been carried out, no satisfactory general formulation of this problem has yet been given. But even if this is not yet possible on account of our scant knowledge of the chemistry of proteins and the salt systems involved, accumulation of further data and introduction of new aspects should bring about a better understanding of this problem.

Addition of neutral chlorides to common chrome liquors (basic sulfates) generally leads to increased hydrogen-ion concentration, greater stability of the chromic salt toward alkali, and decrease in the tanning property of the chromic sulfate. Wilson and his collaborators[2] consider the increase in actual chrome concentration and hydrogen ion due to hydration of the neutral salt and the decrease in chrome fixation by hide, to be in part at least, a result of the increased hydrogen-ion concentration of the solution. The relative efficiency of the neutral chlorides in regard to increase in hydrogen ion and retardation of tanning was in the same order as their degree of hydration. It was further shown by Thomas and Baldwin[3] that neutral sulfates added to acid solutions decrease the hydrogen-ion concentration of the solutions. Retardation of chrome fixation by hide substance occurs also in this case.[4] Accordingly, the view of the regulating influence of pH and the actual concentration of chrome upon the rate and extent of chrome fixation could not be of general applicability. This was pointed out by the above investigators, and Thomas and Foster concluded that formation of complex double salts with lessened affinity for hide was probably the main factor, with hydration as a secondary cause.

Phases of Problem to Be Considered

The basic chromic salts in the form generally employed in tanning are undoubtedly definite chemical compounds, although only in a few instances has their preparation in crystalline form been possible. This is not unexpected in view of their high sensitiveness to structural rearrangement upon changes of the conditions in their solutions which lead to alterations in the degree of aggregation and electrochemical behavior of the salt. This important phase of the neutral salt problem has not heretofore been considered, and the systems of neutral salt and chromic salt have been treated similarly to solutions containing hydrogen ions in general with a possible complex compound formation as an additional factor. The composition of the chromic salt, especially in regard to the internal sphere, is determined by a number of factors, such as basicity, concentration, temperature, age, the nature of anion of chromic salt, and the quantity and character of added foreign ions. On adding a neutral salt to a solution of chromic salt, the degree of hydrolysis changes. It follows that the concentration of chromic cation or complex should show a similar increase due to hydration. The changes in ionic conditions have been indicated to affect the composition of the cationic chromium complex, in regard to the number of acidic and probably also the nature of the basic groups associated directly with chromium.[5] These changes further affect the electrochemical behavior—that is, the number of charges of the complex and its sign. This internal rearrangement may further change the extent of hydrolysis and ionization of the resulting chromic salt and also the degree of aggregation of the chrome complex. Formation of stable complexes with lessened degree of ionization between the added salt and the chrome compound may also occur. In systems not possessing a common anion double decomposition between salt pairs further complicates the problem. The direct and indirect effects of the neutral salt upon the protein is another factor worthy of consideration. At the pH values generally met in chrome tanning, the specific ion effect of the salt upon protein is probably insignificant compared with that of hydrogen ions, especially for the commonly employed sodium chloride and sulfate. The change in hydrogen ion by neutral salt addition may also affect the constitution of the protein and its degree of activation.

In extremely basic salts of colloidal character the neutral salt effect upon the colloidal constituents must also be considered. Thus, extremely basic chromic sulfates may under certain conditions show increased chrome fixation by hide in the presence of sodium chloride of certain concentrations, whereas for ordinary basic salts the reverse is true. The colloidal factor plays a prominent role in the behavior of the basic aluminum sulfates, which show a greater agglomerating tendency than the chromic sulfates of corresponding percentage acidity. Addition of neutral chlorides and sulfates to the aluminum sulfates affects the pH in a manner similar

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[1] Presented under the subtitle before the Divison of Leather and Gelatin Chemistry at the 72nd meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926. Received March 23, 1927.

[2] *J. Am. Leather Chem. Assocn.*, **15**, 273 (1920); *J. Am. Chem. Soc.*, **42**, 715 (1920).

[3] *Ibid.*, **41**, 1981 (1919).

[4] Wilson and Kern, *J. Am. Leather Chem. Assocn.*, **15**, 273 (1920); Thomas and Foster, This Journal, **14**, 132 (1922).

[5] Gustavson, *J. Am. Leather Chem. Assocn.*, **19**, 446 (1924); *Collegium*, No. **671**, 97 (1926).

to that found for chromic salts. In this case also the neutral sulfates decrease the fixation of aluminum sulfate by the hide protein. Neutral chlorides in moderate concentrations, however, bring about greater fixation of the tanning agent from moderately basic aluminum sulfate. In extremely basic state or high concentration of added salt the reverse occurs. Variations in the concentration of the aluminum salt lead to similar apparent irregularities in the action of neutral chlorides. The formation of very stable complexes, in part of anionic type, between neutral sulfate and aluminum sulfate, leading to an increased degree of dispersity of the colloidal complexes, is probably the main factor in this particular retardation of tanning by neutral sulfates. The action of neutral chlorides seems to be due in part to their aggregating influence upon the aluminum salt. In this case the increase or decrease in tanning potency of aluminum sulfate in the presence of salts seems to depend primarily upon the degree of agglomeration of the aluminum complex.

Evidently, the experimental conditions and the type of salt in question must be considered as chiefly determining the relative prominence of any of the many factors that have to be considered. Weiser's[6] suggestion that "a great deal of the effect of neutral salts is due to their adsorption by the hide, which cuts down the adsorption of hydrous chromic oxide," is too simple to be true. Its absurdity is evident from data to be presented in this paper.

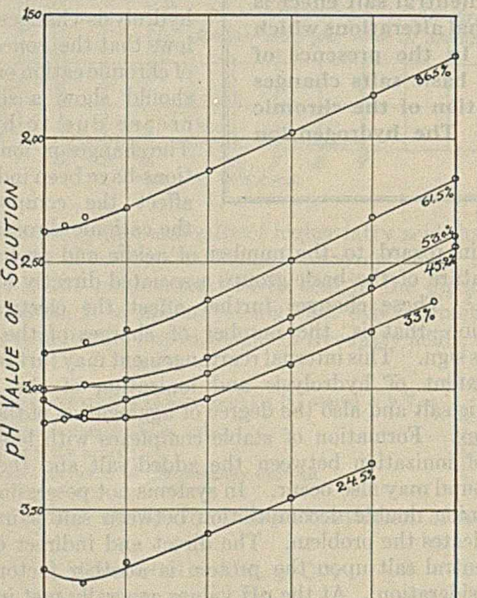

Figure 1—pH Values of Solutions of Chromic Chlorides as a Function of Their Molality in Sodium Chloride

Experiments were carried out to determine the effect of neutral chlorides upon the tanning property of chromic chlorides, as measured by their chrome fixation by hide powder. The neutral salt effect in tanning is generally associated with the concept of diminished tanning property. In this particular case, the action of the neutral salt gives rise to a very considerable increase in the tanning potency of the chromic salt.

EXPERIMENTAL

In most of the experiments sodium chloride was used on account of its technical importance. The basic chlorides were prepared from concentrated solutions of an 86 per cent acid chromic chloride of c. p. grade employing sodium hydroxide as neutralization agent. The neutral salt solutions were tested for their reaction (neutral) and the absence of sulfate. The stock solutions of basic chloride were kept until hydrolysis equilibria were established. The diluted solutions with added neutral salts as used for tanning had also reached pH equilibria. The analytical methods have been previously described.[7]

The lack of an accurate method for the determination of combined chloride in leather is deplorable. Therefore, the figures given for the percentage of acidity of the chrome-collagen compound should be considered as only approximate. The per cent acidity of the chromic salt at which a permanent turbidity was observed and the pH values of the original solutions are included in the tables. For a detailed treatment of these phases reference is given to a previous article.[8] In Figure 1 the pH values of the tanning solutions with established pH equilibria are plotted against the molality of solution in sodium chloride.

Comparison of Dry and Hydrated Hide Powder

In the first series portions of dry hide powder equal to 5.00 grams of protein were treated under continuous rotation at room temperature with 200-cc. portions of the chomic chloride containing increasing amounts of sodium chloride. Table I and Figure 2 contain the data.

Table I—Action of NaCl upon Chrome Fixation by Dry Hide Powder from Solutions of Chromic Chloride

No.	NaCl Molality	pH of Original Soln.	Acidity at Which Pptn. Occurs %	Cr_2O_3 %	Cl %	Collagen %	Cr_2O_3 on Collagen Basis %	Acidity of Chrome-Collagen Compd. %
			86.3% Acid Chromic Chloride, Concn. 6.7 g./l. Cr_2O_3					
1	0.0	2.38	12.5	1.96	1.8	85.3	2.29	65
2	0.25	2.35	32.3	2.02	2.1	85.1	2.37	73
3	0.5	2.32	35.5	2.18	2.4	84.8	2.57	79
4	1.0	2.28	52.0	2.34	2.5	84.4	2.78	76
5	2.0	2.13	54.2	2.58	2.6	84.1	3.07	72
6	3.0	1.98	56.8	2.77	2.7	83.0	3.34	70
7	4.0	1.82	56.8	3.01	2.7	80.2	3.67	65
8	5.0	1.65	56.8	3.39	2.8	79.2	4.28	60
			61.5% Acid Chromic Chloride, Concn. 9.4 g./l. Cr_2O_3					
1	0.0	2.88	20.5	4.12	3.1	83.3	4.94	53
2	0.5	2.83	31.4	4.98	3.9	80.5	6.19	56
3	1.0	2.77	35.7	5.62	4.1	79.5	7.07	51
4	2.0	2.66	40.0	5.83	4.1	79.1	7.38	50
5	3.0	2.49	41.1	6.07	4.1	78.5	7.73	49
6	4.0	2.32	42.3	6.15	4.2	77.0	8.00	49
7	5.0	2.15	42.7	6.34	4.2	76.2	8.32	48
			53.0% Acid Chromic Chloride, Concn. 10.0 g./l. Cr_2O_3					
1	0	3.01	15.8	5.38		81.2	6.62	
2	0.5	2.96	27.6	5.99		79.0	7.58	
3	1.0	2.90	32.2	6.40		78.1	8.20	
4	2.0	2.89	34.5	6.92		77.5	8.93	
5	3.0	2.72	35.2	7.13		76.2	9.36	
6	4.0	2.55	35.2	7.33		75.7	9.68	
7	5.0	2.38	35.7	6.80		76.8	8.85	
			45.2% Acid Chromic Chloride, Concn. 7.6 g./l. Cr_2O_3					
1	0	3.155	12.4	6.22	3.2	80.1	7.77	36
2	0.125	3.145	19.6	6.69	3.4	78.6	8.52	36
3	0.25	3.13	21.6	6.80	3.5	77.9	8.73	36
4	0.50	3.11	24.9	7.21	3.7	78.0	9.24	37
5	1.00	3.045	28.2	7.64	3.9	74.7	10.23	36
6	2.00	2.94	30.8	8.07	4.0	74.4	10.84	37
7	3.00	2.77	32.1	8.34	4.2	73.2	11.39	37
8	4.00	2.60	32.8	7.96	4.1	73.0	10.90	37
9	5.00	2.43	33.5	7.31	3.9	73.4	9.96	38
			33.3% Acid Chromic Chloride, Concn. 8.4 g./l. Cr_2O_3					
1	0	3.06	22.2	7.73	2.6	85.8	9.01	24
2	0.5	3.13	26.3	8.78	2.8	82.8	10.60	23
3	1.0	3.13	28.1	9.80	3.9	81.6	12.01	22
4	2.0	3.05	28.7	9.36	3.1	77.9	12.02	24
5	3.0	2.91	29.3	8.94	3.5	83.6	10.69	28
6	4.0	2.78	30.0	8.15	3.5	85.8	9.50	31
7	4.75	2.66	30.0	6.94	3.5	87.2	7.96	36
			24.5% Acid Chromic Chloride, Concn. 9.6 g./l. Cr_2O_3					
1	0	3.76	19.5	10.55	2.7	77.1	13.68	18
2	0.5	3.80	22.7	11.53	3.2	71.7	16.08	20
3	1.0	3.74	23.8	11.80	3.3	71.4	16.53	20
4	2.0	3.60	24.5	11.32	3.2	72.2	15.68	20
5	3.0	3.45	24.5	10.01	3.2	78.1	12.82	23
6	4.0	3.30	24.5	8.70	3.0	80.1	10.86	25

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[6] "The Hydrous Oxides," p. 328, McGraw-Hill Book Co., New York, 1926.

[7] Gustavson and Widen, This Journal, **17**, 577 (1925); *Collegium*, No. **672** (1926).

[8] This Journal, **17**, 945 (1925).

The use of hide powder without previous hydration as an evaluator of tanning agents of colloidal character under certain conditions produces an artificial maximum in the curve of fixation of tanning agent. This is probably due in part to an overtanning of the surface of the hide powder, whereby the diffusion of the aggregated particles through the hide gel is retarded. It is therefore possible that the maxima in chrome fixation noted in the series with extremely basic liquors of high molalities in sodium chloride are artificial. These solutions were turbid and semicolloidal. Accordingly, in the following series with these extremely basic liquors hydrated hide powder was employed. All solutions were diluted immediately before the start of experiment, with the exception of the 24.5 per cent acid one which had been aged for 8 weeks.

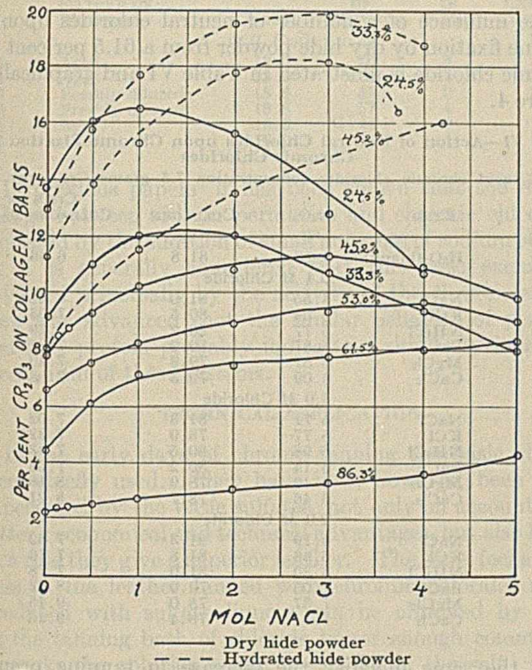

Figure 2—Degree of Chrome Fixation by Hide Powder from Solutions of Chromic Chlorides as a Function of Their Molality in Sodium Chloride

Table II—Action of NaCl upon Chrome Fixation by Hydrated Hide Powder from Solutions of Chromic Chlorides

No.	NaCl Molality	Cr_2O_3 %	Collagen %	Cr_2O_3 on Collagen Basis %
45.2% Acid Chromic Chloride, Concn. 7.6 g./l. Cr_2O_3 (Freshly Diluted Solutions)				
1	0	7.04	88.0	8.00
2	0.5	8.00	83.8	9.55
3	1.0	9.10	79.2	11.49
4	2.0	10.52	78.3	13.44
5	3.0	10.84	77.4	14.01
6	4.2	11.94	74.6	16.01
33.3% Acid Chromic Chloride, Concn. 8.4 g./l. Cr_2O_3 (Freshly Diluted Solutions)				
1	0	8.95	80.1	11.10
2	0.5	11.80	75.4	15.64
3	1.0	12.58	72.1	17.45
4	2.0	13.70	70.2	19.52
5	3.0	13.81	70.2	19.67
6	4.2	12.53	71.6	18.89
24.5% Acid Chromic Chloride, Concn. 8.7 g./l. Cr_2O_3 (Aged Solutions)				
1	0	8.42	83.6	10.07
2	0.5	10.58	77.1	13.72
3	1.0	11.47	74.6	15.38
4	2.0	12.62	71.7	17.60
5	3.0	12.83	70.7	18.15
6	3.75	12.10	74.7	16.19

Portions of hide powder equal to 4.00 grams of protein were soaked in 50 cc. of water for 12 hours. The chromic solutions containing increasing amounts of sodium chloride were then added and the tanning processes carried out for 48 hours under continuous rotation. The data in Table II, showing the concentration of the chromic solutions and their molalities in sodium chloride, refer to the values of the final solutions as used in tanning.

Evidently, the use of dry hide powder with chromic chlorides of low acidities gives an incorrect evaluation of their tanning property, particularly in solutions containing large amounts of added salt. In view of these data and also in order to obtain conditions similar to those in actual tanning practice, hydrated hide powder should be used in investigations of tanning systems of low dispersity. In studies of changes in the degree of hydrolysis in solutions resulting from chrome fixation by hide, dry hide powder is desired and its use is also justified for systems without any marked colloidality, such as the chrome liquors commonly employed. The two kinds of hide powder give similar reactions with such chromic salts. In comparing data from the series with dry and hydrated hide powder, it must be borne in mind that the experiments with the 33 and 45 per cent acid salts using hydrated hide powder were carried out with freshly prepared solutions. This also explains the reversal of the chrome fixation from the 33 and 24.5 per cent acid chlorides by the hydrated hide powder.

Effect of Aging

For such extremely basic salts as the last one mentioned the "aging" leads to decrease in tanning property of solution, probably due to agglomeration that has proceeded too far. The resulting low degree of dispersity of the chrome complexes retards the diffusion of the chrome salt through the protein gel and indirectly also the tanning process. The tanning capacity of solutions of chromic chlorides of acidities and concentrations as usually employed in practice improves with time. In this instance changes affecting the internal sphere, and indirectly also the degree of aggregation and hydrolysis, probably explain the increase in chrome fixation.

The time factor in tanning with a 45 per cent acid chromic chloride is given in Table III.

Hide powder equal to 5.00 grams of protein was soaked with 50 cc. water and thereafter 200-cc. portions of freshly diluted–aged solutions were added. The final concentration was 15.4 grams per liter; the time of tanning was 48 hours.

Table III—Age of Solutions of Chromic Chloride as a Factor in Tanning

No.	Age	Molality in NaCl	pH of Liquor	Cr_2O_3 on Collagen Basis %	Acidity of Chrome-Collagen Compd. %
1	Freshly diluted	0	2.25	10.44	36
2	One year	0	3.03	12.97	33
3	Freshly diluted	4	2.03	15.82	30
4	One year	4	2.49	18.31	30

Effect of Cr_2O_3 Concentration

The solutions described above were of moderate concentrations in Cr_2O_3, similar to those employed in practice. It was deemed of theoretical interest to ascertain the influence of sodium chloride upon chromic chlorides of various concentrations. The data are given in Table IV and Figure 3.

Hide powder equal to 3.00 grams of protein, after being soaked in 25 cc. of water, was treated with 125-cc. portions of a 52 per cent acid chromic chloride. The solutions were prepared immediately before beginning the tanning experiment. The concentrations of Cr_2O_3 and molalities in sodium chloride refer to the final solution employed in tanning.

Table IV—Action of Sodium Chloride upon 52 Per Cent Acid Chromic Chloride of Various Cr_2O_3 Content

Final Molality in NaCl	Final Concn. of Solns. in g./l. Cr_2O_3			
	5.0	25.0	50.0	100.0
	Grams Cr_2O_3 on collagen basis in tanned stock			
0	6.62	10.80	14.52	18.24
0.5	8.42	11.72	14.24	17.55
1.0	9.63	12.25	14.60	17.02
2.0	11.36	13.08	13.95	15.83
3.0	13.98	13.83	15.12	14.30

In dilute and moderately concentrated solutions the accelerating effect of sodium chloride upon the chrome fixation is enormous. With increase in Cr_2O_3 content of solutions, the presence of sodium chloride is less effective and in concentrations as high as 100 grams per liter Cr_2O_3, in this special instance, addition of sodium chloride leads to diminished chrome fixation.

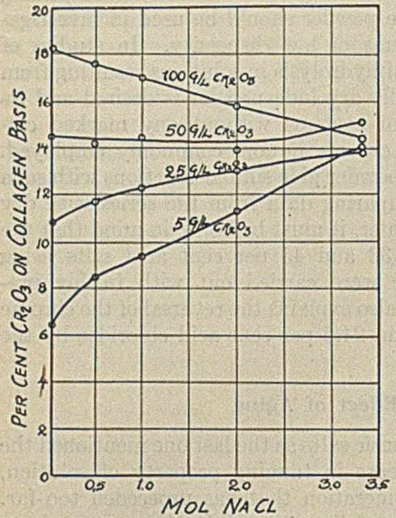

Figure 3—Influence of Sodium Chloride upon Chrome Fixation by Hide Powder from a 52 Per Cent Acid Chromic Chloride of Varying Cr_2O_3 Content

The blank solutions of the 24.5 and 33.3 per cent acid chromic chlorides were clear. On addition of sodium chloride a marked turbidity was produced, and upon standing a precipitation of insoluble constituents was observed in solutions of the 24.5 per cent acid salt containing high molalities in sodium chloride.

Effect of Degree of Colloidality

An indication of the degree of colloidality of solutions of chromic chlorides at various acidities and the influence of sodium chloride upon this property is afforded by the comparison of chrome fixation by hide powder peptized with potassium thiocyanate and hide powder proper. It has been found that cationic chromic salts of crystalloid nature show practically the same values of fixed Cr_2O_3 by regular hide powder and peptized stock.[9] With increase in colloidality of chromic salt the tanning agent has greater affinity for the peptized stock. In the case under consideration no anionic chromium is formed and accordingly the behavior of these two kinds of hide powder toward solutions of chromic chloride with and without addition of salt is expected to depend principally upon the degree of agglomeration of the chromic complexes.

Hide powder that had been treated in 1 *M* potassium thiocyanate solution for 14 days, then freed from salt and dehydrated with alcohol in portions equal to 2.00 grams of protein, was soaked in 25 cc. of water, and a 100-cc. solution of freshly diluted chromic chloride added to give the final concentration of Cr_2O_3 and molalities in sodium chloride as stated in Table V. The tanning process lasted 48 hours. The hide powder blanks had undergone similar treatment after the hydration process.

Table V—Agglomerating Effect of Sodium Chloride upon Chromic Chloride

No.	Acidity	Final Concn.	Molality in NaCl	Cr_2O_3 on Collagen Basis: Regular hide powder	Cr_2O_3 on Collagen Basis: KCNS-treated hide powder
	%	*G./l. Cr_2O_3*		%	%
1	67.0	10.2	0	5.36	5.42
2	67.0	10.2	4	10.44	11.69
3	44.0	9.6	0	6.41	7.02
4	44.0	9.6	4	14.37	17.80
5	33.0	10.2	0	12.48	14.95
6	33.0	10.2	4	20.73	30.64

The 67 per cent acid chromic chloride without added sodium chloride shows practically the same chrome fixation by regular and peptized hide powder. In the solution made four molal in sodium chloride the increase in Cr_2O_3 fixed by the KCNS-treated stock indicates that agglomeration processes have taken place in the chrome complex. With decrease in the acidity of the blank solutions of chromic chloride greater chrome fixation by peptized hide powder compared with blank hide powder is recorded, as would be expected. A considerable increase in the colloidality of extremely basic solutions due to the neutral chloride is evident.

Influence of Various Neutral Chlorides

The influence of a number of neutral chlorides upon the chrome fixation by dry hide powder from a 61.5 per cent acid chromic chloride is illustrated in Table VI and graphically in Figure 4.

Table VI—Action of Neutral Chlorides upon Chrome Fixation from Chromic Chlorides

(61.5% acid chromic chloride; concentration 7.5 grams Cr_2O_3 per liter)

No.	Kind	Cr_2O_3	Collagen	Cr_2O_3 on Collagen Basis
		%	%	%
1	H_2O (blank)	5.28	81.8	6.46
		0.4 *M* Chloride		
1	NaCl	5.55	81.0	6.85
2	KCl	5.66	80.5	7.03
3	NH_4Cl	5.77	80.2	7.19
4	$BaCl_2$	5.87	80.2	7.32
5	$MgCl_2$	5.87	79.3	7.40
6	$CaCl_2$	6.09	79.3	7.68
		1.0 *M* Chloride		
1	NaCl	5.71	81.3	7.02
2	KCl	5.77	78.9	7.32
3	NH_4Cl	5.98	80.5	7.43
4	$BaCl_2$	6.14	80.2	7.66
5	$MgCl_2$	6.46	78.9	8.18
6	$CaCl_2$	6.46	78.7	8.21
		2.0 *M* Chloride		
1	NaCl	6.19	81.3	7.62
2	KCl	5.66	81.8	7.76
3	NH_4Cl	6.30	81.0	7.78
4	$BaCl_2$	7.05	79.0	8.92
5	$MgCl_2$	7.37	78.0	9.45
6	$CaCl_2$	7.41	78.4	9.45

At the same molality the increase in tanning property by the neutral chlorides is in the following order: $CaCl_2 > MgCl_2 > BaCl_2 > NH_4Cl > KCl > NaCl > H_2O$.

In a previous article[8] the hypothesis was advanced that the effect of sodium chloride upon the degree of alkali stability of chromic chloride is intimately connected with changes in the coördinated sphere, as an increase in chloride ions of the solution would be expected to increase the amount of chloro groups. The order of efficiency of a number of neutral chlorides in transferring solutions of hexaquo-chromi chloride into chloro compounds was found by Bjerrum[10] to be the same as their degree of ionization. From the data of chrome fixation in the presence of neutral chlorides in Table VI, it is evident that the degree of ionization of the neutral chlorides does not control the chrome fixation, but that the degree of hydration of the neutral chlorides is a factor of fundamental importance.

Effect of Salt on Acidity of Chloro-Chromi Complex

The hide powder tanned with basic chlorides contains a part of the chlorine directly associated with chromium, but most of the acid is held by the protein. Treatment of tanned stock with a 4 per cent pyridine solution removes the protein-bound acid but leaves the acido complex intact. In order to ascertain the per cent acidity of the chloro-chromi complex fixed by hide protein from solutions of chromic chloride and the influence of sodium chloride upon the internal sphere, specimens of hide powder were tanned with chromic chloride with and without addition of sodium chloride and then treated with pyridine solution. The data from the treated stock are given in Table VII.

In moderately acid salts the presence of sodium chloride slightly increases the acidity of the chloro complex. No appreciable change in this figure is evident in the less acid salts. In view of the slight differences found and the con-

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[9] Gustavson, Colloid Symposium Monograph, Vol. IV, p. 79, The Chemical Catalog Co., New York, **1926**.

[10] *Z. physik. Chem.*, **59**, 581 (1907).

siderable analytical discrepancy in the determination of chloride, further discussion of this question will be left to investigations.

Table VII—Influence of NaCl upon Acidity of Chloro-Chromi Complex

No.	Nature of Solution	Concn.	Acidity of Solution	Molality in NaCl	Acidity of Chloro-Chromi Complex
		G./l. Cr_2O_3	%		%
1	Aged	13.0	70	0	9
2	Aged	13.0	70	4	13
3	Freshly diluted	18.8	57	0	18
4	Freshly diluted	18.8	57	4	18
5	Aged	13.0	44	0	8
6	Aged	13.0	44	4	7

In previous papers[5] it has been shown that the base exchange between sodium permutite and chromic chlorides is increased by the addition of small amounts of sodium chloride. As it is generally considered that this base exchange is governed principally by the activity of the chromic salt, the view was advanced that the similar behavior of permutite and hide protein probably indicates a similarity in reaction mechanism of these systems.

TECHNICAL APPLICATION

In the early days of chrome tanning the basic chlorides were chiefly used. They have now, however, been largely superseded by the basic sulfates, not only on account of the latter's economical and technical advantages, but also because as a rule they give a superior leather. The same feel and fullness in the leather tanned with chromic chlorides as that produced with sulfate liquors can be obtained by adding to the tanning bath of chloride liquor enough common salt to make the solution about one molal in the salt. On experimenting with pieces of calfskin, the empty and thin leather produced by basic chlorides was turned into a very satisfactory product by such an addition.

From these practical experiments and the theoretical findings in this investigation the following *modus operandi* of tanning with basic chromic chlorides is suggested:

> The tanning is begun with a basic chloride of moderate percentage acidity, containing a small amount of salt to prevent swelling of the stock. After a short pretannage sufficient common salt is added to give a solution of about one molal strength in salt. Alkali is added in the last stage of the operation. The suitable quantities of salt and alkali, duration of pretannage, and the acidity of the chrome liquor must, of course, be governed by the particular conditions, such as the extent of pickle, concentration of solution, temperature, tanning equipment, etc.

This mode of tannage fulfils the theoretical requirements, as a fixation of the hide occurs in the pretannage with a solution of slow tanning action. By addition of salt the rate of tanning is greatly increased in the main stage, which is desirable, and the decreased alkali stability of the chromic salt in the presence of common salt will result in a heavy retannage after alkali addition in the last stage of the process. A similar control of the degree of tanning by addition of sodium sulfates to chromic chlorides has been described.[11]

THEORETICAL CONSIDERATIONS

According to Wilson's hydration theory, the addition of neutral chlorides to chromic chlorides should lead to an increase in concentration of all the constituents of the chrome liquor, referred to the amount of solvent available. Accordingly, with increasing amounts of added neutral salt the chromium cation would behave as existing in a more and more concentrated solution. The fixation of chromium by hide powder from chromic chlorides increases steadily with increase in chrome concentration of solutions for all chlorides examined in this investigation except the 24.5 per cent acid one. Therefore, the data presented in Figure 2 are on the whole in harmony with the hydration viewpoint. This applies also to the curves in Figure 4, where at the same molality of added chlorides the heavily hydrated chlorides of alkaline-earth metals are more effective in increasing the chrome fixation than the alkali chlorides, implying that the importance of stabilization of chloro groups by chlorine ions is secondary to the hydration effect.

The maximum amounts of chrome fixed by hydrated hide powder as a function of Cr_2O_3 concentration of the solutions are considerably greater than the optimal values of Cr_2O_3 fixed by hydrated hide powder from the corresponding 24.5 and 33 per cent acid chromic chlorides in the presence of sodium chloride. The data represented in Figure 3 are, however, difficult to reconcile with the hydration concept, as this 61.5 per cent acid liquor up to the highest possible concentrations of Cr_2O_3 shows a steady increase in chromium fixed by hide substance. The hydration hypothesis would also suffice in this instance, with the aid of the assumption that in concentrated solutions of chromic chlorides addition products between the same and added salt are formed, possessing lessened affinity for hide, or if the added neutral chlorides greatly depress the ionization of the chromic salt. Such a radically different action of sodium chloride upon chromic chlorides of low and high concentrations seems less likely, however. There is also the possibility that at low concentrations the constitutional changes in the chromic salt largely eliminate the effect of hydrogen ion, whereas in concentrated solutions of chromic salt the constitutional factor is of minor importance compared with the predominating action of hydrogen ion.

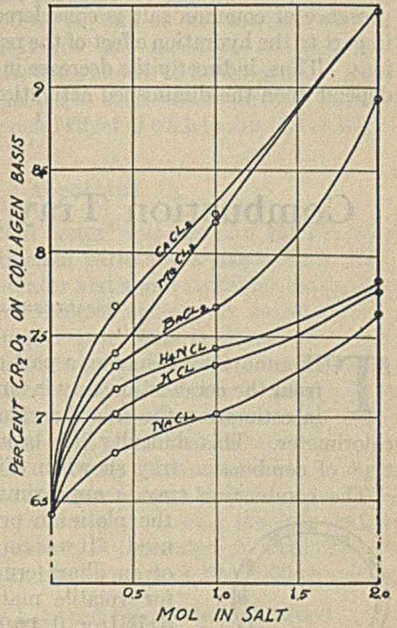

Figure 4—Influence of Various Neutral Chlorides upon Chrome Fixation by Hide Powder from Solutions of 61.5 Per Cent Acid Chromic Chloride

It is evident, however, that the changes the chromic chloride undergoes in the presence of neutral chlorides are intimately connected with alterations in its structure and indirectly with the degree of aggregation of the complex. The concentration factor in the fixation of Cr_2O_3 by hide can be adequately explained by the assumption that with increase in concentration of Cr_2O_3 the charge of the cationic complex is gradually diminished by increase in amounts of chloro groups. In the case under consideration a similar action of the neutral chlorides, leading to decrease in electrical charge of the complex by the hydration tendency of the salt and the action of chloride ions, would satisfactorily explain the data obtained. As a rule addition of neutral chlorides in concentrations up to two molal gives proportionally the greatest acceleration of the tanning process. The constitutional changes as evaluated by alkali stability are also greatest in the molalities of sodium chloride up to two. In concentrated solutions the greater percentage of coördi-

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[11] *J. Am. Leather Chem. Assocn.*, **18**, 568 (1923).

nated chlorine will materially reduce any influence of neutral chloride in regard to alterations in the cationic complexes.

Marked colloidality of the 33 per cent acid liquor containing large amounts of sodium chloride was evident. Concentrated solutions of the same chromic chloride gave no marked indication of colloidality. Therefore, the aggregation changes in this case are probably of most importance, and the decrease in tanning action of these colloidal electrolytes containing great molalities of sodium chloride is probably due to too great agglomeration of the colloidal micelles. From this viewpoint optimum charge, secondary valency activity, and colloidality of the chromic salt seem possible. The view of the formation of colloidal products as a requisite for chrome tanning agents is, however, untenable in view of the data presented in the experiments with the 86 per cent liquor. In this instance any formation of products of colloidal dispersities seems very improbable. The constitutional factor no doubt plays the primary role here, whereas in extremely basic liquors the degree of aggregation of the chrome complex and the colloidal influence of salt enter as additional factors. The reversal in tanning properties of solutions of chromic chlorides of normal acidities on the one hand and the extremely basic ones on the other hand, upon aging, although in both instances the hydrogen-ion concentration is decreased upon standing, gives further indication that the pH factor in chrome tanning is only a secondary and circumstantial function. Instead, the data point to the importance of structural, and therefore colloidal, changes of the chromic salt.

From the ampholytic concept of hide protein it follows that the amount of ionized acidic protein groups should decrease with increase in hydrogen-ion concentration. The decrease in fixation of chromium from chromic sulfates in the presence of common salt is considered by Wilson to be due in part to the hydration effect of the neutral salt upon chromic ions. Thus, indirectly the decrease in chrome fixation should depend upon the diminished activation of the protein caused by the decrease in pH due to the addition of salt. This view is based on the assumption that the hide protein possesses the same number of free acidic and basic groups independent of the hydrogen-ion concentration, which probably is not true. Considering the hide powder in the vicinity of the isoelectric point to consist, at least partly, of internally compensated structures, it would instead be expected that increase in hydrogen ion to a certain extent would manifest itself in an increase in the number of free acidic protein groups although their ionization would be less. According to this view, the influence of pH upon the protein should consist of two opposing reactions. Increased chrome fixation should result from the opening up of the internal protein structure, due to increase in hydrogen ion, whereas the decrease in activation of free acidic protein groups by the decrease in pH would be expected to lead to diminished reactivity of the protein for chromic ion. The relative magnitude of these opposing influences is probably controlled largely by the nature of the chromic salt and the hide protein. This complicated influence of hydrogen ion is not readily conceivable in the system under consideration on account of the predominance of the constitutional influence of the chromic salt.

In tanning practice the osmotic and similar effects of the neutral salt upon the hide and its attendant degree of swelling very likely influence the tanning process.

Conclusion

As previously pointed out, our present concept of the neutral salt effect in tanning is rather inadequate. The main finding of this investigation is that the degree of chrome fixation is not regulated by the hydrogen-ion concentration, but largely by the constitution of the chromic salt.

It is hoped that the investigation of the nature of chromic salt which Professor Stiasny[12] is now carrying out will also greatly extend our knowledge of this important problem.

[12] *Collegium*, No. **677**, 408 (1926).

Combustion Tray for Determination of Heating Value of Coal[1]

By Geo. B. Watkins and J. V. Hunn

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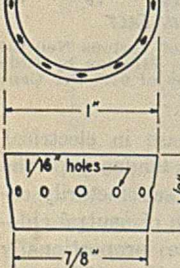
THE annoyance of having a part of the coal sample blow from the combustion tray is familiar to all experienced in estimating the calorific value of coals in the bomb calorimeter. This difficulty has been overcome by using a type of combustion tray shown in Figure 1.



Combustion Tray

The combustion tray is approximately twice as deep as the platinum or nickel tray ordinarily used. It was constructed from the cover of an illium crucible, of the type used for volatile matter determinations, by drilling 0.159-cm. (1/16-inch) holes through the sides of the cover approximately 0.64 cm. (1/4 inch) apart and half way up.

The unbriquetted coal sample is placed in the tray and heaped into the form of a cone. The loop of the iron fuse wire connecting the electrodes in the head of the bomb is bent down to touch the apex of the sample when the tray is in position. As the combustion proceeds, oxygen is drawn in through the holes in the tray, producing a baseburner effect and completely burning the coal sample.

Coals having a high volatile content and high calorific value usually give the most trouble. Several parallel runs have been made on such coals using the ordinary type of nickel tray and the one described. The relative merits of these trays will be seen from the table, which shows the test runs made on a bituminous coal before satisfactory heating value checks were obtained.

Table I—Heating Value Tests, Showing Relative Merits of Trays

RUN	NICKEL TRAY *Cal. per gram*	TRAY DESCRIBED *Cal. per gram*
1	Incomplete combustion[a]	7623
2	Incomplete combustion	7563
3	Incomplete combustion	7596
4	7628	
5	Incomplete combustion	
6	Incomplete combustion	
7	7604	
8	Incomplete combustion	
9	Incomplete combustion	
10	Incomplete combustion	
11	7580	
12	Incomplete combustion	
13	7617	
14	Incomplete combustion	

[a] "Incomplete combustion" refers to test runs in which a part of the coal sample escaped combustion by falling from the combustion tray during the burning period.

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[1] Received April 21, 1927.

The Electrical Resistance of Wood as a Measure of Its Moisture Content[1]

By Alfred J. Stamm

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

This investigation indicates broadly the effects of moisture and certain associated experimental and natural factors on the electrical resistance of wood, thus defining in greater detail than hitherto the limitations of resistance methods for determining average moisture contents and showing that such methods would be of practical value in the lumber trade only in special cases.

The experiments check Hasselblatt's general findings that below the fiber saturation point the logarithm of the electrical resistance of the wood decreases directly as the moisture content increases. The variation is such that the resistance increases 1.8 fold for a decrease of one per cent absolute moisture content. At a given moisture content the ordinary resistance law for the dimensions of solid conductors $\left(R \propto \frac{l}{A}\right)$ seems to hold. The degree of tightness with which the surface electrodes are clamped changes the observed resistance considerably, but with electrodes of proper type and with careful clamping, the error in calculated moisture content introduced by slight differences in pressure may be neglected. In making moisture determinations by this method, the effects of species and density of wood, direction of flow of current through the wood (parallel or perpendicular to the fibers), temperature, ash content (within reasonable limits of variation), and extent of specimens beyond the electrode surfaces either are negligible or can be corrected for in many cases. Condensed moisture on surfaces parallel to the direction of flow of current and uneven distribution of moisture in the wood must be avoided. By the resistance method as here described, the moisture content of specimens below the fiber saturation point having a uniform distribution of moisture can be, in general, determined within one per cent absolute moisture content.

For specimens of non-uniform moisture content, the use of pointed or blade electrodes which may be inserted into the board is suggested as a means of determining moisture content at the center of the piece.

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PREVIOUS investigations on soil,[2] wood,[3] and other hygroscopic materials[4] of low conductivity show that their electrical resistance decreases very rapidly with an increase in moisture content. Hasselblatt's data for birch indicate that the logarithm of the electrical resistance decreases in direct proportion to the increase of moisture content up to what appears to be the fiber saturation point. Above fiber saturation Hasselblatt found very little change in resistance with increased moisture content. A decrease to 56.8 per cent of the original resistance corresponded roughly to a moisture increment equal to one per cent of the weight of the dry wood. As any definite multiple change in the resistance corresponds to the same absolute additive change in moisture content, all deviations considered in this paper will be presented on the basis of the absolute deviation in moisture content rather than on a percentage deviation basis. It must be borne in mind that the percentage deviations at low moisture contents will be much greater than at high moisture contents for the same absolute deviation. The findings of Kujirai and Akahira indicate a similar logarithmic relationship between the moisture content and the electrical resistance for the fibrous materials which they studied.

This rapid change in resistance with moisture content below fiber saturation suggests the possibility of developing a quick and simple electrical method of determining the moisture content of wood. The accuracy of such a method and its adaptability to commercial requirements depends upon the effect of a number of factors associated with the test—namely, the amount of pressure applied and the type of contact between electrodes and wood, dimensions of specimens, extent of specimens beyond the electrode surfaces, direction of flow of current through the wood (parallel or perpendicular to the fibers), species and density of the wood, temperature, ash content, distribution of moisture in the specimens, and the presence of moisture on surfaces parallel to the flow of current. All these factors, as well as the fundamental relationship between resistance and moisture content were therefore examined in the experiments to be described. Only sufficient data were collected in each case to show in a semi-quantitative way the general effect of each factor on the measurements.[5]

Apparatus

The Megger insulation tester[6] was used for the electrical measurements. Its principal parts are a hand-driven 1000-volt, direct-current generator and a galvanometer, both operating between the same electromagnets. A constant voltage is assured when the generator crank is rotated at a speed above 120 r. p. m., as a friction clutch on the armature shaft automatically slips at that speed so that the armature speed is not increased. The circuit containing the material whose resistance is to be measured is connected in series with the generator and in parallel with the galvanometer, so that the greater the resistance of the specimen to be tested, the larger will be the proportion of the current flowing through the galvanometer. The instrument is calibrated to read directly in megohms resistance and has a range of 1 to 2000 megohms.

Type of Contact between Electrodes and Wood

Three different kinds of surface electrodes were tried—(1) plain copper plates 7.5 by 7.5 cm. made from 1-mm. plate; (2) 7.5 by 7.5 heavy brass plates with routings 2 mm. wide and 2 mm. deep cut in both directions to give a rough cleated surface that could be pressed into the surface of a board;

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[1] Received April 25, 1927.

[2] Whitney, Gardner, and Briggs, *Bur. Soils, Bull.* **6** (1897).

[3] Hiruma, Extracts *Bull. Forest Expt. Sta., Meguro* (*Tokyo*), 59 (1915); Hasselblatt, *Z. anorg. allgem. Chem.*, **154**, 375 (1926).

[4] Curtis, *Bur. Standards, Bull.* **11**, 359 (1915); Kujirai and Akahira, *Sci. Papers, Inst. Phys. Chem. Research* (*Tokyo*), **1**, 96 (1923).

[5] Since this investigation was completed, a publication by Meyer and Rees, New York State College of Forestry, *Tech. Bull.* **26**, No. 19 (1926), has appeared on the determination of the fiber saturation point of wood by an electrical resistance method. The authors suggest that the method might be used for determining the moisture content of wood, but no examination of the various factors involved was attempted by them.

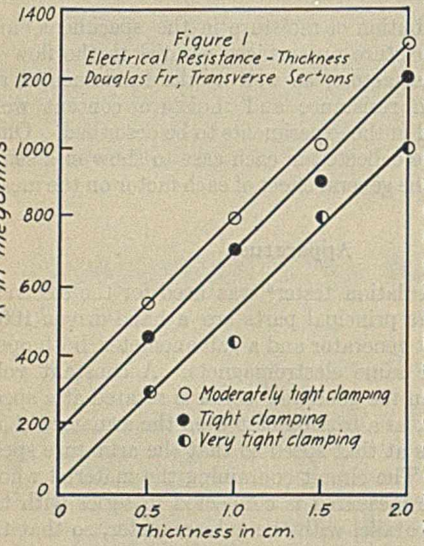
[6] Thanks are due the Wisconsin Power & Light Company for the use of this instrument.

(3) 5.0 by 5.0 cm. brass plates with soft lead faces which, under pressure, would conform to the surface of the board. Threefold deviations in the resistance of a one-inch specimen were obtained when the plain copper-plate electrodes were held with a wooden screw clamp. The same order of deviations was noted by Butterfield[7] when using sheet-iron electrodes backed with fine sand. The other two types of electrodes, when set at a reasonably firm pressure, gave results that generally checked within 20 per cent, the routed electrodes requiring the tighter clamping for equal constancy of readings. The lead-faced brass electrodes were therefore used in most of the experiments. The wood surfaces were all plane, but were not specially dressed or surfaced before making the measurements.

Dimensions of Specimen

The effect of the thickness of the specimen (distance between electrodes) for different degrees of tightness of electrodes was tested on a series of transverse sections of Douglas fir 5 cm. square. These had stood exposed to room conditions for months, equal moisture content and uniform moisture distribution being thus assured. The results (Figure 1) show that the resistance varies directly with the thickness, within experimental error, over the range tested. The three lines represent three different degrees of tightness of electrodes. When the clamping is as firm as can be made by hand without a special mechanical device, the contact resistance is negligible in comparison with the effect of other uncontrollable variables for all but very thin sections, as will be seen later.

The effect of the conductor cross section was tested with two one-inch specimens of Sitka spruce of the same moisture content, one 5 cm. square and the other 7.5 cm. square. The first, fitted with the 5-cm. lead-faced electrodes, showed a resistance of 82 megohms. The second, fitted with the 7.5-cm. plain electrodes, gave 42 megohms, and with the routed brass electrodes, 35 megohms. All three resistance figures are averaged from six determinations each. These results, calculated to unit cross section by the inverse law of areas, are 2050 megohms for the first specimen and 2360 and 1970 megohms, according to the electrodes, for the second. The second value is naturally high because of the impossibility of reducing the contact resistance of the plain brass electrodes to a negligible value. The good agreement between the first and last values is considered as a close enough verification of the inverse law of areas for the purposes of this study.



Direction of Current with Respect to Grain

The resistance of several cubes 5 cm. on a side were determined in each of the three structural directions of the wood—namely, the longitudinal (parallel to the length of the fibers), the tangential (perpendicular to the fibers and to the radius of the log), and the radial (perpendicular to the fibers and to the annual rings). The results are shown in Table I.

Table I—Variations in the Electrical Resistance of Wood in Its Different Structural Directions

Species	Density	Moisture Content	Electrical Resistance, R Longitudinal	Radial	Tangential
		Per cent	Megohms	Megohms	Megohms
Western red cedar	0.336	14.0	9	22	24
Sitka spruce	0.417	15.7	10	18	20
Alaska cedar	0.547	15.6	18	27	27
Douglas fir	0.584	15.3	11	21	23

The resistance in the tangential direction is only slightly greater than in the radial direction but about twice as great as in the longitudinal direction. The same sort of variation was found by Hiruma. The practical equality of radial and tangential resistance is of interest because it eliminates the "grain" factor in two directions as a variable in making resistance-moisture determinations.

Moisture Content—Species—Density

Table II is a summary of experimental data on moisture content and electrical resistance of wood in a transverse direction at 28° C. for several species of different densities and variable thickness of specimen. The lead-faced electrodes were used. To make the results comparable they have been converted to a specific resistance basis, which has been previously shown to be justifiable. The data for all the species plotted in Figure 2 show that within the moisture range examined the logarithm of the specific resistance has a linear relationship to moisture content. The data show no appreciable variation on account of the simultaneous variation of species and density. Hasselblatt found that variations in the electrical resistance were entirely within experimental error for the different specimens of birch of variable density which he used and also for changes from heartwood to sapwood. It is thus very probable that variations in the species alone would have the same negligible effect. The slope of the average line through all the points indicates that the resistance decreases to 55.0 per cent of its original value for an increase of one per cent moisture content. This corresponds closely to the decrease to 56.8 per cent calculated from Hasselblatt's data between the same moisture-content limits. The calculated moisture contents for the different specimens taken from the curve are given in the last column of Table II and show the order of deviations from the straight-line relationship.

Table II—Actual and Calculated Moisture Contents for Different Species

Species	Density	Thickness	Moisture Content Observed	Total Resistance, R	Specific Resistance, R_s	Moisture Content Obtained from Curve
		Cm.	% wt. dry wood	Ohms × 10^{-6}	Ohms × 10^{-8}	% wt. dry wood
Western red cedar	0.336	5.0	13.0	40	2.0	14.4
	0.336	5.0	14.0	24	1.2	15.4
	0.336	2.25	6.3	2000	222.0	7.0
	0.336	2.25	9.4	340	37.8	9.8
	0.336	2.25	14.4	18	2.0	14.5
Sitka spruce	0.417	5.0	14.7	26	1.3	15.2
	0.417	5.0	15.7	20	1.0	15.7
	0.417	1.45	7.3	1600	276.0	6.7
	0.473	2.7	10.45	320	29.6	10.3
Alaska cedar	0.547	5.0	14.3	35	1.75	14.7
	0.547	5.0	15.6	27	1.35	15.2
	0.547	2.4	8.1	1600	156.0	7.8
	0.547	2.4	6.9	2000	208.0	7.3
Douglas fir	0.584	5.0	14.1	30	1.5	15.1
	0.584	5.0	15.3	23	1.15	15.4
	0.584	1.65	6.3	2200	334.0	6.3
	0.584	1.65	6.8	1800	273.0	6.7
Basswood	0.395	2.0	8.1	800	100.0	8.3
Western hemlock	0.407	1.7	7.3	1800	265.0	6.9

It is the steep logarithmic relationship thus established that permits considerable variation in the resistance without

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[7] Electrical Engineering Thesis, Purdue University, 1910.

largely affecting the calculated moisture content. The unimportant effect of variations in species and density, however surprising, is no doubt a consequence of the same relationship. The lightest of the woods tested, western red cedar, tends to give slightly lower resistance than the others, but practically the deviations are within the experimental error. If the measurements were so made that the current flowed longitudinally instead of transversely through the wood, the moisture content as determined from Figure 2 would be consistently one per cent too high; for, as has been shown, the longitudinal resistance is practically one-half of that in the transverse direction.

Extent of Specimen beyond Electrodes

If the method is to be of any practical value, it is highly desirable that the resistance measurements be made upon specimens the cross sections of which are infinitely large in comparison with the area of the electrodes, thus eliminating the necessity of cutting specimens from the boards to be tested. A few experiments were therefore made to investigate the decrease of resistance when the wood extended appreciably beyond the electrodes. A basswood specimen 21.5 by 19.5 cm. and 2.7 cm. thick gave 450 megohms with the 5 cm. square lead-faced electrodes, whereas a section 5 by 5 cm. cut from the same piece gave 800 megohms. Similarly, a Sitka spruce specimen 10 by 15 by 2.7 cm. gave 240 megohms, whereas a 5 by 5 cm. section of the same thickness gave 350 megohms. In the first case increasing the cross section of the specimen 16.4 times caused a decrease in resistance of 44 per cent; in the second a sixfold increase in cross section caused a decrease in resistance of 32 per cent. This shows that the rate of decrease in resistance diminishes rather rapidly with an increase in the total cross section. The thinner the section the less important becomes the decrease in resistance upon extension. Sections 5 cm. square and 18 by 24 cm. cut from 0.2 cm. thick veneer gave 1800 and 1600 megohms, respectively, showing a decrease in resistance of only 11 per cent for a surface 17.3 times as great as the original.

From the theoretical considerations it would be expected that the tendency of current density to become uniform over the whole specimen, rather than to drop off abruptly beyond the part immediately between the electrodes, would increase with an increase in conductivity—in wood, specifically, an increase in moisture content—and an increase in the thickness of the specimen. Thus, in pieces of large area and considerable thickness the resistance would become an exceedingly complex function of the moisture content, so that a complete tabulation of the moisture-resistance relation for large-size stock between zero moisture content and fiber saturation could best be worked out empirically.

Nevertheless, within a very common range for practical determinations, the correction of moisture value necessitated by extent of wood surface is small, and in some cases can be evaluated with sufficient accuracy or be neglected altogether. Thus for reasonably dry veneer, no correction for extent of specimens need be made, while for reasonably dry 1 $^1/_4$-inch stock it appears that the correction would not exceed a subtractive correction of more than one per cent absolute moisture content when making calculations from Figure 2. It would be preferable in general practice, however, to use a standard computation curve obtained upon the type of stock under consideration.

Temperature

The effect of temperature change was tested on a Sitka spruce specimen 2.7 cm. thick, fitted with the brass-routed electrodes. A hole was bored in the end of the piece 2 cm. deep and a mercury thermometer inserted. The electrodes were heated while clamped in place and then allowed to stand until the temperature of the wood and that of the electrodes differed by less than 1° C. The electrical resistance of the wood was then determined. The results, shown in Table III, indicate a falling off of resistance with increasing temperature, a phenomenon contrary to the behavior of ordinary solid conductors but similar to that of electrolytic conduction. Butterfield found that the resistance doubled when the temperature was lowered by 11° C., a result which checks the present findings fairly well. Thus it appears that for measurements made at 16° C., one per cent would have to be added to the moisture content, and for measurements at 40° C. one per cent would have to be subtracted from the moisture content obtained from Figure 2, which was determined at 28° C.

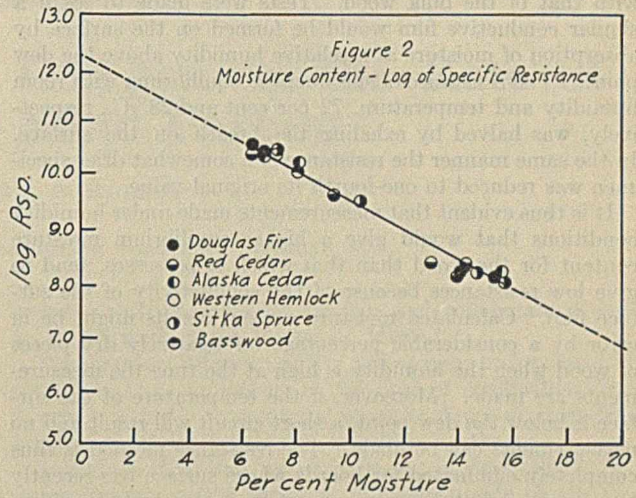

Table III—Effect of Temperature on Electrical Resistance

Determination	Temperature	R	Temperature Drop Corresponding to Doubling of R
	° C.	Megohms	° C.
1	28.5	75	
	32.5	55	
	40.0	40	12.3
2	28.2	130	
	32.0	100	
	39.2	80	12.8

Ash Content

As stock of considerably variant ash content was unavailable, the ash content was varied by the absorption of sodium chloride from solution. A specimen which had absorbed 1.1 per cent of the salt showed a resistance, corrected to the original moisture content, of 120 megohms, as compared with an original resistance of 490 megohms. Thus the resistance is reduced to one-fourth its original value by an increase of about one per cent sodium chloride, or (apparently) halved by each increase of about 0.5 per cent. Only in exceptional cases is the variation in ash content as great as this; furthermore, as a large part of the natural ash in wood is insoluble, it is probable that the variations in calculated moisture content introduced by variations in the natural ash content are much less than one per cent.

Butterfield investigated the effect of zinc chloride on the resistance. He found that the resistance, at several different moisture contents, of sections containing 1.5 per cent zinc chloride is about one-fifth that of the untreated sections. In this case, also, the resistance seems to vary inversely with the concentration of the salt in the wood, so that at a given moisture content the resistance would be halved for an increase of about 0.6 per cent zinc chloride.

Surface Moisture

The effect of a film of surface moisture was examined. A dry specimen that offered a resistance of 2000 megohms was moistened in a streak from electrode to electrode with a wet cloth. The instrument was short-circuited, indicating a resistance of less than one megohm and thus showing the extremely high conductivity of the surface film in comparison with that of the bulk wood. Tests were made to see if a similar conductive film would be formed on the surface by absorption of moisture at a relative humidity above the dew point. The resistance of specimens in equilibrium with room humidity and temperature, 72 per cent and 28° C., respectively, was halved by exhaling the breath on the surface. In the same manner the resistance of a somewhat drier specimen was reduced to one-fourth its original value.

It is thus evident that measurements made under humidity conditions that would give a higher equilibrium moisture content for the wood than that which it possesses, tend to give low resistances because of the conductivity of the surface film. Calculated moisture content results might be in error by a considerable percentage for relatively dry pieces of wood when the humidity is high at the time the measurements are made. Moreover, if the temperature of the surface is below the dew point, a short circuit will result and no measurements can be made. The resistance method is thus completely eliminated for boards whose surface has recently been wet, and it becomes uncertain under high humidity conditions.

Unequal Moisture Distribution

Measurements were made to determine the effect of variations in the moisture distribution through a section. Four pieces of veneer 0.2 cm. thick at moisture contents of 15.0, 27.7, 6.4, and 6.2 per cent, respectively, and averaging 13.8 per cent, were clamped together between the electrodes. With the first and second outside, the resistance was 450 megohms; with the first and second inside the resistance was 560 megohms.

These results show a relatively inconsiderable effect of the arrangement of the layers, greater moisture content on the surface giving only a slightly lower resistance when it is not continuous between electrodes. Under normal conditions there would be a moisture gradient in all three directions in a piece of wood rather than only (as in this experiment) in one direction. This in itself would tend to produce a considerable difference in electrical resistance between specimens having a drying or an absorbing moisture gradient, even though the moisture contents were equal.

Surface conductivity is not the worst part of an uneven distribution, however, as will be seen from the moisture content, 7.8 per cent and 7.4 per cent, respectively, calculated from the above resistances. The reason for this large deviation from 13.8 per cent, the actual average moisture content, can be readily understood when the individual resistances of the sections as measured separately—namely, 1 megohm, less than 1 megohm, 400 megohms, and 400 megohms; total, 801 megohms—are added together, giving a calculated moisture content of 6.9 per cent.

It is because of the logarithmic relationship between resistances and moisture content that it is impossible to get an arithmetic average of moisture contents of the laminae. This effect is further illustrated by resistance measurements on a 76 by 10 by 5.4-cm. piece of Sitka spruce that was coated on the ends and edges with shellac and tinfoil while green and then dried for 18 hours at 160° F. (71° C.) and 15 per cent relative humidity. Its moisture condition, as calculated by Tuttle,[8] was then as follows:

Depth Cm.	Moisture Per cent
At surface	2.8
0.63	13.0
1.26	20.0
1.89	25.5
2.52	25.6
Average	19.7

This piece of wood had a resistance across the gradient of 1700 megohms, giving an apparent moisture content of 7.7 per cent as compared with an actual moisture content of nearly 20 per cent. This result again shows that when the resistances of the various laminae in series are added together, it is the high values that are most effective in determining the calculated moisture content.

Electrolysis and Electroendosmose

No effort was made to study the effect of electrolytic action and the extent of electroendosmose caused by the use of direct current at moisture contents below the fiber saturation point, as has been done in the case of saturated sections.[9] An unpublished Forest Products Laboratory report by Taylor[10] shows that the d. c. resistance may build up to twice the a. c. resistance after a considerable time. Taylor attributes the effect entirely to polarization, but at least a part of it may be due to the building up of an uneven moisture distribution by the electroendosmotic motion of the water.[11] For the purpose of the present study, however, such relatively gradual changes in resistance are unimportant as compared with the immediate and large effect of moisture content.

Conclusions

The results of this investigation show that the determination of the electrical resistance of wood as a means of measuring its average moisture content using surface electrodes is practical only within narrow limits. For stock in which the moisture content is below the fiber saturation point and approaches an equilibrium condition (does not possess a steep moisture gradient), and which does not have an appreciable surface film of condensed moisture tending to short-circuit the electrodes, the average moisture content can be determined by the resistance method to an accuracy of about one per cent absolute content moisture. Factors such as contact resistance, species and density of wood, direction of flow of current, temperature, ash content (within ordinary limits of variation), and extent of specimen beyond the electrodes are either negligible or corrections can, in many cases, be made for them. Although the limitations to which it is subject eliminate resistance measurement as a method of determining the average moisture content of wood under widely variable conditions, it may possibly be applied in special cases as the measurement of the moisture content of thin veneers, which soon attain moisture equilibrium with their surroundings and are not likely to retain steep moisture gradients. It could be used for any wood, such as furniture stock, that had been thoroughly seasoned and had been kept for a considerable time under fairly constant humidity conditions. The method is not applicable for following the seasoning of stock in a dry kiln, or for determining the moisture content of ordinary lumber shipments which may have been only partially seasoned or may have been exposed to extreme humidity changes in transit.

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[8] *J. Franklin Inst.*, **203**, 609 (1925).

[9] Stamm, "Electroendosmose through Wood Membranes" (Saturated Sections), Colloid Symposium Monograph, Vol. IV (1926).

[10] "Effect of the Electrolysis of Maple Wood on Its Electrical Conductivity."

[11] Electroendosmose has been regarded by Evershead, *J. Inst. Elec. Eng.* (*London*), **52**, 51 (1914), as the cause of variation in resistance of moist porous insulators with change in applied d. c. voltage.

These experimental results suggest, however, that the method could be used for determining center moisture content of stock, over a sufficiently small thickness range so that the moisture gradient effect would be small, by using side-insulated point or knife-blade electrodes which can be pressed into the interior of the wood. Experiments along this line are now being carried on by the author at the Forest Products Laboratory. Though the method is obviously limited in its application, it is hoped that it can be used to meet several special needs perhaps better than the over-all resistance method using surface electrodes as described in this paper.

Influence of Diffusion of Oxygen on the Rate of Combustion of Solid Carbon[1]

By J. T. Ward,[2] and J. B. Hamblen

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FROM gas analyses and other data taken during the operation of a hand-fired furnace at firing rates of 19.7 to 185 pounds of fuel per square foot per hour, the U. S. Bureau of Mines[3] showed that the oxygen disappeared 3 to 6 inches above the grate, that the carbon dioxide reached a maximum at about 4 inches from the grate, and that the composition of the gases was practically independent of the rate of air supply.

W. K. Lewis[4] averaged these gas analyses and from the shape of the resulting smooth curves concluded that the rate of the reaction $C + O_2 = CO_2$ is limited only by the rate of diffusion of oxygen through the gas film around each particle of carbon. This conclusion was based on the following facts: (1) The carbon dioxide content of the gases rises rapidly at the start, and its initial slope varies but little with the air velocity; (2) the oxygen content falls sharply at the start practically independent of air velocity; (3) in the initial stages the carbon dioxide curve is approximately the reverse of the oxygen curve.

Although in the Bureau of Mines tests the air velocity was increased approximately tenfold, the oxygen disappeared at nearly the same distance above the grate in every case. Since the increase in air velocity gives decreased time of contact, this may be explained only on the basis that diffusion is the controlling factor or that the specific reaction rate increases in proportion to the velocity. The data show that the increase in fuel bed temperature is not sufficient to account for such a large increase in the specific reaction rate. However, this oxygen disappearance can be easily explained on the basis that diffusion is the controlling factor. It is known that the thickness of the film on the surface of a solid particle is decreased approximately in proportion to the increase in gas velocity. Furthermore, Rhead and Wheeler[5] have shown that the rate of this reaction increased 400 per cent, even between 350° to 500° C., and hence it may be concluded that the rate of chemical reaction of carbon and oxygen is substantially instantaneous at fuel bed temperatures. Therefore, the rate of combustion must be determined by the rate at which oxygen can diffuse through the film to the surface of the carbon. Further data on gas composition at several points in fuel beds of various thicknesses, which are in accord with those of the Bureau of Mines, have recently been obtained by Haslam and collaborators[6] and by recent work of the Bureau of Mines.[7]

The reaction between carbon and oxygen under fuel bed conditions is so important in the field of combustion that it seems desirable to secure, if possible, direct experimental verification of the validity of the diffusion theory.

A method of attack which consisted in determining the concentrations of the gases on the carbon side of the gas film surrounding a burning carbon particle was suggested by W. K. Lewis. Figure 1 is a diagrammatic representation of the concentration gradients in such a system. The concentration of oxygen on the air side of the film is 21 per cent but decreases to zero on the carbon side.

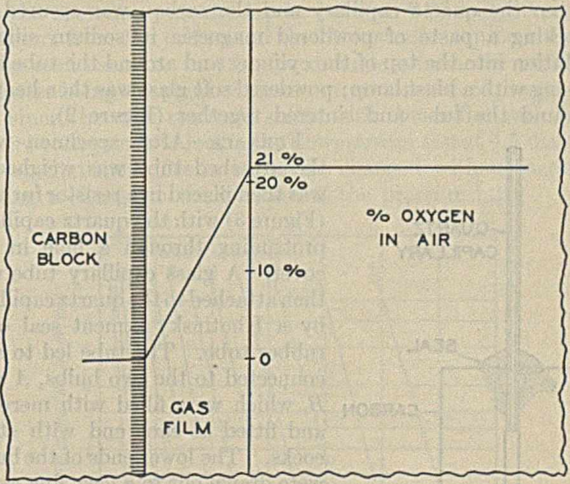

Figure 1—Diagrammatic Representation of Oxygen Concentration in Gas Film

The diffusion velocities of gases are inversely proportional to the square root of their respective molecular weights. When combustion is continuous the oxygen must diffuse in and the resultant carbon dioxide must diffuse out at the same rates. Since the specific diffusion rate constants of oxygen and carbon dioxide are inversely proportional to $\sqrt{32}$ and $\sqrt{44}$, respectively, the concentration of carbon dioxide on the carbon side of the film must be greater than that of oxygen on the air side in order to create a driving force equal to that of the oxygen. If the gases on the carbon side of the film

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[1] Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Assistant professor of chemical engineering at Massachusetts Institute of Technology.

[3] Kreisinger, Ovitz, and Augustine, *Bur. Mines, Bull.* **137** (1914).

[4] This Journal, **15**, 502 (1923).

[5] *J. Chem. Soc.*, **101**, 831, 846 (1912).

[6] Haslam, Entwistle, and Gladding, This Journal, **17**, 586 (1925); Haslam, Mackie, and Reed, *Ibid.*, **19**, 119 (1927); Haslam, Ward, and Mackie, *Ibid.*, **19**, 141 (1927).

[7] American Gas Association, Report of Carbonization Committee, 1926.

are withdrawn so slowly that the film does not collapse, an analysis should show a combined oxygen content greater than that existing on the air side of the film. Such data would be strong proof of the theory that the rate of diffusion is the controlling variable.

The theoretical amount of oxygen which should appear on the carbon side of the film may be derived as follows: The specific diffusion rate constants of carbon dioxide and oxygen are inversely proportional to their concentrations:

$$\frac{\text{Specific diffusion rate constant of } O_2}{\text{Specific diffusion rate constant of } CO_2} = \frac{\text{concn. } CO_2}{\text{concn. } O_2}$$

On a basis of 100 mols of nitrogen there are $21/79 \times 100 = 26.58$ mols of oxygen in the air, and on the carbon side of the film the concentration of oxygen in the form of carbon dioxide, or its equivalent in carbon monoxide, would be $26.58 \div \frac{\sqrt{32}}{\sqrt{44}} = 30.16$ mols.

Experimental Method

To demonstrate the validity of this idea a carbon block was burned in air and, by very slow sampling, the gas was drawn off from the carbon side of the gas film through a quartz capillary sealed into the end of the carbon block.

PREPARATION OF SAMPLE—Samples of carbon were made from $1^1/_2$-inch (38-cm.) electrode carbon cut into $2^1/_4$-inch (5.7-cm.) lengths. A hole, into which a 2-mm. quartz tube could be forced, was drilled in the center of one end of the carbon cylinder $1^1/_2$ inches (3.8 cm.) deep. The first $^3/_{16}$ inch (5 mm.) of this hole was enlarged about $^1/_{16}$ inch (2 mm.) in radius and slightly undercut. The clear quartz capillary tube 5 inches (13 cm.) long was then forced $^3/_4$ inch (2 cm.) into the carbon, leaving a small cavity. A tight joint between the quartz capillary and the carbon was secured by working a paste of powdered magnesia in sodium silicate solution into the top of the cylinder and around the tube and fusing with a blast lamp; powdered soft glass was then heaped around the tube and sintered together (Figure 2).

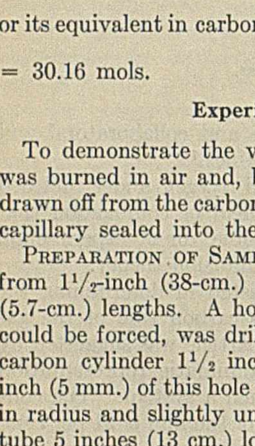

Figure 2—Seal between Quartz Capillary and Carbon

FURNACE—After specimen with the attached tube was weighed it was then placed in a resistor furnace (Figure 3) with the quartz capillary protruding through a hole in the cover. A glass capillary tube was then attached to the quartz capillary by a Khotinsky cement seal over rubber tube. The tube led to a Y connected to the two bulbs, *A* and *B*, which were filled with mercury and fitted at each end with stopcocks. The lower ends of the bulbs were drawn out to a very fine capillary to allow the mercury to escape very slowly and thus draw gas through the carbon at a very slow rate. A second quartz tube, connected with the compressed air line through a meter and a drying tower filled with anhydrous calcium chloride, was inverted through a hole in the cover of the furnace to supply dry air for the combustion.

COLLECTION OF SAMPLES—The furnace was turned on and the carbon specimen brought up to about 1500° F. (816° C.) The air was adjusted to flow at constant rate and the mercury allowed to flow from the first bulb, *A*, at the rate of about 10 cc. per hour. By this means gas was drawn through the carbon until all the air was removed from the carbon and the capillary tubing and collected in the first bulb. After enough gas had collected to have thoroughly scavenged the system of air, the second mercury bulb, *B*, was turned on and from 6 to 9 cc. of the gas were collected over a period of about 90 minutes. The flow of air around the carbon block was sufficient to maintain the atmosphere substantially free from the products of combustion.

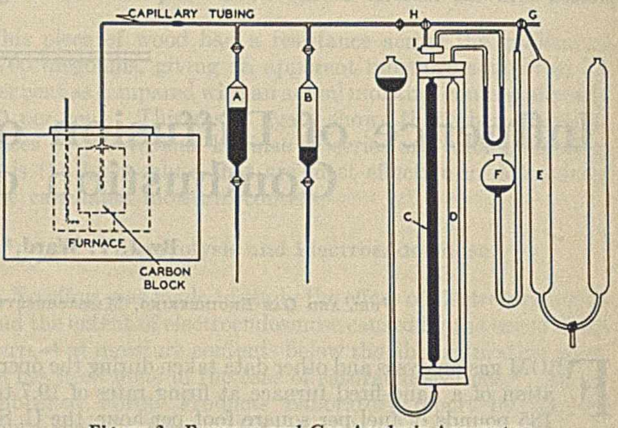

Figure 3—Furnace and Gas Analysis Apparatus

ANALYSIS OF GAS—The gas sample thus collected was analyzed over mercury in an apparatus (Figure 3) which was designed to give very accurate analyses when using small amounts of gas. A 10-cc. graduated buret, *C*, with compensator, *D*, in a water jacket was connected to an absorption pipet, *E*, containing glass tubes. A mercury reservoir, *F*, was connected through the three-way stopcock, *G*, so that when the gas had been exposed to a given reagent the residual gas in the capillaries could be swept back into the measuring buret, *C*. The carbon dioxide was absorbed in potassium hydroxide, the carbon monoxide in acid cuprous chloride, and the oxygen in alkaline pyrogallol. The various parts of the entire apparatus were sealed to form a single unit. The gas sample was transferred to the analytical apparatus without loss or contamination by sealing the sampling bulb onto the tube *H* and evacuating the capillary between the stopcock *I* and that on the sample bulb.

Results

The data secured are given in Table I.

Table I—Gas Analyses

RUN	AIR RATE	CARBON BURNED	TIME OF COLLECTION		SAMPLE	CO_2	O_2	CO	N_2
	Liters per hour	*Grams*	*Hours*	*Min.*	*Cc.*	%	%	%	%
1						16.55	0.68	7.76	75.01
2	325		1	10	8.14	2.46	1.23	29.9	66.41
3	325	62.32	1	35	8.29	1.93	2.06	28.75	67.26
4	350	49.0	1	5	7.06	3.82	0.28	29.45	66.45
5	300	47.55	1	20	9.64	1.04	0.52	33.70	64.74
6	325	36.79			5.72	4.37	0.88	27.5	67.26

Table II contains these data calculated to a basis of 100 mols of nitrogen and also the oxygen-nitrogen ratio corrected for free oxygen and the corresponding nitrogen. These quantities were doubtless present due to leakage and should be excluded in a consideration of the true gases of combustion on the carbon side of the film.

Table II—Gas Analysis on Basis 100 Mols of Nitrogen and Oxygen-Nitrogen Ratio

RUN	CO_2	O_2	CO	RATIO CO_2:CO	RATIO[a] O_2:N_2
	Mols	*Mols*	*Mols*		
1	22.05	0.9	10.33	2.134	28.22
2	3.71	1.85	45.0	0.0824	28.15
3	2.87	3.06	42.7	0.0672	27.41
4	5.75	0.42	44.40	0.129	28.35
5	1.60	0.80	52.0	0.0308	28.45
6	6.5	1.30	40.90	0.159	28.35

[a] Corrected to oxygen-free basis.

As indicated above, the concentration of oxygen inside the gas film that would be expected from diffusion of the gases through an unbroken film is 30.16 mols. On the same basis the ratio of oxygen to nitrogen in air is 26.58 mols. The data of Table II show an average ratio of 28.07 mols. Two additional runs were made in which the oxygen-nitrogen ratio was less than 26.58, but in these cases it was known that absorption of carbon monoxide was incomplete. The data of Table II indicate that the concentration of combined oxygen on the carbon side of the air film was consistently greater than in air and that therefore diffusion took place in accordance with the theory proposed.

Since carbon monoxide was found present in the gases drawn off, one might fear that it complicated the diffusion mechanism. This is not believed to be a fact because the carbon monoxide is a secondary product of the reaction of carbon and oxygen, as has been shown by Langmuir and others. Therefore, the carbon monoxide formed on the carbon side of the film is outside the zone of primary reaction of carbon and oxygen. Any carbon monoxide formed on the air side of the film would be oxidized to carbon dioxide at once on account of the high concentration of oxygen. Therefore it is believed that the net result of the diffusion process is not affected by carbon monoxide formation.

Burkhart[8] made similar experiments, but he collected his samples much more rapidly and used an ordinary Hempel apparatus for gas analysis. His data show an average oxygen-nitrogen ratio of 28.13, exclusive of those runs which are obviously in error.

Conclusion

The conclusion seems justified, therefore, that when solid carbon burns the controlling variable is not the rate of chemical interaction of carbon and oxygen but is, as suggested by Lewis, the rate of diffusion of the combustion gas through the gas film.

Acknowledgment

The writers wish to acknowledge their indebtedness to Professors W. K. Lewis and R. T. Haslam for suggesting the experimental method and for advice.

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[8] M. I. T. Thesis, 1923.

A Slide Rule for Solution of Problems in Flow through Orifices[1]

By H. G. Schnetzler

Standard Oil Company (Indiana), Whiting, Ind.

In testing refinery equipment it is often necessary to measure the flow of liquids or gases in lines where no measuring device is already installed. In many of these cases the simplest and most quickly installed device for measuring the flow is the sharp-edged orifice flowmeter. The conditions under which an orifice may be used and the relation between the pressure drop through the orifice and volume of flow are so well known that quite accurate results are obtained through its use. On account of its accuracy and simplicity it serves as a useful tool in checking refinery operations.

Orifice Coefficients

The general formula for flow through an orifice is

$$Q = C\frac{\pi}{4}d^2\sqrt{2gh} \qquad (1)$$

where Q = flow, cubic feet per second at the downstream density
g = acceleration of gravity, feet per second per second
d = diameter of the orifice, feet
h = head, feet of fluid flowing at the downstream density
C = orifice coefficient

The coefficient C in this equation varies with the conditions under which the orifice is being used, its value depending upon the ratio of the area of the orifice to the cross-sectional area of the pipe and upon the spacing of the pressure taps before and after the orifice for obtaining the pressure drop across the orifice. The relation between these factors and the orifice coefficient has been studied by a number of investigators. Perhaps the most accurate and complete data are those of Spitzglass,[2] who determined the coefficient for various orifice ratios and various pressure tap spacings in pipes from 3 to 12 inches in diameter.

As a result of these studies Spitzglass has recommended that the upstream pressure tap be between 0.75 and 2.0 pipe diameters from the orifice and the downstream tap be either at the *vena contracta* or 4.5 pipe diameters from the orifice, the latter being the point of maximum restoration of pressure. But since the *vena contracta* shifts with the orifice ratio, it is more convenient to locate the downstream tap at 4.5 diameters so that the orifice ratio may be changed without necessitating a change in the location of the pressure tap.

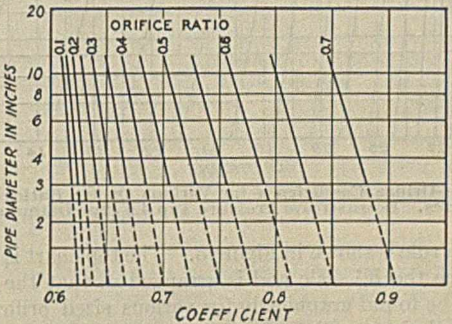

Figure 1—Orifice Coefficients for Various Orifice Ratios and Pipe Sizes. Downstream Pressure Tap at the *Vena Contracta*

The values of the orifice coefficients found by Spitzglass are plotted in Figures 1 and 2. The dashed portions of the lines represent extrapolations to smaller pipe diameters. Several checks on these extrapolated values have shown them to be reasonably accurate. However, if it is desired to rely only upon Spitzglass' experimental data, the line can in many cases be enlarged to 3 inches for sufficient length (20 pipe diameters upstream and 10 pipe diameters downstream from the orifice) to give accurate readings.

The orifice coefficients shown in Figure 2 were used in constructing the slide rule described herewith for the solution of problems in flow through orifices.

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[1] Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *J. Am. Soc. Mech. Eng.*, **44**, 919 (1922).

Construction of Rule

In order to save time and eliminate errors in calculation of results of orifice measurements a slide rule has been devised for making the necessary calculations. For calculating the flow of a liquid in cubic feet per hour, the pressure drop across the orifice being measured by means of a mercury manometer, equation (1) takes the form

$$Q = 3600C\,\frac{3.1416}{4}\,\frac{d^2}{144}\sqrt{\frac{62.4 \times 64.4 \times 13.6}{12}}\sqrt{\frac{l}{p}} \qquad (2)$$

where Q = flow, cubic feet per hour at downstream conditions
C = orifice coefficient
l = pressure drop across orifice, inches of mercury
p = density of flowing liquid, pounds per cubic foot at downstream conditions
d = orifice diameter, inches

This reduces to

$$Q = 1325\,Cd^2\sqrt{\frac{l}{p}} \qquad (3)$$

For a given orifice size in a given pipe size equation (3) becomes

$$Q = K\sqrt{\frac{l}{p}} \text{ or } Q^2 = K^2\,\frac{l}{p} \qquad (4)$$

where Q = flow, cubic feet per hour
K = a constant

This equation can be solved for Q^2 on the ordinary slide rule containing two logarithmic scales with one setting of the rule when K^2, l, and p are known. Therefore, to make a slide rule to solve directly this equation for problems in flow, we require a fixed logarithmic scale graduated in values of K^2, a sliding logarithmic scale graduated in values of p, a second sliding logarithmic scale graduated in values of l, whose position relative to the first sliding scale is fixed, and lastly another fixed logarithmic scale graduated in values of Q^2.

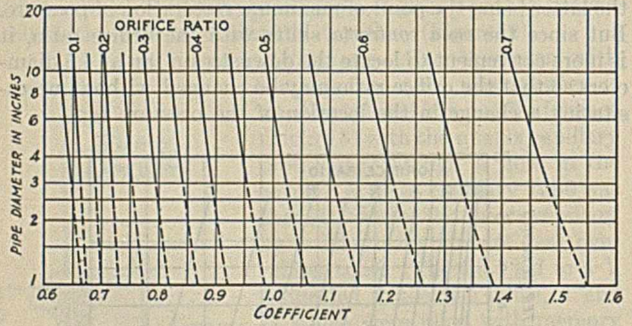

Figure 2—Orifice Coefficients for Various Orifice Ratios and Pipe Sizes. Downstream Pressure Tap 4.5 Pipe Diameters

Such a rule is shown in Figure 3. The top chart is designed to replace the K^2 scale and is arranged so that the value of K^2 may be found graphically for various sized orifices in various sized pipes. The orifice diameters, in inches, are represented by the straight lines running at an angle of 45 degrees across the chart. The pipe sizes are represented by the curved lines across the chart. Where any of these lines intersect the value of K^2 is represented by the vertical line through the point of intersection. Numerical values of K^2 are not shown, since this is usually not of interest. This chart, then, is used to solve graphically for K^2 and in addition provides a logarithmic scale for K^2 at the base.

Under the chart is a blank space in which the sliding scales at the bottom of the figure fit. The chart may be cut out to use as a slide rule, preferably when cemented to a board containing the proper sized slider. It will be noted that there are several scales on the top half of the slider. These are for obtaining Q^2 in the proper units. Thus, if it is de-

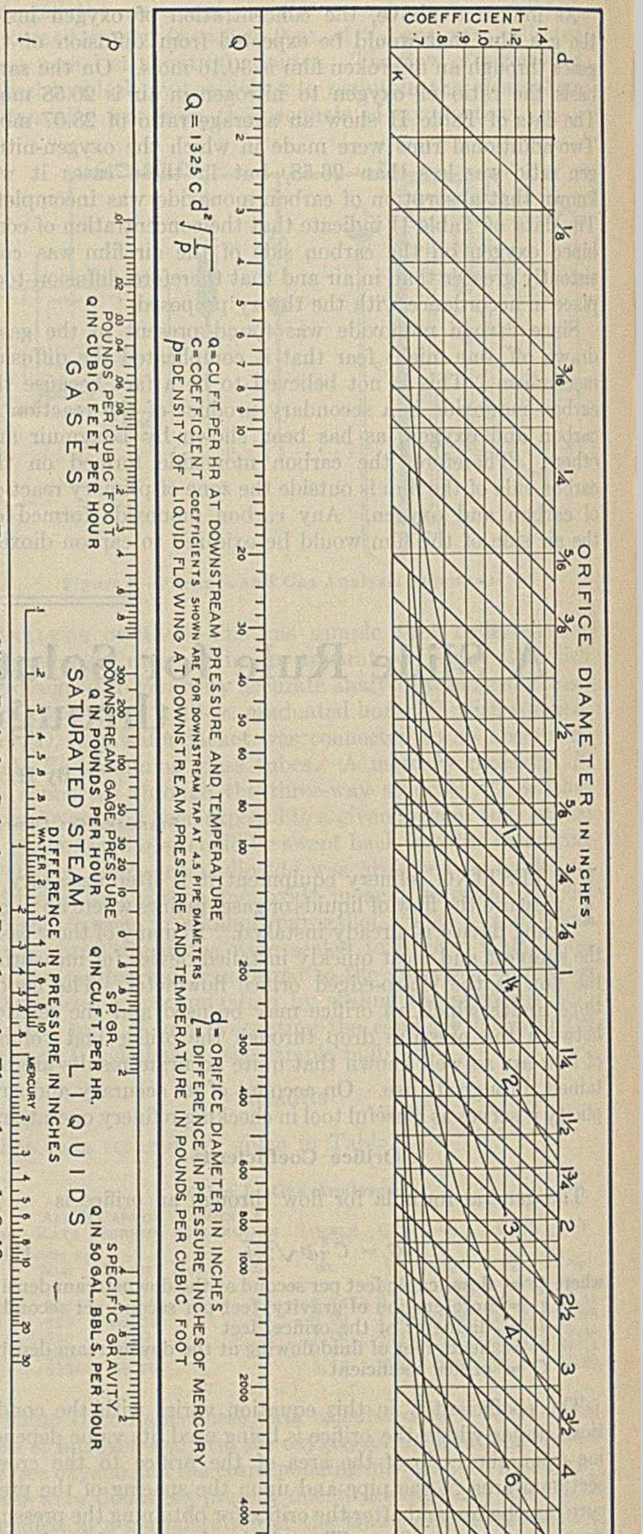

Figure 3—Slide Rule for Solution of Problems in Flow through Orifices

sired to know Q^2 in units other than cubic feet per hour, this may be readily found by shifting the positions of the sliding scales for l and p relative to one another. Under each scale for p is given the unit in which the Q^2 scale will read. The lower or l scales on the slider are graduated directly in inches of water and mercury. Then, fitting the slider in the blank space on the figure, we have under the p scale a fixed logarithmic Q^2 scale, which is labeled in units of Q for convenience.

To solve a problem locate K^2 by the intersection of the lines for the proper orifice diameter and pipe sizes; set the appropriate value of p under the vertical line through this intersection; under the correct value of l read Q in the units given under the p scale.

If for any reason the orifice coefficient is desired, it may be read directly from the chart, since the horizontal lines passing through the intersection of the pipe and orifices sizes lines represent the coefficient and the numerical values are shown at the left of the chart.

The rule also permits rapid estimation of the proper sized orifice to be placed in the line where it is desired to measure the flow.

Copies of this slide rule in size for more convenient use (7 by 20 inches) are being distributed by the Petroleum Division to its members, and may be obtained by others for 25 cents. Orders should be sent to F. W. Padgett, University of Oklahoma, Norman, Okla.

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o-Dichlorobenzene—An Excellent Cleaner for Metals[1]

By P. H. Groggins and Walter Scholl

Color Laboratory, Bureau of Chemistry, Washington, D. C.

O-DICHLOROBENZENE is obtained as a by-product in the chlorination of benzene, particularly in the process of preparing *p*-dichlorobenzene, which has found extended use as a deodorant for lavatories and as an insecticide and fungicide. About one million pounds of the ortho compound are produced annually in this country. Thus far, only limited commercial applications have been found for it, chiefly in the role of solvent.

During an investigation of its properties and possibilities *o*-dichlorobenzene was found to be an excellent cleansing agent for some commonly used non-ferrous metals. One of the samples of commercial *o*-dichlorobenzene submitted to the Color Laboratory possessed the following characteristics: clear and free from suspended matter; almost water-white; penetrating and persistent odor; specific gravity at 60° F. (15.6° C.) (by hydrometer), 1.300; no stain left on paper after 30 minutes; flash point (with open cup tester) 154° F. (68° C.)

Distillation Results

Per cent over	° *C.*
Initial boiling point	168
18	168 to 175
68	175 to 180
9	180 to 185
3	185 to 196

The residue, 2 per cent (by difference), gives a neutral reaction.

Experimental

In working with *o*-dichlorobenzene it was observed that when the liquid fell upon tarnished metals and was rubbed off the tarnish was removed. This suggested the possibility of its use to clean or polish metals.

Practical applications were first investigated. Subsequently analytical data of a fundamental character were obtained to explain and substantiate its success in practice. At first commercial *o*-dichlorobenzene (containing other chlorinated benzenes) was used alone. Later it was found advantageous to apply this active cleansing ingredient mixed with non-gritty powders to form a paste. A paste prepared by adding one part of precipitated chalk to five parts of the liquid forms a clot on the polishing cloth, thereby facilitating its economical application to metal surfaces, and is sufficiently fluid to be poured from a narrow-mouth bottle. A paste of this kind was used in the experiments to be described. Other non-gritty mineral absorbents were also utilized in preparing heavier pastes suitable for dispensing in collapsible tubes.

Copper plates and pipes were rubbed with a cloth containing some of the thin paste. It was found that even the heaviest tarnish or coating was quickly removed and a bright luster imparted to the metal surfaces.

Treating nickel-plated automobile radiator shells with this paste quickly gave a high polish. A comparison with two commercial polishing compounds showed that *o*-dichlorobenzene is more efficacious in removing rain spots from such surfaces.

The cleaner was then tried in homes on silver and aluminum ware. Here also it proved its merit. Comparative tests were made on silver-plated articles with two polishes, one of which cost but 10 cents a bottle and the other, a well advertised product, distributed only by agents of the manufacturers, 85 cents a tube. Some of each polish on a soft cloth was rubbed ten times over the metal surface. After testing repeatedly in this way and after making various other tests, it could be stated definitely that the *o*-dichlorobenzene paste acted more rapidly than the other two.

In attempting to explain the detergent action of *o*-dichlorobenzene, it was assumed that the liquid possessed a solvent action, not only on any greasy coating that might be present, but also on the metal oxides. Confirmatory evidence was sought, inasmuch as it was particularly important to know whether the metal itself was also simultaneously attacked by the solvent.

The effect of *o*-dichlorobenzene upon silver, nickel, copper, and aluminum and upon the oxides of these metals was made the subject of investigation. For the tests, sheet-copper strips, aluminum turnings, a nickel dish, and a silver coin were used. The aluminum was first cleaned with dilute sodium hydroxide; the others were treated with dilute nitric acid. The metals were then washed, first with water and then with alcohol, after which they were quickly dried. After a preliminary rinsing with some *o*-dichlorobenzene, each metal was placed in a 25-cc. portion of the preparation and allowed to stand at 100° C. for 15 minutes.

Two grams of each of the powdered oxides of the four metals mentioned were also placed in 25-cc. portions of *o*-dichlorobenzene and kept under the conditions prescribed for the metals. The eight mixtures were then promptly poured on dry filters. The filtrates were evaporated to dryness on the steam bath in porcelain dishes. After adding 10 cc. of 50 per cent sulfuric acid to each of the dishes con-

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[1] Received May 14, 1927. 137th Contribution from the Color Laboratory, Bureau of Chemistry.

taining the dried residues, heating was continued until the contents were well charred, after which the dishes were cooled. Concentrated nitric acid (5 cc.) was added to each and heating was resumed until heavy fumes of sulfuric acid were evolved. The nitric acid treatment was repeated until the residues became light in color and remained so after evaporation to dryness.

The dried material in each dish was completely dissolved in 8 cc. of 30 per cent sulfuric acid and 10 cc. of water.[2] Qualitative tests were then made for the metals in each of the eight solutions thus obtained. Standard analytical procedure was followed.

Solvent Action of *o*-Dichlorobenzene on Metals and Metal Oxides

METAL OR OXIDE	SOLVENT ACTION	METAL OR OXIDE	SOLVENT ACTION
Cu	Nil	Ni	Faint trace
CuO	Appreciable	NiO	Appreciable
Ag	Nil	Al	Faint trace
Ag_2O	Appreciable	Al_2O_3	Trace

Discussion of Results

The analytical tests showed that the oxides of the four metals treated are susceptible to the solvent action of *o*-dichlorobenzene. This action is more pronounced with the help of frictional rubbing. The negative tests for silver and copper were conclusive. The action on nickel was extremely slight. The test for metallic aluminum was not conclusive.

o-Dichlorobenzene paste when used as a metal polish possesses the following merits: It contains no acid or alkali; it is not dangerous to handle nor is it inflammable at room temperatures; it does not scratch or corrode metal; it does not vaporize rapidly.

It has been found that the incorporation of small quantities of aromatic oils will mask the persistent odor characteristic of *o*-dichlorobenzene. Table utensils treated with this polish need to be dipped in boiling water before they are used again. In industrial practice, metal articles may be merely dipped into a vat containing *o*-dichlorobenzene and then brushed briskly to produce a bright luster. The paste polish is particularly adaptable for door plates and knobs, where it performs the dual role of dissolving accumulated grease and removing tarnish.

Summary

Commercial *o*-dichlorobenzene is an excellent cleansing agent for metals. In some industries it may be used unmodified. For domestic use it may be put up as a thin paste in bottles, or as a heavier paste in collapsible tubes or jars. It acts as a solvent for the oxides of nickel, silver, copper, and aluminum. Its action on the metals is practically negligible.

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[2] Noyes, "Qualitative Chemical Analyses," p. 54.

Influence of Temperature on the Tensile Strength of Reclaimed Rubber[1]

By Henry F. Palmer

THE XYLOS RUBBER CO., AKRON, OHIO

The effect of the temperature of the test strips and the surrounding atmosphere during test upon the resulting tensile of vulcanized reclaimed rubber mixtures is quite marked. The tensile, stress, and elongation decrease with rise in temperature.

The large number of tests on whole-tire reclaim shows that within normal room temperature limits of 18° to 32° C. the relation tends to be linear. Some variations from the linear relation have been observed, and may be due to variation in temperature rise in the strips during stressing or to error in the method.

The percentage decrease in tensile for vulcanized reclaimed rubber mixtures with rise in temperature is appreciably greater than for vulcanized new rubber mixtures, as found by other investigators, being between 16 and 24 per cent for the former and well under 12 per cent for the latter.

It is possible to use a correction chart for practical purposes, the error involved in the case of the whole-tire reclaim studied being approximately that which may occur in a series of tests on the same vulcanized mixture at one temperature, or ±3.5 per cent when eight strips are tested.

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SEVERAL investigators[2 to 7, inc.] have pointed out that the tensile strength of vulcanized new rubber is influenced by the temperature at which the tests are conducted. In general they have concluded that as the temperature increases the elasticity and elongation increase and the tensile decreases, and that the tensile of low-grade rubber is influenced to a greater extent by temperature changes than that of high-grade rubber.

The present investigation shows that the percentage change in tensile strength with changes in testing temperature is more marked in the vulcanized mixture prepared from reclaimed rubber than when prepared from new rubber, although actual numerical differences are not so greatly different. This is of particular significance to the reclaimed rubber industry, since the product is often sold on a specification basis and seasonal variations in testing temperatures may result in the rejection of material in the summer months that would be quite acceptable during the winter.

Conditions of Work

The data recorded herein were obtained according to the standard practice recommended by the Physical Testing Committee of the Division of Rubber Chemistry.[6] The stocks were mixed on an 8 by 16-inch (20 by 40-cm.) mill having a roll ratio of 3:2, the slow roll making 14 r. p. m. Cures were made at 141.1° C. in a platen press which was checked by means of a calibrated thermometer inserted in a special mold. Tests were made on a

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[1] Presented before the Division of Rubber Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Breuil, *Caoutchouc & gutta-percha*, **8**, 5298 (1911).

[3] Wormeley, "The Rubber Industry," p. 246 (1914).

[4] *Bur. Standards, Circ.* **38**, 60, 83 (1921).

[5] Nuckolls, *India Rubber World*, **67**, 79 (1922).

[6] Report of Physical Testing Committee of Division of Rubber Chemistry, THIS JOURNAL, **17**, 535 (1925).

[7] Boone and Newman, *Ibid.*, **18**, 539 (1926).

calibrated Scott machine having a jaw separation under load of 22.5 inches (57 cm.) per minute. Although the room in which tests were conducted did not have thermostatic control, when once the desired temperature had been obtained it invariably remained constant to within ±0.5° C. during the period of exposure and testing. The test strips were exposed to the temperature at which they were to be tested for at least 2 hours, this time being sufficient for the establishment of equilibrium. The relative humidity during the tests remained between 20 and 40 per cent, being determined by a sling psychrometer. According to Stringfield[8] in the case of new rubber mixtures relative humidity changes between 40 and 60 per cent are taken care of by proper exposure. The samples of reclaimed rubber were exposed for 16 to 24 hours in the uncured state after mixing at a room temperature of 20° to 23° C., and after curing for 20 to 24 hours at the same temperature and for at least 2 hours within ±0.5° C. of the testing temperature.

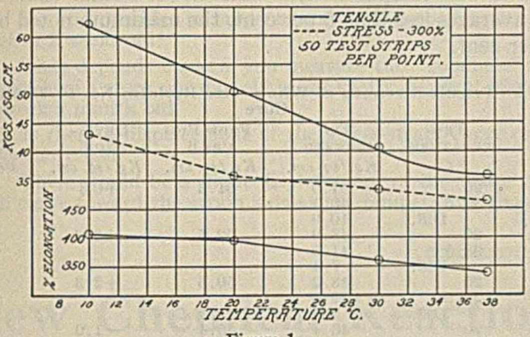

Figure 1

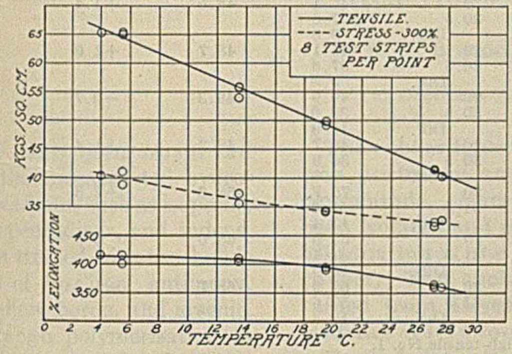

Figure 2
Whole-Tire Reclaim No. 1, 25-Minute Cure

Whole-Tire Reclaim

In a mixture of 100 parts of whole-tire reclaim No. 1 and 5 parts of sulfur the maximum physical properties are obtained in 25 minutes when vulcanized at 141.1° C. This cure was chosen for the more exhaustive investigation and in order to simplify the work. The reclaim was very well blended both before and after mixing in the sulfur. Tests were conducted at 10°, 20°, 30°, and 37.5° C., fifty test strips being broken at each temperature. The probable error for all temperatures as calculated by the method of least squares averages ±0.6 per cent from the tensile given by the arithmetical mean. The results (Figure 1) show that the effect of temperature on tensile here is best represented linearly up to about 32° C., where with increased temperature the tensile appears to tend toward a minimum value. The stress at 300 per cent elongation also decreases with increased temperatures, but to a lesser degree than tensile. The elongation decreases with increased temperature, whereas with new rubber mixtures[2 to 7, inc.] it has been found to increase. Subsequent tests on three different samples of the same stock tested at 4°, 5.5°, 13.5°, 19.5°, 27°, and 27.5° C., eight strips being tested for each point, check very closely and the slope of the curve obtained agrees with that obtained from the fifty test strips. These results are shown in Figure 2.

The above findings have further been established for other reclaimed rubbers as given below.

Solid-Tire, Tube, and Carcass Reclaims

Five parts of sulfur were mixed with 100 parts of each reclaim and the mixture cured 25 minutes at 141.1° C. In the case of the carcass reclaim 1 per cent of di-*o*-tolylguanidine was also added. The results are given in Figure 3. The tensile and stress in each case decrease with increased temperature, as does the elongation for the solid tire and carcass reclaims. With the tube reclaim the elongation shows a slight increase from 10° to 20° C. Further tests have shown that there is a tendency for the elongation of the tube reclaim to decrease, but this decrease is not marked.

Effect of Cure and Process

Whole-tire reclaim No. 1 was cured 15, 25, and 35 minutes, ten strips being tested at 10°, 20°, 30°, and 39° C. The results (Figure 4) show the same trend as those in Figures 1 and 2. These results, as well as other check tests (in which the 45-minute cure was included), show no particular effect of cure on the curve except to displace it, as the magnitude of the physical properties varies with the cure. Figure 4 also shows that maximum physical properties are obtained with the 25-minute cure. The curves are very similar to those of Nuckolls[5] for a low-tensile, new-rubber mixture.

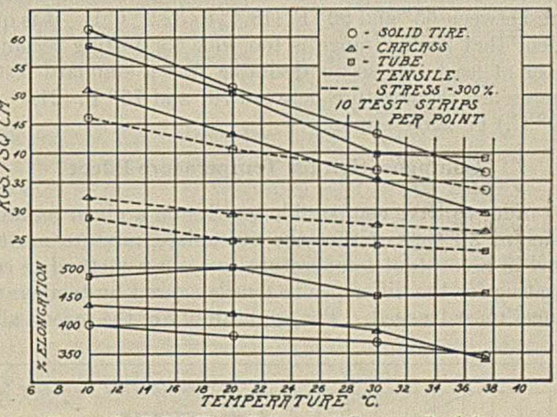

Figure 3—Solid-Tire, Tube, and Carcass Reclaims

Two other whole-tire reclaims, Nos. 2 and 3, which were processed on different factory equipment, were tested. Five parts of sulfur were mixed with 100 parts of each of the reclaims and the mixture cured 25 minutes. Ten strips were tested at 5.5°, 20°, 30°, and 37° C., with the results shown in Figure 5. The effect of temperature on tensile does not appear to be modified by the type of process.

Discussion of Results

It has been observed that the points do not always fall on a straight line, especially when fewer strips were tested. Further tests on carcass and tube reclaims showed a slight dip in the curves at 20° C. These irregularities may be due to a temperature variation during stressing, as described by Boone and Newman,[7] or to error in the tests, which is ±3.5 to 4.0 per cent for eight to ten test strips.

The data show that as the temperature increases from 20° to 30° C. the tensile of whole-tire reclaim No. 1 (25-minute cure) decreases approximately 21 per cent. The drop in tensile in this same range for the 15- and 35-minute cures of

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[8] This Journal, **17**, 833 (1925).

whole-tire reclaim No. 1, 25-minute cures of whole-tire reclaims Nos. 2 and 3, solid-tire, tube, and carcass reclaims as shown in the curves, ranges between 16 and 24 per cent. The percentage decrease in tensile for vulcanized new rubber mixtures[4,6,7] from 20° to 30° C. appears to be well under 12 per cent. While the numerical magnitude of the decrease in tensile of reclaimed rubber with increase in testing temperature is in many cases no greater or as great as that for vulcanized new rubber mixtures, the percentage change is much greater as vulcanized reclaimed rubber has in general a much lower tensile strength. It has been recommended[4,9] that tests on rubber goods be conducted at a room temperature between 65° and 90° F. (18.4° to 32.2° C.). It is quite evident that such a range is too wide for testing reclaimed rubber at least. It seems desirable that a standard testing or reference temperature between 70° and 75° F. (21.1° and 23.9° C.) be agreed upon.

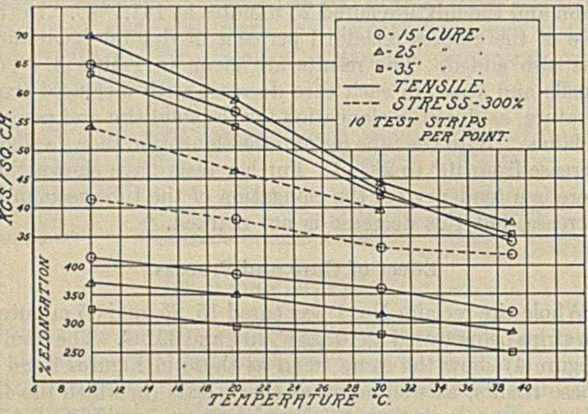

Figure 4—15-, 25-, 35-Minute Cures, Whole-Tire Reclaim No. 1

Compensation for Temperature Effect

In order to have comparable tensiles on a given reclaimed rubber at all times either the vulcanized mixture must be tested in a constant temperature room or a method of compensating for the difference in tensile caused by temperature changes must be used. The applicability of the second alternative has been tried out quite thoroughly in the case of whole-tire reclaim No. 1. For this purpose Figure 6 was used, in which a series of straight lines has been drawn parallel to the tensile curves shown in Figures 1 and 2. By means of this chart tensiles obtained at any temperature within the limits given may be referred to any desirable reference temperature.

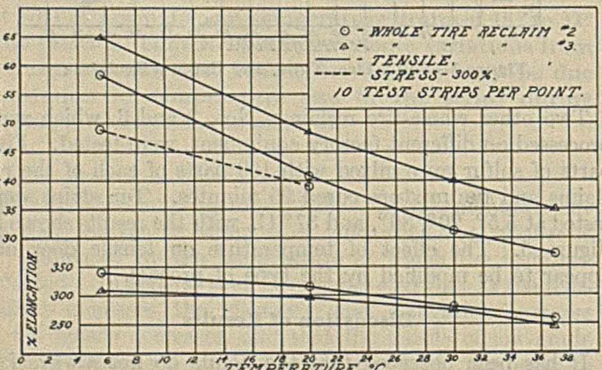

Figure 5—Whole-Tire Reclaims Nos. 2 and 3, 25-Minute Cure

Table I gives eleven tests on different samples of whole-tire reclaim No. 1 in which eight strips were tested at 20°, 30.5°, and 31.5° C. The figures obtained at 30.5° and 31.5° C. were referred back to 20° C. on the chart and the figure thus obtained was compared with that of the actual test. The error averages less than 5 per cent, the maximum noted being 7.3 per cent.

Table I—Tensile Strength of Whole-Tire Reclaim No. 1—25-Minute Cure

Test	Temperature	Observed	From Figure 6	Deviation	Error
	° C.	Kg./sq. cm.	Kg./sq. cm.	Kg./sq. cm.	Per cent
A	20	51.0	51.3	+0,3	+0.6
	30.5	40.1			
	Diff.	10.9			
B	20	48.9	52.5	+3.6	+7.3
	30.5	41.5			
	Diff.	7.4			
C	20	48.2	50.5	+2.3	+4.8
	30.5	39.4			
	Diff.	8.8			
D	20	46.4	45.4	−1.0	−2.2
	30.5	34.4			
	Diff.	12.0			
E	20	47.1	48.5	+1.4	+3.1
	30.5	37.3			
	Diff.	9.8			
F	20	47.1	48.7	+1.6	+3.4
	30.5	37.6			
	Diff.	9.5			
G	20	49.9	49.3	−0.7	−1.4
	30.5	38.0			
	Diff.	11.9			
H	20	46.7	48.2	+1.4	+3 0
	30.5	36.9			
	Diff.	9.8			
I[a]	20	70.7	68.2	+2.3	+3.3
	31.5	57.3			
	Diff.	13.4			
J[a]	20	65.0	65.0	0.0	0
	31.5	54.1			
	Diff.	10.9			
K[a]	20	69.9	68.7	−1.2	−1.7
	31.5	57.6			
	Diff.	12.3			

[a] High-tensile No. 1.

The error in testing this reclaim has been found to be approximately ±3.5 per cent when eight test strips are used. This method of compensation is therefore quite applicable and, although it has not been tested thoroughly in other cases, gives indications of being satisfactory for practical purposes. It is sufficiently accurate as a control check, but where several reclaimed rubbers are to be studied at various times it would be inconvenient to determine the specific correction curve for each one. For such work a constant-temperature room is desirable. Possibly humidity control should be combined with temperature control, though the magnitude of the effect of humidity changes on the tensile of reclaims has not been published.

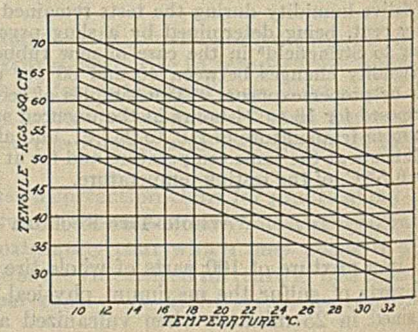

Figure 6—Correction Curves for Whole-Tire Reclaim No. 1

Discussion

Q. Was any sample, after exposure to higher temperature, dropped back again to a lower temperature and tested to eliminate any possible effect of post-vulcanization?

A. No, not exactly that. The effect of overcure on the general slope of the curve appears small, from the data given on 15-, 25-, and 35-minute cures of whole-tire reclaim No. 1. In another test a 45-minute cure was also made. Further, strips held at the warmer temperatures 2 to 3 hours were found to give results which checked with those of strips held at the warmer temperatures for 10 to 12 hours.

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[9] *Bur. Standards, Circ.* **232**, 6 (1925).

Q. Do the curves on freshly made reclaimed rubber follow the same general trend as that which has been developed?

A. I think that they would. The tests given were on reclaims at least one day old. The magnitude of the tensile for more freshly made stock—that is, say one hour old—is less, but I would expect a similar effect of temperature changes.

Q. Do you consider reclaim one day old as good as one, say, a week or 2 weeks old?

A. That depends on how you measure the "goodness" of it. The tensile of a stock one day old is not vastly different from that of a stock a month old.

Q. Is there a displacement of the stress-strain curve or is it merely shortened?

A. There would be a slight displacement of the entire stress-strain curve toward the strain axis as the temperature rises.

Q. Will an overcured stock follow the same curve in tensile strength as undercured stock?

A. I gave the three cures 15, 25, and 35 minutes. The longest cure made on the whole-tire reclaim was 45 minutes, but up to 45 minutes there was no change in the general slope of the curve, so it would be my conclusion that the effect of temperature on tensile would be the same with the different cures, the curves being displaced as the magnitude of the tensile changes with the degree of cure.

Q. Would the same curve obtain on reclaims mixed with rubber definitely proportioned to rubber, say one-third to one-half?

A. It would be the same type of curve but have a different slope.

Note—The answers in this discussion are by the author in each case.

New Chemical Reactions of Rubber Hydrocarbons[1]

Reactions with Metallic Halides

By H. A. Bruson, L. B. Sebrell, and W. C. Calvert

The Goodyear Tire & Rubber Company, Akron, Ohio

The rubber hydrocarbon adds the halide salts of tin, iron, antimony, and titanium to form colored addition compounds. A stable addition product with $SnCl_4$ has been isolated and possesses the formula $(C_5H_8)_{10}.SnCl_4$. Elimination of the $SnCl_4$ by alcohol gives a polymer of rubber. Two such isomeric products have been obtained from Hevea rubber which furnish additional evidence of its two-phase nature. The action of halide salts on balata, isoprene, and polymerized isoprene is described.

It has been observed that unsaturated hydrocarbons, such as isoprene, cyclopentadiene, and indene, when treated with the halide salts of tin, iron, antimony, titanium, boron, and arsenic, undergo polymerization to yield compounds of apparently high molecular weight.[2] Such polymerized products are white amorphous powders. The halide salt first forms a colored addition product, after which an exothermal polymerization occurs at room temperature. By treatment with alcohol the addition product is decomposed, quantitatively liberating the polymerized hydrocarbon component.

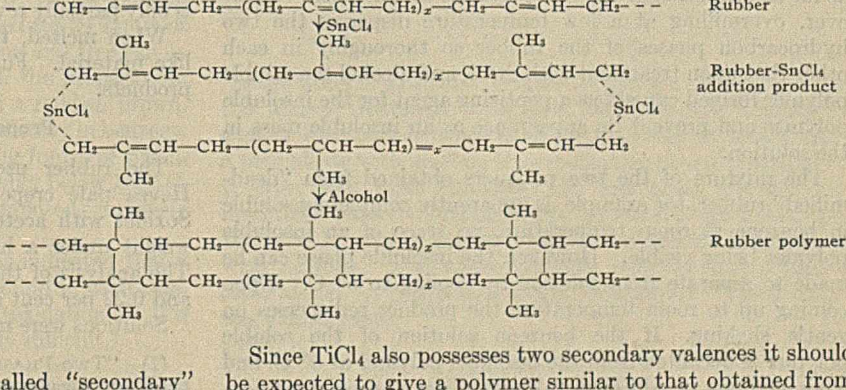
It seemed probable, therefore, that rubber, gutta-percha, or balata hydrocarbons, when treated analogously, would react in a similar manner to yield first an addition product and then a polymeride. This has been found to be the case.

Formation of Additive Compounds

When rubber solutions were treated with anhydrous $SnCl_4$, at room temperature in an inert nitrogen atmosphere, chemical addition occurred with the formation of a colored compound. The addition product was fairly stable in dry nitrogen, but readily split off the metallic halide when treated with alcohol or acetone. The $SnCl_4$-rubber addition product possessed the empirical composition $(C_5H_8)_{10}.SnCl_4$. Upon treatment with alcohol the $SnCl_4$ split off, simultaneously precipitating the hydrocarbon $(C_5H_8)_x$ as a white amorphous powder. $TiCl_4$, $FeCl_3$, and $SbCl_5$ reacted in a similar way.

Each of these halides possesses so-called "secondary" valences of the Werner type, which enable it to add to many classes of organic compounds that contain an unsaturated atom or a double bond.[3]

The addition of $SnCl_4$ to rubber hydrocarbon occurs at the most reactive point in the molecule. According to Staudinger's theory of end valences,[4] addition of the halide salt should take place at the ends of the hydrocarbon chain. Since $SnCl_4$ possesses two reactive secondary valences, it is probable that two molecules of rubber hydrocarbon add to the $SnCl_4$ in such a manner that upon subsequent treatment with alcohol some of the double bonds of the hydrocarbon bridge across to form rings in the more reactive positions of the double molecule, leaving other unsaturated bonds intact. This would explain the decreased unsaturation. Isoprene and balata would be expected to behave similarly, but would, of course, yield different polymers. The mechanism of the reaction with rubber may be formulated as follows:



Since $TiCl_4$ also possesses two secondary valences it should be expected to give a polymer similar to that obtained from $SnCl_4$. On the other hand, $FeCl_3$, with three secondary valences, and $SbCl_5$, with one secondary valence, should

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[1] Received June 3, 1927. For a preliminary report of some of this work see Dinsmore, This Journal, **18**, 1140 (1926).

[2] Bruson and Staudinger, This Journal, **18**, 381 (1926); Staudinger and Bruson, *Ann.*, **447**, 110 (1926); Bruson, Dissertation, Zürich, E. T. H., 1925.

[3] A comprehensive survey is given by Pfeiffer, "Organische Molekulverbindungen," F. Enke, Stuttgart, 1922.

[4] *Ber.*, **57**, 1203 (1924); *Kautschuk*, August, 1925, p. 5.

give different polymers. This was found to be in accord with the experimental facts.

Application to Structure of Rubber

Another feature of the reaction throws some light on the structure of rubber. Ordinary unmilled, purified Hevea rubber yields a mixture of two isomeric addition products analyzing $(C_5H_8)_{10}.SnCl_4$. The polymer obtained by splitting off $SnCl_4$ from this mixture consists of two hydrocarbons, each analyzing $(C_5H_8)_x$. One of these is readily soluble in cold benzene and forms 75 per cent of the total weight of the polymer. The other hydrocarbon forms the remaining 25 per cent and is insoluble in all the usual solvents.

However, if the same original, unmilled, purified rubber is first subjected to an ether diffusion process as described by Feuchter[5] and the portion which diffuses into the ether is then treated with $SnCl_4$ as described above, only one addition product, $(C_5H_8)_{10}.SnCl_4$, is formed. The polymer obtained from this product by treatment with alcohol is completely soluble in benzene.

Furthermore, quantitative ether-diffusion experiments showed that close to 75 per cent of the weight of unmilled, extracted Hevea rubber diffuses in ether, the remaining 25 per cent forming the insoluble gel skeleton. These results indicate that the benzene-soluble polymer is derived from the hydrocarbon phase of Hevea rubber which is diffusible in ether, and that the insoluble polymer is formed from the non-diffusible phase of the rubber.

The experiments show chemically that Hevea rubber does actually consist of two distinct isomeric hydrocarbons, thus confirming the physical evidence already observed by other investigators.[5,6]

Tin tetrachloride adds separately to each phase. The fact that the mixture of the two $SnCl_4$-rubber addition compounds obtained from two-phase rubber has the same empirical composition as the addition product derived from the diffusible phase alone, indicates that both phases have the same combining capacity for $SnCl_4$, but differ from each other either in molecular weight or in the spacial arrangement of their atoms.

Effect of Milling

The physical and chemical properties as well as the relative amounts of the two polymers obtained from cold overmilled rubber were the same as those of the polymers obtained from unmilled rubber, showing that cold milling has no appreciable chemical action upon rubber hydrocarbon, as far as formation of the two polymers is concerned. However, overmilling at a low temperature disperses the two hydrocarbon phases of the rubber so thoroughly in each other that upon treatment with $SnCl_4$ and alcohol the soluble polymer formed can act as a peptizing agent for the insoluble polymer and prevent its appearance as an insoluble mass in the solution.

The mixture of the two polymers obtained from "dead-milled" rubber, for example, is apparently completely soluble in benzene at room temperature, no trace of an insoluble polymer being visible. However, the insoluble phase can be made to separate from solution by cooling to 5° C. Upon coming up to room temperature the product redisperses on gentle shaking. If the benzene solution of the soluble polymer is decanted from the insoluble polymer at 5° C. and fresh benzene is added to take its place, the polymer does not redissolve. It can no longer be redispersed, even when all the soluble polymer originally present is put back into the solution. The phenomenon is a curious example of colloidal behavior and peptizing action.

If unmilled or slightly milled rubber is used, the insoluble polymer obtained with $SnCl_4$ and subsequent treatment with alcohol at first disperses only in boiling benzene but subsequently becomes insoluble. The peptizing action of the soluble polymer is very small in this case, apparently because it is contained within the interior of the particles of the insoluble polymer and can be reached by the benzene only after the insoluble cell walls have been penetrated. This seems to indicate that a dispersion of *unmilled* rubber in benzene consists of discrete swollen particles possessing a two-phase hydrocarbon structure as noted in the case of latex particles by Freundlich and Hauser.[7] The ether-diffusible hydrocarbon is located inside the globule and is surrounded by the non-diffusible hydrocarbon envelope. This accounts for the phenomenon of swelling, diffusion, and the characteristic behavior of milled and unmilled rubber with $SnCl_4$.

Effect of Heat

Rubber that had been heated in an inert atmosphere at 163° C. for 24 hours in the solid state or in solution at a temperature of 80° C. or above was found to yield only one polymer. This polymer was completely soluble in benzene. It had a lower melting or decomposition point than the soluble polymer obtained from unheated rubber. No trace of an insoluble polymer was present. Apparently a temperature of 80° C. is sufficient to bring about depolymerization of one or both hydrocarbon phases in solution, so that subsequent treatment with $SnCl_4$ and alcohol gives lower polymers than those produced in the cold. Rubber that had been milled for 45 minutes at 100° C. gave both polymers, showing that ordinary hot milling as carried out in factory practice does not destroy the insoluble phase.

Properties of Rubber Polymers

The polymers of rubber produced by the action of $SnCl_4$ possess a lower degree of unsaturation and a higher melting or decomposition point than rubber itself. They have no elastic properties whatever. They are more inert toward oxidation than rubber, but they do autoxidize appreciably. Like rubber they form gels with S_2Cl_2 and still are able to add to metallic halides to form colored additive compounds. Whether or not the addition products thus formed are identical with those produced with the original rubber has not yet been determined, but the indications are that the reaction is only partially reversible.

When melted, the polymers form a hard, brittle, shellac-like material. Further heating yields liquid decomposition products.

Preparation of Rubber Solutions

The rubber used was high-grade, unmilled, plantation Hevea pale crepe. The thin sheets were extracted in a Soxhlet with acetone for 24 hours, then dried to constant weight under a high-vacuum pump at room temperature. The analysis of the dried rubber was 0.48 per cent nitrogen and 0.22 per cent ash.

Solutions were made up from this rubber as follows:

(I) "TWO-PHASE" RUBBER—A 2 per cent (by weight) dispersion of the above rubber in anhydrous, thiophene-free benzene.

(II) PURIFIED TWO-PHASE RUBBER—Solution (I) diluted with twice its volume of benzene was allowed to stand several weeks in an atmosphere of nitrogen. The clear supernatant solution was decanted from the bottom protein layer and precipitated with three times its volume of alcohol. The precipi-

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[5] *Kolloidchem. Beihefte*, **20**, 434 (1925).

[6] Gladstone and Hibbert, *J. Chem. Soc.* (*London*), **53**, 679 (1888); Weber, *J. Soc. Chem. Ind.*, **19**, 680 (1900); Spence, *Quart. J. Inst. Comm. Res. Tropics*, **1907**, No. 13; Beadle and Stevens, *J. Soc. Chem. Ind.*, **31**, 1099 (1912); Caspari, *Ibid.*, **32**, 1041 (1913); Freundlich and Hauser, *Kolloid-Z.* (Zsigmondy Festschrift), **36**, 15 (1925).

[7] *Loc. cit.*

tate was redissolved in benzene and precipitated with alcohol a total of three times, then dried *in vacuo* to constant weight. Analysis: N 0.09 and ash 0.09 per cent. This rubber was dissolved in pure anhydrous benzene to give a solution containing 1.8 grams per 100 cc.

(III) "KD"-DIFFUSION RUBBER—Thirty grams of the rubber were allowed to stand in 2 liters of ordinary ether for 1 month. The clear upper solution was decanted off from the gel skeleton, filtered through cotton to remove small particles of insoluble gel, and precipitated by stirring into 5 liters of alcohol. The precipitate was dried *in vacuo* to constant weight and dissolved in pure anhydrous benzene to give a solution containing 1.8 grams per 100 cc. Analysis of dried rubber: N 0.09 and ash 0.10 per cent.

(IV) ETHER-INSOLUBLE RUBBER—The residue from (III) was placed in 1 liter of fresh ether and allowed to stand several weeks. The supernatant ether was poured off and the residue treated with alcohol and dried. It was milled 5 minutes on a cold, tight mill to assist dispersion, and 3.6 grams were placed in 200 cc. of pure benzene.

(V) OVERLY MILLED RUBBER—The rubber was milled 30 minutes on a cold mill and dissolved in pure benzene to give a 2 per cent (by weight) solution.

Preparation of $SnCl_4$ Addition Compounds

Preliminary experiments showed that autoxidation occurred unless the reactions were conducted out of contact with the air. An ordinary 500-cc. Erlenmeyer suction flask fitted with dropping funnel, gas inlet, and exit tubes was used. Both inlet and exit tubes were fitted with stopcocks, so that after the rubber solution had been added, and the air displaced with pure dry nitrogen, the $SnCl_4$ could be run in through the dropping funnel and the system then closed. The nitrogen was passed through two Fisher gas-washing bottles containing alkaline pyrogallol, then through two gas washers containing concentrated sulfuric acid, and finally through a tower of soda lime. The flushing of the reaction flask was continued until an indicator solution, consisting of sodium indigo disulfonate which had previously been exactly decolorized by carefully adding a dilute sodium hydrosulfite solution, was no longer affected by gases leaving the apparatus.

Two hundred cubic centimeters of diffusion rubber (solution III) were placed in the flask and the flushing with nitrogen was continued for 4 to 5 hours until all air had been displaced. Ten cubic centimeters of freshly distilled, anhydrous $SnCl_4$ were then run in through the dropping funnel and the system was closed. The flask was allowed to stand 24 hours at 20–30° C. The solution became non-viscous and a deep red color developed. There was no precipitate. The exit tube of the reaction flask was then connected to a vacuum pump and the excess $SnCl_4$ and benzene distilled off at 10 mm. over a water bath kept at 70° C. A vacuum of 2 mm. was then continuously maintained for 24 hours at 30° C. to remove the final traces of benzene and free $SnCl_4$. At no time did air come into contact with the preparation.

The residue in the reaction flask formed a reddish brown, brittle, vitreous solid. It dissolved with difficulty in benzene. In moist air it slowly decomposed, evolving fumes of $SnCl_4$. When heated it did not decompose appreciably below 150° C. At 170° C., it suddenly swelled and decomposed, copiously evolving $SnCl_4$.

Analysis of several separate preparations indicated that a definite amount of $SnCl_4$ was chemically bound in each case. (The hygroscopicity and readiness of autoxidation of this compound make exact analyses exceedingly difficult.)

Analysis: I—0.1016 gram substance: 0.0764 gram H_2O and 0.2377 gram CO_2
0.1172 gram substance: 0.0722 gram AgCl
II—0.1113 gram substance: 0.0906 gram H_2O and 0.2557 gram CO_2
0.1522 gram substance: 0.0233 gram SnO_2

$(C_5H_8)_{10}.SnCl_4$	% C	% H	% Cl	% Sn
Calcd.:	63.75	8.57	15.07	12.61
Found: I	63.86	8.42	15.24	...
II	62.74	9.14	...	12.05

A longer reaction period with excess $SnCl_4$ did not change the composition of the product.

Two-phase rubber, solution (II), under exactly the same conditions gave a similar product.

Analysis: 0.0892 gram substance: 0.0656 gram H_2O and 0.2038 gram CO_2
0.1484 gram substance: 0.0850 gram AgCl

$(C_5H_8)_{10}.SnCl_4$	% C	% H	% Cl
Calcd:	63.75	8.57	15.07
Found:	62.33	8.24	14.24

Preparation of Polymers from $SnCl_4$ Addition Products

It was found best to prepare these compounds without isolating the intermediate addition products. To prevent oxidation during the alcohol precipitation process, the reaction flask was fitted with an extra tube reaching to the bottom of the vessel. By means of nitrogen pressure applied at the exit tube of the suction flask the contents could be pumped over into a bottle containing alcohol, also under nitrogen.

(A) WITH TWO-PHASE RUBBER (UNMILLED)—Two hundred cubic centimeters of solution (II) were treated with 10 cc. of anhydrous $SnCl_4$ under nitrogen as previously described and allowed to stand for 24 hours. The red solution was then forced over by means of nitrogen pressure into 500 cc. of 95 per cent ethyl alcohol under nitrogen. As fast as the red benzene solution came in contact with the alcohol it was completely decolorized. Simultaneously a white, amorphous powder precipitated out. This was allowed to remain in the alcohol for 2 to 3 hours, during which time the $SnCl_4$ was quantitatively split off by the alcohol, with which it combines to form an alcohol-soluble compound.[8]

The white powder was filtered off by suction and dried. The yield was quantitative.

Separation of Soluble Polymer. The powder was shaken with 200 cc. of benzene and the supernatant liquid decanted off from the insoluble gel. The gel was boiled for several minutes with 200 cc. additional benzene and filtered hot. It went partly into solution. Upon cooling the filtrate to 5° C., the gel separated out again. The supernatant benzene was again decanted off and combined with the previous benzene solution which had been decanted. The combined cold benzene-soluble solutions were precipitated with 500 cc. of 95 per cent alcohol. The white powder was reprecipitated a total of five times from benzene solution with alcohol for purification, and dried at 100° C. *in vacuo* to constant weight for analysis. The product was free from chlorine.

Analysis: 0.1068 gram substance: 0.1141 gram H_2O and 0.3441 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash
Calcd.:	88.15	11.85	
Found:	87.88	11.98	0.10

Separation of Insoluble Polymer. The gel remaining after the above treatment with cold benzene was repeatedly shaken with cold benzene until the washings no longer gave a precipitate with alcohol, thus indicating that all the soluble polymer had been removed. At this point the gel was insoluble even in boiling benzene. It was allowed to stand in 100 cc. of alcohol to harden it and then extracted in a Soxhlet with acetone. The white crumbly material was dried *in vacuo* at 100° C. to constant weight for analysis. The product was chlorine-free.

Analysis: 0.1026 gram substance: 0.1098 gram H_2O and 0.3311 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash
Calcd.:	88.15	11.85	
Found:	88.01	12.00	0.11

When the same experiment was repeated with extracted, unmilled pale crepe which had not been purified, solution

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[8] Rosenheim and Schnabel, *Ber.*, **38**, 2778 (1905).

(I), the results were not so good; a typical analysis being C 81, H 10.5, ash 1.6, N 0.4 per cent. This is due to the presence of the protein-$SnCl_4$ reaction product as impurity in the rubber. Quantitative experiments showed that the ratio of soluble to insoluble polymer in this case was 75 to 25.

Properties of Soluble Polymer. The soluble polymer is a fine, white powder which is very electrostatic in the dry state. The x-ray spectrogram was kindly examined for us by E. A. Hauser, in Frankfurt, Germany, and by Edward Mack, at Ohio State University. Both investigators found the material to be completely amorphous. It is very soluble in the usual rubber solvents, difficultly soluble in ether, and insoluble in acetone or alcohol. Its solutions are non-viscous except at concentrations over 50 per cent. On evaporation such solutions deposit a transparent, colorless or slightly yellow, brittle film. The polymer softens at 220–225° C., gradually becoming pasty and melting at about 280° C. with decomposition. The melt upon cooling solidified to a black, shiny, vitreous mass which is soluble in benzene.

On evaporation such solutions deposit a brownish, adherent, varnish-like film.

The degree of unsaturation of the soluble polymer is considerably less than that of rubber, but exact values by any of the standard procedures, such as direct bromine titration or the McIlhiney[9] and Kemp-Wijs[10] methods, could not be obtained.

Note—The data on a large number of runs by all these methods at 0° C. under different conditions of time and concentration indicated a large amount of substitution. In fact, the McIlhiney method gave negative unsaturation due to a splitting out of HBr from the bromine addition product during the titrations, leading to erratic results. The Kemp-Wijs method gave check values on any particular run, but when the time of reaction was increased or the concentration of the Wijs solution changed, entirely different values were obtained, which in some cases amounted to a 100 per cent difference in the unsaturation values. Kemp observed similar reactions with various cyclic hydrocarbons.

In air the compound oxidizes readily. A sample that had stood in an oxygen-filled desiccator over P_2O_5 in the sunlight for 5 months increased in weight 12 per cent. A similar sample, on aging in an oxygen bomb at 50° C. and 10.5 kg. per sq. cm. pressure, showed a weight increase of 17.6 per cent after 31 days.

The molecular weight determination cryoscopically in benzene gave very small depressions, the molecular weight increasing with the concentration. Values obtained ranged from 3300 to 10,000 and even higher—typically colloidal results.

Properties of Insoluble Polymer. The insoluble polymer is a white, fibrous, inelastic material resembling shredded asbestos. It possesses a characteristic toughness which makes it difficult to powder. It is insoluble in all the usual solvents. When heated it sinters at about 255° C., gradually softening and decomposing above 300° C. A pure sample of the insoluble polymer which had stood in a loosely stoppered bottle for 7 months analyzed C 86.99, H 11.77 per cent, showing that it oxidizes very slowly under ordinary conditions. A sample kept in an oxygen bomb for 31 days at 50° C. and 10.5 kg. per sq. cm. oxygen pressure showed 11.8 per cent increase in weight. The x-ray spectrogram showed this material to be completely amorphous.

(B) WITH TWO-PHASE RUBBER (OVERMILLED)—Two hundred cubic centimeters of solution (V) were treated exactly as in (A). The white powder obtained by treatment with alcohol was completely soluble in benzene at 25° C. Upon cooling the solution to 5° C., a white flaky material separated out. The mixture was centrifuged while still cold and the supernatant benzene poured off from the matted gel. The gel was redispersed in warm benzene, cooled to 5° C., centrifuged, and the top layer again decanted. After the third or fourth repetition of this process the gel became insoluble even in hot benzene. The soluble polymer was precipitated from the collected supernatant cold benzene and amounted to 75 per cent of the rubber used. The insoluble gel, after standing with excess alcohol, hardened and could be pulverized. The properties of the two polymers were exactly the same as those shown by the polymers from unmilled rubber. Several quantitative experiments were run with $SnCl_4$ for various lengths of time ranging from 24 to 96 hours. In each case the ratio of soluble to insoluble polymer was closely 75 to 25.

(C) WITH DIFFUSION RUBBER—"KD"—The polymer obtained by treating solution (III) with $SnCl_4$ and alcohol as described in (A) was completely soluble in benzene even at 0° C. There was no separation of any insoluble polymer. The yield was quantitative.

Analysis: 0.1033 gram substance: 0.1106 gram H_2O and 0.3328 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash	% N
Calcd.:	88.15	11.85		
Found:	87.79	12.01	0.10	0.07

The properties of this compound were the same as those of the soluble polymer obtained in (A) and (B).

(D) WITH ETHER-INSOLUBLE PHASE—Solution (IV) contained a swollen mass which did not dissolve appreciably. Upon treatment with tin tetrachloride as described under (A) the mass went into solution but precipitated a gelatinous product after about 20 hours. The polymer obtained upon subsequent treatment with alcohol contained some soluble polymer, which was removed with benzene. The insoluble gel was purified as in (A). The analysis of the final product was unsatisfactory owing to the ash and protein which is concentrated in this fraction. (C 83.2, H 10.3, ash 0.58, N 2.28 per cent.) For this same reason the $SnCl_4$ addition product was not prepared, since it would not have been possible to separate the protein from the ether-insoluble residue.

EFFECT OF HEAT—Two hundred cubic centimeters of solution (I) were boiled under reflux in nitrogen for 2 hours, then cooled, and finally treated with $SnCl_4$ and alcohol as previously described. It gave only a soluble polymer.

Similarly when 200 cc. of solution (I) were boiled with 10 cc. of $SnCl_4$ under reflux for 4 hours in nitrogen, only a soluble polymer was formed. This product contained a small amount of chlorine (0.2 per cent).

Analysis: 0.1441 gram substance: 0.1348 gram H_2O and 0.4619 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash	% N
Calcd.:	88.15	11.85		
Found:	87.42	10.48	0.19	0.12

It showed a lower decomposition point than the soluble polymer prepared at room temperature. It became soft and plastic at 185–200° C. and melted with decomposition at 250–260° C. On cooling, the melt formed a dark, brittle, shellac-like mass.

Action with Other Halides

In the preparation of addition products with $TiCl_4$, $SbCl_5$, and $FeCl_3$ benzene cannot be used as a solvent because it reacts with the halides. Pure anhydrous carbon tetrachloride or chloroform was therefore used as the rubber solvent. The addition products of $SbCl_5$ and $FeCl_3$ with rubber are insoluble and precipitate out within a few minutes after the reagents have been added. $TiCl_4$ behaves like $SnCl_4$, giving both the soluble and insoluble polymers of rubber. However, $FeCl_3$ and $SbCl_5$ give only insoluble polymers.

WITH $FeCl_3$—Ten grams of anhydrous, resublimed $FeCl_3$ were thoroughly shaken with 200 cc. of ordinary chloroform

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[9] *J. Am. Chem. Soc.*, **21**, 1084 (1899); Fisher, Gray, and Merling, THIS JOURNAL, **13**, 1031 (1921); Lewis and McAdams, *Ibid.*, **12**, 573 (1920).

[10] *Ibid.*, **19**, 531 (1927).

(containing 1 per cent alcohol) and the solution filtered; 35 cc. of this solution were added to 100 cc. of a 2 per cent solution of purified two-phase rubber in carbon tetrachloride or chloroform and the mixture was shaken. The solution gradually became darker and in about 5 minutes deposited a brownish jelly. This mixture when placed in 150 cc. of 95 per cent alcohol turned white as the $FeCl_3$ split off, and deposited a fibrous, crumbly material. The product was broken up and washed with alcohol until the washings were no longer yellow and then extracted in a Soxhlet, first with alcohol, and then ether. The final product was a white, crumbly powder insoluble in all reagents. The yield was quantitative.

Analysis: 0.1050 gram substance: 0.1124 gram H_2O and 0.3365 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash
Calcd.:	88.15	11.85	
Found:	87.42	12.00	0.26

Diffusion rubber behaved in the same way. $SbCl_5$ gave a similar product.

Reactions with Isoprene, Polymerized Isoprene, and Balata

Isoprene—Twenty-five cubic centimeters of pure isoprene (b. p. 33–34° C.) prepared by cracking dipentene *in vacuo*[11] were mixed with 25 cc. of pure dry benzene under nitrogen in a flask fitted with reflux. A solution of 4.6 cc. of anhydrous $SnCl_4$ in 10 cc. of benzene was then slowly added through a dropping funnel. In about 5 minutes the solution turned yellow and began to evolve heat. The reaction was allowed to continue for about 1 hour, during which time the solution reached 50° C. and became deep brown. It was filtered from a small amount of insoluble matter through a cotton plug and precipitated with 300 cc. of 95 per cent alcohol. A flocculent white precipitate first separated, which immediately coagulated to a glistening rubber-like mass. The supernatant liquid was poured off, and the mass washed with alcohol. It was reprecipitated three times from benzene solution with alcohol, followed by precipitation with alcohol from solution in ether. The product was dried *in vacuo* (1 mm.) at 85° C. During the drying the rubbery mass swelled to a spongy solid which, when completely dried, could be powdered. It formed a snow-white powder which oxidized very rapidly in the air with formation of a yellow color.

Analysis: 0.1008 gram substance: 0.1048 gram H_2O and 0.3218 gram CO

$(C_5H_8)_x$	% C	% H
Calcd.:	88.15	11.85
Found:	87.06	11.65

The polymer is very soluble in ether and in the usual rubber solvents, in all of which it gives non-viscous solutions. It is insoluble in alcohol or acetone. The compound softens at 110° C., becomes pasty at 120° C., and melts with decomposition above 135° C. It therefore differs from the soluble polymer obtained from natural rubber at room temperature.

Polymerized Isoprene—Isoprene was polymerized by heating in a sealed tube for 7 months at 50° C. The rubber-like mass was treated in benzene solution at room temperature with $SnCl_4$ and alcohol as described under (A). It gave a red addition product which, after splitting with alcohol, formed a fine, white powder that was completely soluble in benzene at 0° C. This polymer softened at 175–180° C. The product was not entirely oxygen-free.

Analysis: 0.1060 gram substance: 0.1052 gram H_2O and 0.3287 gram CO_2

$(C_5H_8)_x$	% C	% H
Calcd.:	88.15	11.85
Found:	84.57	11.12

Balata—Balata which had been purified by freezing out from gasoline solution followed by acetone extraction reacted similarly at room temperature with $SnCl_4$, giving a white powder completely soluble in cold benzene. There was no indication of a second hydrocarbon phase. The polymer softens at 200° C. and melts with decomposition at 250° C.

Analysis: 0.1004 gram substance: 0.1040 gram H_2O and 0.3209 gram CO_2

$(C_5H_8)_x$	% C	% H	% Ash
Calcd.:	88.15	11.85	
Found:	87.17	11.61	0.12

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[11] Staudinger and Klener, *Ber.*, **44**, 2215 (1911).

Some Accelerator Characteristics as Revealed by Coefficients of Vulcanization[1]

By A. F. Hardman and Frank L. White

Kelly-Springfield Tire Company, Cumberland, Md.

When a simple unaccelerated mixture of rubber and sulfur is vulcanized at constant temperature, the combination of sulfur proceeds at a uniform rate to a point where the sulfur approaches exhaustion. Where organic accelerators are used, the rate of combination usually decreases as the cure proceeds, in some cases becoming almost zero. Various accelerators were examined in respect to this property of persistence during cure and some significant differences are pointed out.

In the earlier days of rubber chemistry the coefficient of vulcanization—that is, the percentage of chemically combined sulfur calculated to 100 parts rubber hydrocarbon—was considered an index of considerable importance in determining the state of cure. Furthermore, various investigators[2] established the fact that in the ordinary types of soft rubber mixtures vulcanized at constant temperature for different periods of time the coefficients of vulcanization are directly proportional to the time of heating up to a point where the free sulfur approaches exhaustion.

With the advent of organic accelerators it was early realized that the old idea that correctly vulcanized rubber should have a coefficient of 3 to 5 was no longer true. It was further discovered that different accelerators, even when used in proportions that would give equivalent physical cures under the same condition of vulcanization, did not produce the same coefficients of sulfur combination.[3] In fact, variations were so wide that the coefficient of vulcanization as an index of cure has been generally discarded.

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[1] Presented before the Division of Rubber Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Whitby, "Plantation Rubber and Testing of Rubber," p. 313, Longmans, Green & Co., London.

[3] Shepherd and Krall, This Journal, **14**, 951 (1922).

A few observers[4] have mentioned the fact that when certain accelerators are used the vulcanization coefficients of a series of cures plotted against the time of cure fall, not on a straight line, but on a curve concave to the time axis. An especially notable example of this change of direction of the combined-sulfur curve, as affected by the metallic xanthates, is shown by Twiss and Thomas.[5] They point out that, when curing at low temperatures with such accelerators in the presence of zinc oxide, the active curing period during which sulfur is combining with the rubber hydrocarbon is extremely short and the rate of reaction decreases rapidly almost to zero as measured by the combined sulfur of the cured rubber. They explain this phenomenon by assuming that the accelerator is involved in two distinct reactions: (1) that in which the sulfur is activated and caused to combine with the rubber, and (2) a decomposition and loss of accelerating potency brought about by the heat.

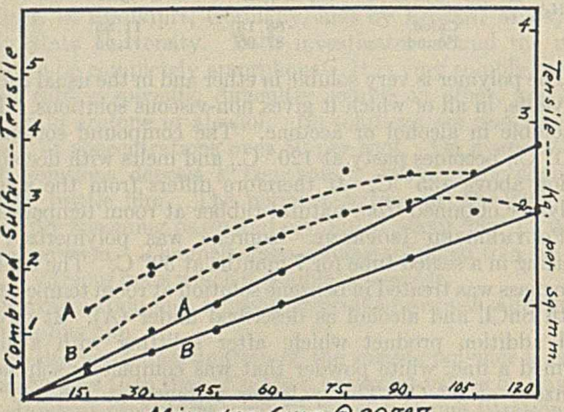

Figure 1. A—Hexamethylenetetramine, 0.8 Part; B—Triphenylguanidine, 1.5 Parts per 100 Rubber

The second influence is so marked, even at very moderate curing temperatures such as 5 or 10 pounds steam pressure, that relatively large amounts of these accelerators are necessary to produce a full cure before their effect is nullified by thermal decomposition. At higher temperatures the rate of decomposition becomes so rapid that the accelerating effect is almost entirely lost. Whitby and Simmons[6] illustrate what they term "transient catalysis" by sulfur curves obtained with di-α-thionaphthoyl disulfide as accelerator, and observe that it is their experience that all ultra-accelerators in the classes of disubstituted dithiocarbamates or corresponding thiuram sulfides, or salts of the dithiocarboxylic acids and the corresponding dithioacyl disulfides, are active but for a limited time during the cure. While the ultra type affords the most striking example of what have been termed "fugitive" or "transient" accelerators, nearly all organic accelerators exhibit this property to a greater or less extent and since the number of accelerators now available is rather large and so little has been published in regard to their "persistent" or "transient" qualities during the cure, it was thought that a series of comparisons of these properties of several of the commonly used accelerators would be of interest and practical value to the rubber compounder.

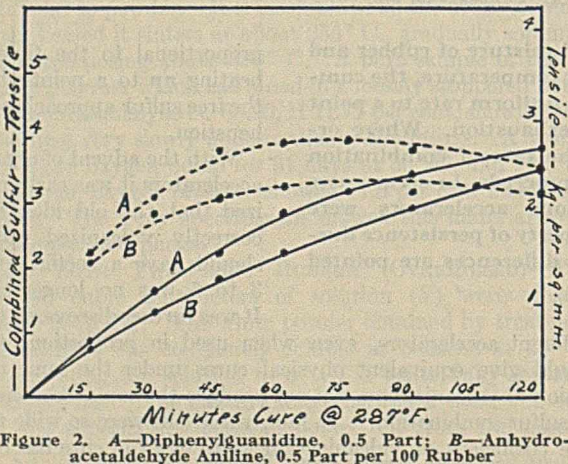

Figure 2. A—Diphenylguanidine, 0.5 Part; B—Anhydroacetaldehyde Aniline, 0.5 Part per 100 Rubber

(*Note:* Curve B represents the mean results obtained with four different samples of hard, resinous products obtained from three different manufacturers.)

Experimental Method

The simple formula—rubber 100, sulfur 5, and zinc oxide 5 parts—was used as the base, to which was added such an amount of each accelerator as would give fairly equivalent cures and would show a tensile maximum within the curing range selected. Blended smoked sheet was the rubber used. Slabs about 1/8 inch (3 mm.) thick were cured in the steam-heated platen press, usually at intervals of 15 minutes to 2 hours. The physical properties were determined on a Scott testing machine, two or more test pieces being broken from each slab and the best value taken as the tensile strength. The combined sulfurs were determined by difference. Samples were extracted overnight and the free sulfur was oxidized with bromine and determined as barium sulfate in the usual way. By deducting the values obtained from the total sulfur added to the compound, the figures for combined sulfur were obtained.

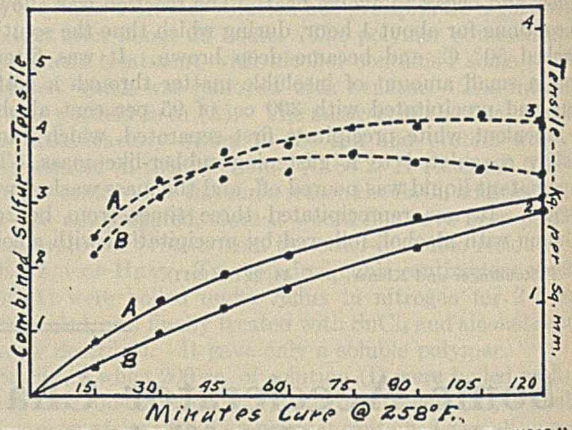

Figure 3. A—Mercaptobenzothiazole, 0.5 Part; B—"808," 0.5 Part per 100 Rubber

The method is subject to certain errors, in that no allowance is made for the small amounts of sulfur that may combine with the zinc or materials other than the rubber hydrocarbon, nor for the sulfur which is a constituent part of certain of the accelerators themselves; but since the chief interest in this investigation is the shape of the sulfur curve relative to the time axis, and not the degree of sulfur combination at any particular cure, the method selected is quite accurate enough to give consistent comparative values.

Results

Twelve different accelerators, most of them well known, were examined in the manner described. The results are graphically represented in Figures 1 to 5, where both the combined sulfur (continuous lines) and the tensile at break (dotted lines) are plotted against the time of cure. In the case of the tensile curves each unit of the scale on the left represents

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[4] Whitby, *Op. cit.*, p. 315.

[5] *J. Soc. Chem. Ind.*, **42**, 499T (1923).

[6] This Journal, **17**, 931 (1925).

1000 pounds per square inch, while the corresponding values in kilograms per square millimeter are shown on the right. All other physical tests, such as elongation at break and load at certain fixed elongation, have been omitted in order to avoid tedious and space-consuming tables. It should be mentioned that, when mixing the compounds containing as accelerators the lead and zinc salts of dithiofuroic acid, 0.5 per cent cottonseed oil was added to each batch to promote accelerator dispersions. The accelerator and oil were mixed together to form a paste before being added to the rubber batch. Without such treatment these accelerators have a tendency to stick on the rolls of the mill and form lumps which cannot subsequently be broken up and therefore cause spotting when the mix is cured.

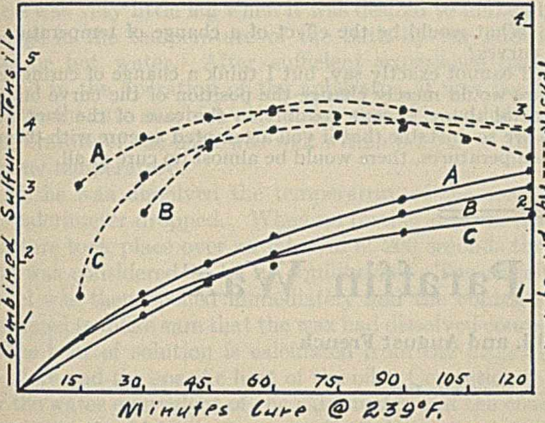

Figure 4. *A*—Zinc Diethyl Dithiocarbamate, 0.2 Part; *B*—Tetramethylthiurammonosulfide, 0.125 Part; *C*—Tetramethylthiuramdisulfide, 0.125 Part per 100 Rubber

Discussion

The twelve accelerators examined fall broadly into three classes. One class, represented by hexamethylenetetramine, triphenylguanidine, and "808," consists of persistent accelerators, the sulfur curve for which is a straight line from beginning to end. Another class, represented by lead and zinc dithiofuroate and zinc ethylxanthate, consists of highly transient accelerators, the sulfur curve for which rapidly becomes parallel to the time axis. The accelerators in this class exert their full effect during the first 15 or 30 minutes of vulcanization, and thereafter become inert. Intermediate between these two classes is a class, represented by the remaining accelerators, which may be called semipersistent, and which give a sulfur curve concave to the time axis.

The tensile curve for the stock containing hexa (Figure 1) is represented only as far as the 105 minutes' cure, since with this particular mixture the rubber became brittle during the last 15 minutes of cure and its tensile strength fell off almost to zero. Other investigators[7] have reported somewhat similar results with this accelerator, so this tendency to an abrupt overcure may be considered characteristic of hexa and probably of any fairly powerful persistent accelerator. Triphenylguanidine, although also a persistent accelerator, is much slower than hexa, and in consequence no sudden break was reached in the tensile curve during the curing period.

The sulfur curve for the accelerator known commercially as "808" (Figure 3), although not quite a straight line, is sufficiently close to one to justify the classification of the accelerator as persistent. It appears that the stability of this accelerator at 20 pounds steam pressure approaches that of hexa at 40 pounds.

The curing power of the semipersistent accelerators falls off, but does not disappear with increasing period of vulcanization. The falling off with diphenylguanidine (Figure 2) is relatively uniform, the sulfur curve being a fairly regular arc; but with the other semipersistent accelerators it is more rapid during the earlier than the later part of the curing period, the sulfur curves showing a deflection in the early part.

The sulfur curve for tetramethylthiurammonosulfide (Figure 4) is less concave than that for the corresponding disulfide. The corresponding zinc dithiocarbamate shows about the same initial rate of cure as the disulfide, but does not fall off at the same rate as the latter.

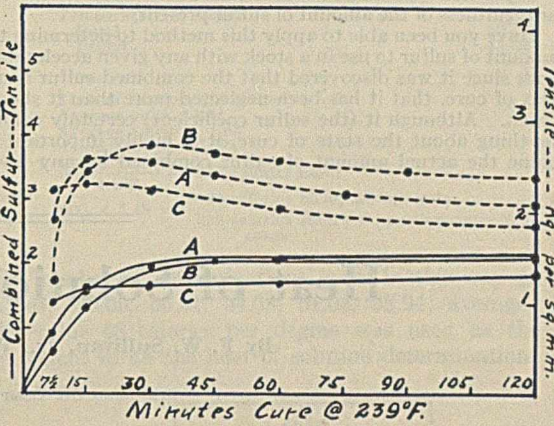

Figure 5. *A*—Zinc Dithiofuroate, 0.2 Part; *B*—Lead Dithiofuroate, 0.3 Part; *C*—Zinc Ethylxanthate, 2.5 Parts per 100 Rubber

The lead salt of dithiofuroic acid (Figure 5) is a little slower at the beginning of the cure than the zinc salt. The extreme case of transient acceleration is found in zinc ethylxanthate. The instability of this accelerator is so much greater even than that of the salts of dithiofuroic acid that more than ten times as much xanthate is required as of the latter to produce equivalent cures.

Conclusion

No attempt has been made to evolve a theory to explain the different behavior of these various accelerators, since each one seems to be a case of its own. But it is evident that both the stability of the accelerator itself towards heat and towards the other vulcanizing agents and the nature of the decomposition products formed are the factors which determine the shape of the sulfur curve. In other words, an accelerator that is quickly decomposed, whether by heat or by reaction with sulfur, etc., into inert decomposition products will give sulfur curves which are typified by the xanthates or salts of the dithiocarboxylic acids. On the other hand, with an accelerator which is extremely resistant to the disintegrating influences during vulcanization or one in which the various decomposition products continue to exert a curing action equivalent to that of the original substance, there would be produced the persistent, straight-line cure as shown by hexa and triphenylguanidine, and between these two extremes the majority of the now commonly used accelerators may be placed, all of which indicate by their sulfur curves progressive changes in curing effect during the course of vulcanization.

It is believed that a study of these changes as revealed by sulfur coefficients will prove an aid to the compounder in choosing the accelerator best suited to any particular article of rubber manufacture.

General Discussion

Q. What happens to the accelerator in these straight-line cures? I assume the reason the sulfur curves become straight is that the accelerator changes in such a way that it will no longer function when a proper cure is reached.

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[7] Trickey and Leuck, This Journal, **18**, 812 (1926).

A. It is assumed that the accelerator decomposes into inactive products. What they are I am unable to say.

Q. Was any work done on combinations of accelerators along that line?

A. Not in this particular investigation.

Q. For a stock to be non-blooming with one of these accelerators, would the accelerator disappear during the cure?

A. To make non-blooming stocks the sulfur would have to be kept very low so that the free-sulfur ratio would not be more than about 1 per cent on the rubber. The accelerator would disappear regardless of the amount of sulfur present.

Q. Have you been able to apply this method to determine the best amount of sulfur to use in a stock with any given accelerator? It seems, since it was discovered that the combined sulfur is not an index of cure, that it has been neglected more than it should have been. Although it (the sulfur coefficient) certainly cannot tell anything about the state of cure, it is highly important to determine the actual amount of sulfur combined by any given accelerator. This paper seems to be valuable in its suggestiveness of what may be developed along these lines.

Q. Is it not possible that the flattening of the curves is due to the mass action of the sulfur rather than to the decompositions of the accelerator?

A. No, it has been established by a number of investigators that mass action does not seem to enter into it at all until the free sulfur is almost gone. It would make little difference whether the sulfur content were 5 or 10 per cent, the accelerator of this fugitive type would combine just about the same amount of sulfur.

Q. What would be the effect of a change of temperature on these curves?

A. I cannot exactly say, but I think a change of curing temperature would merely change the position of the curve but not its general shape, except possibly in the case of the xanthates, which are so unstable that if you attempted to cure with them at high temperatures, there would be almost no cure at all.

Heat of Solution of Paraffin Wax[1]

By F. W. Sullivan, Jr., W. J. McGill, and August French

Standard Oil Company (Indiana), Whiting, Ind.

IN CALCULATIONS concerning refrigeration requirements for the chilling of wax bearing distillates, 63.27 B. t. u. per pound is commonly used as the heat of solution of the wax. This figure seems to have been taken from the 1894 edition of Landolt-Börnstein's "Tabellen."[2] Graefe[3] gives a value of 70.2 B. t. u. per pound; Batelli,[4] 63.0 B. t. u. per pound; Kozicki and Pilat,[5] 70 B. t. u. per pound for 126° F. (52.2° C.) melting point paraffin wax and 78.9 B. t. u. per pound for 149.6° F. (65.3° C.) melting point wax.

In making heat balances for refrigerating operations on wax distillate, discrepancies have been found which it was thought might be due to the use of this commonly accepted figure of 63.27 B. t. u. per pound. The heat of crystallization of the wax found in the wax distillate cut from midcontinent crude was consequently determined and found to be 72.5 B. t. u. per pound.

Apparatus

An adiabatic calorimeter was used in this work (Figure 1). The inner vessel, *a*, consisted of an old 1-quart, wide-mouth vacuum bottle, the vacuum of which had been broken. It was left mounted in its original jacket. It was fitted with a thermometer, *t*, graduated in 0.2° C., a heating coil, *c*, of No. 24 nichrome resistance wire, a 1/2-inch (13-mm.) opening, *o*, fitted with a glass tube for introducing the wax, and a stirrer, *s*. The stirrer was of the reciprocating type consisting of two flat rings, *r*, mounted on two upright wires and spaced above each other 2 inches apart. These rings were of sheet copper of about 2 inches outside diameter and 1 inch inside diameter and had 1/4-inch (6-mm.) holes drilled about 1/2 inch (13 mm.) apart midway between the two edges. The ends of the upright wires were sealed into narrow glass tubing with cement. The glass tubing passed through brass sleeves in the cork covering the inner vessel. The stirrer was driven by a string which passed over a pulley, *p*, actuated by a crank attached to a reducing gear driven by an electric motor.

This stirrer mixed the contents of the calorimeter very thoroughly. The amount of heat developed thereby was negligible in these experiments. In 45 minutes of stirring at room temperature in a vacuum bottle the temperature of the oil was raised only 0.1° C.

The water bath was kept at a constant level by means of tube, *e*, attached to a suction line. The bath was adjusted to any desired temperature by running in water from the hot-water line, *h*, or the cold-water line, *f*.

The heating coil was operated by current from a 24-volt storage battery. The current consumed was measured by means of a voltmeter and ammeter which were read at 50-second intervals.

Materials

The oils were pressed distillate from midcontinent crude and a wax-free gas oil. With the latter it was possible to work close to room temperature because of its greater solvent effect for the wax.

The wax was obtained by recrystallization of a slack wax until it was practically oil-free. This wax was ground in a food chopper into particles less than 1/8 inch (3 mm.) in diameter. These were formed into the shape of an easily crumbled rod by plunging a cork-borer into a pile of the wax particles several times and then ejecting the wax from the cork-borer with one of the next smaller size. These rods disintegrated readily upon being introduced into the oil so that the wax dissolved completely in a short time.

Procedure

Four hundred grams of the oil were weighed out into the calorimeter. The motor driving the stirrer was started and the speed was adjusted by means of the regulator until the stirrer made 60 cycles per minute. The oil was brought to the desired temperature by means of the electric heating coil. Some of the first experiments were done at higher temperatures, but the later ones were done close to room temperature to reduce any possible errors due to radiation losses. When the desired temperature was reached the current was shut off and the stirring continued. Meanwhile the temperature of the water bath was adjusted by adding either hot or cold water until it was exactly the same as the temperature of the calorimeter proper. When no increase or decrease in the temperature of the calorimeter

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[1] Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Day, Handbook of the Petroleum Industry, Vol. II, p. 823, John Wiley & Sons, Inc., 1922.

[3] "Laboratoriumsbuch für Braunkohlenteerindustrie."

[4] *Physik. Z.*, **9**, 671 (1908).

[5] *Petroleum*, **14**, 12 (1918).

was observed for 5 minutes the wax was added as rapidly as possible through the tube. The temperature of the wax had been noted at this time.

Readings were taken on both the calorimeter and bath temperatures at intervals of 50 seconds. The bath temperature was adjusted so that at all times it was exactly the same as the calorimeter temperature. The air current used for stirring was sufficient to mix the water thoroughly, so that there was very little lag when it was desired to make a quick change in the temperature of the bath by the addition of cold or hot water. After sufficient experience had been gained in the operation of the apparatus, it was possible so to gage the rate at which cold water should be added that the temperature of the bath was well within 0.2° C. of the calorimeter temperature.

As the wax dissolved the temperature of the contents of the calorimeter dropped. When no further drop in the temperature took place over an interval of 200 seconds the solution was considered to be at equilibrium. The calorimeter vessel was then opened immediately and the contents were examined to make sure that the wax had dissolved completely.

The heat of solution is calculated from the drop in temperature and the specific heat of the oil. Correction is made for the water equivalent of the calorimeter and the change in temperature which the wax itself undergoes.

Calculations for One Determination

Gas oil: 400 grams; specific heat, 0.386
Wax: 20 grams; melting point, 125° F. (51.7° C.); specific heat, 0.6

TEMPERATURES	° C.
Room	28.3
Oil in calorimeter:	
Initial	30.48
Final	26.95
Drop	3.53
Wax:	
Initial	28.30
Final	26.95
Drop	1.35
	Calories
Heat given up by oil: 400 × 0.386 × 3.53 =	545.0
Heat given up by wax: 20 × 0.6 × 1.35 =	16.2
Water equivalent of calorimeter: 58 × 3.53 =	204.7
Total heat absorbed when 20 grams of wax dissolved	765.9

Note—The value for the specific heat of solid paraffin wax was taken as 0.6. This value was obtained by averaging the few values given in the Landolt-Börnstein "Tabellen" and was considered to be close enough in these determinations, since the temperature changes in the wax involved a relatively small amount of heat.

The heat of solution is therefore 765.9 ÷ 20 = 38.3 calories per gram.

Determination of Water Equivalent

Four hundred grams of water were put into the inner vessel and heated by means of the heating coil to a temperature approximating the final temperatures obtained in the heat of solution experiments. The temperature of the water bath was adjusted to that of the calorimeter and the stirring was continued until there was no change in the calorimeter temperature over a period of 200 seconds. The current in the heating coil was then turned on and a stop watch was started simultaneously. Readings of the voltage and amperage on the coil, as well as the calorimeter and bath temperatures, were taken at 50-second intervals. The bath temperature was adjusted to that of the calorimeter by running hot water into it. The heating was continued over a temperature range corresponding to the drop in temperature in the heat of solution determinations. When the desired temperature was reached the current was shut off and the stirring was continued until no further rise in temperature was observed. The voltage and amperage were averaged over the time that the current was on and the product of these averages gave the average wattage over the period. The input in calories was calculated from the formula:

$$\frac{\text{Time in seconds} \times \text{watts}}{4.182} = \text{calories}$$

The water equivalent is 323 ÷ 5.48 = 58.9 calories per degree.

Calculations for One Determination

	° C.
Temperature of water:	
Final	50.74
Initial	45.26
Increase	5.48

Time of heating, 450 seconds
Average volts, 14.34
Average amperes, 1.63
Average watts, 23.37

$$\frac{450 \times 23.37}{4.182} = 2515 \text{ calories input}$$

$$400 \times 5.48 = \frac{2192 \text{ calories absorbed by water}}{323 \text{ calories absorbed by calorimeter over } 5.48° \text{ C. range}}$$

A number of determinations made in this way gave the values: 59.05, 56.31, 54.38, 61.08, 58.94; average, 57.95. The value 58 calories per degree was used as the water equivalent in all the heat of solution determinations.

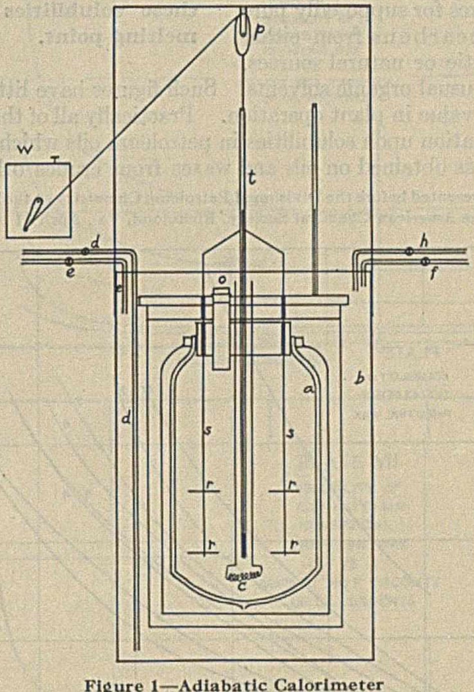


Figure 1—Adiabatic Calorimeter

Specific Heats of the Solvent Oils

The specific heats of the oils used were determined in the same way that the water equivalent was determined.

Heat of Solution of 125° F. (51.7° C.) M. P. Paraffin Wax

EXPT.	OIL	SPECIFIC HEAT OF OIL	TEMPERATURE Initial	TEMPERATURE Final	TEMPERATURE Room	HEAT OF SOLUTION	
			° C.	° C.	° C.	*Cal./g.*	*B.t.u./lb.*
1	Pressed distillate	0.438	50.27	48.15	23.3	40.6	73.2
2	Pressed distillate	0.438	51.80	47.32	26.0	39.5	71.0
3	Pressed distillate	0.438	51.08	46.65	25.6	39.0	70.2
4	Pressed distillate	0.438	49.79	45.16	25.6	42.2	75.9
5	Gas Oil	0.386	35.30	31.10	26.1	41.6	74.9
6	Gas Oil	0.386	30.48		28.3	38.3	68.9
7	Gas Oil	0.386	31.28		25.0	40.7	73.2
					Average	40.3	72.5

The Universal Oil Products Company announces that the British American Oil Refineries, Limited, will install immediately a 1000-barrel Dubbs Cracking Unit at their refinery at Toronto.

Solubility of Paraffin Wax in Oil[1]

By F. W. Sullivan, Jr., W. J. McGill, and August French

Standard Oil Company (Indiana), Whiting, Ind.

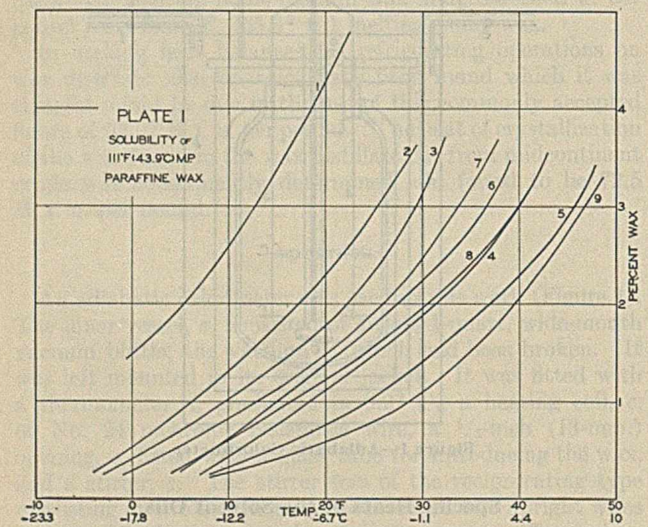
Paraffin waxes of 111° F., (43.9° C.), 125° F. (51.7° C.), and 145° F. (63.8° C.) Saybolt melting points and containing relatively few individual hydrocarbons have been obtained by the repeated fractionation of 125° F. (51.7° C.) Saybolt melting point commercial paraffin wax from midcontinent crude. The solubilities of these fractionated waxes and of the 125° F. (51.7° C.) melting point commercial wax itself have been determined in petroleum ether (boiling point 21.0° to 82.0° C.) and in a number of midcontinent petroleum oils of varying viscosities. Some of the oils represent narrow cuts from a fractional vacuum distillation; others are blends of oils of widely separated viscosities. Solubilities were determined at various concentrations and curves were constructed showing the variation of these solubilities with temperature, viscosity, and melting point.

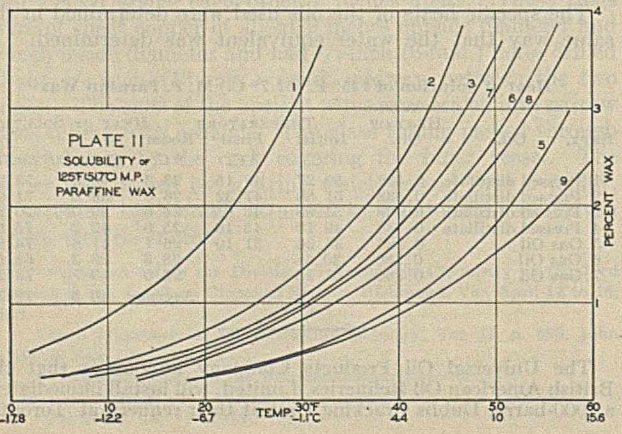
A KNOWLEDGE of the solubilities of paraffin wax in petroleum oils at various temperatures, and of the effect of viscosity of solvent and the melting point of the wax upon solubility, is of considerable practical value in filter-pressing wax distillates to remove the wax. It is also useful in making calculations involving the refrigeration of wax-bearing oils. Solubility data in the literature consist principally of figures for supposedly pure hydrocarbons from either synthetic or natural sources, in the usual organic solvents. Such figures have little or no direct value in plant operation. Practically all of the meager information upon solubilities in petroleum oils which is available was obtained on oils and waxes from crudes other than midcontinent, and hence its value is doubtful for calculations involving this crude.

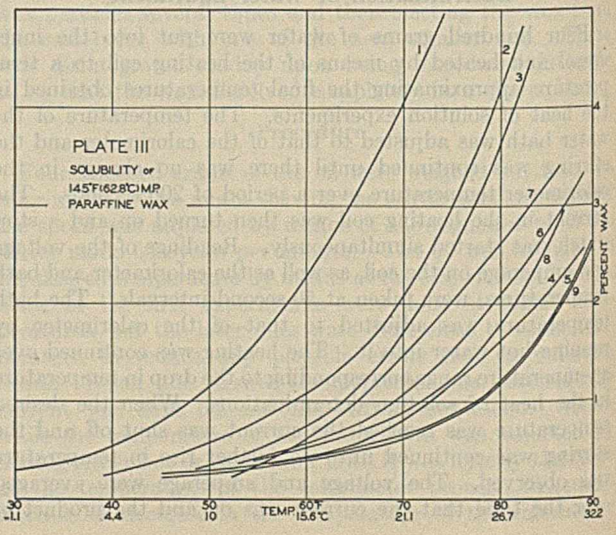
Preparation of Waxes

The waxes used in these experiments were fractions from the vacuum distillation of 50 liters of 125° F. (51.7° C.) melting point wax obtained from the wax refinery. This wax had been sweated from intermediates, and consequently did not contain the highest melting waxes separated in pressing.

For the fractional distillation of the wax, a still of 10 liters capacity was made. The body of the still consisted of a 9-inch (23-cm.) length of 10-inch (25-cm.) pipe with plates welded at either end and appropriate openings for charging and draining. The fractionating column was a 2$^1/_2$-inch (6-cm.) pipe 18 inches (46 cm.) long, filled with plates of $^3/_8$-inch (1-cm.) mesh wire screen spot-welded at 2-inch (5-cm.) intervals on a thin rod running through the center of the tower. An iron pipe $^1/_2$ inch (1.3 cm.) in diameter and 30 inches (76 cm.) long served as an air condenser. The receiving system consisted of a 500-cc. balloon flask with a stopcock outlet. Two Cenco oil pumps were used to maintain the vacuum at 5 mm. When all the fittings had been carefully tightened after the threads had been painted with graphite paste, a 5-mm. vacuum was readily maintained under operating conditions. In fact, one pump was at times sufficient. From one to four Meker burners supplied the heat. The tower was wound with electrical resistance wire. It was found convenient to heat the tower at the beginning of the run, both to save time and to break any foaming caused at the beginning of the distillation by the evolution of gas and moisture from the wax on the application of heat and vacuum. After the distillation had once started







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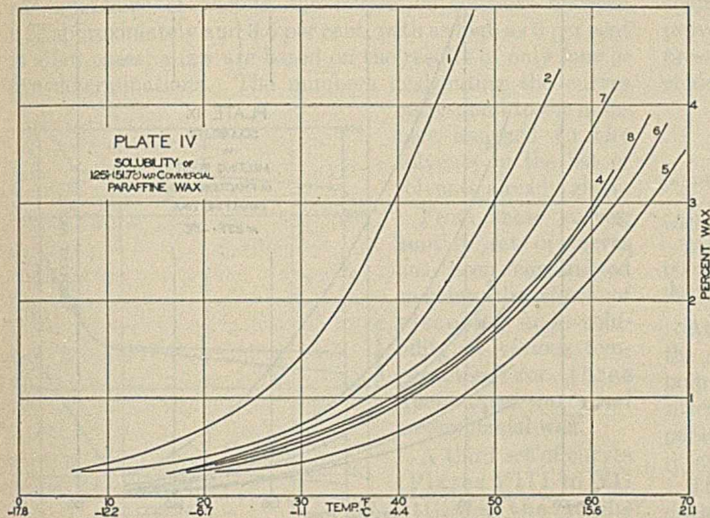
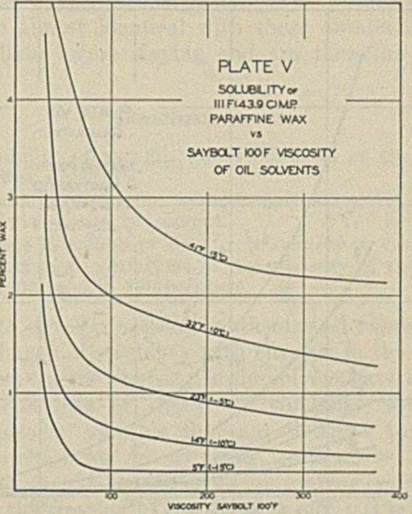
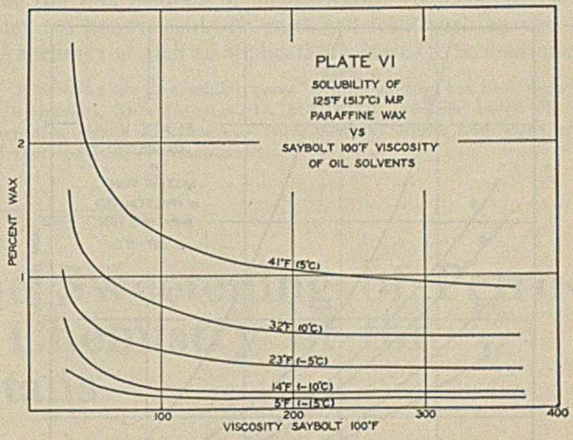
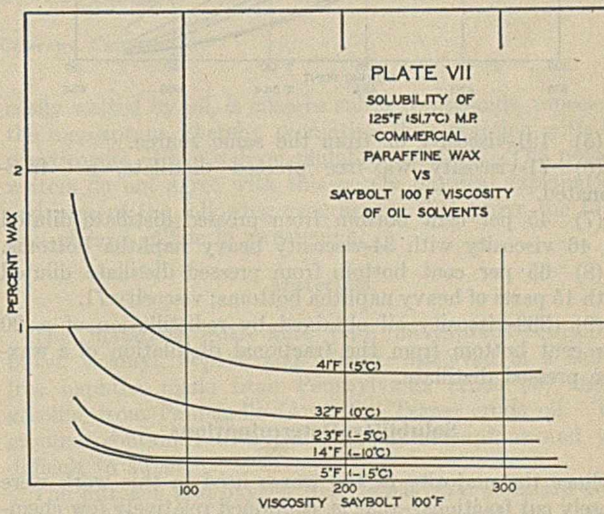
[1] Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.









all heating of the tower was found to be unnecessary and was therefore discontinued.

Five such distillations of 10-liter charges of 125° F. (51.7° C.) melting point refined wax were made. In general, the melting points of like cuts checked each other fairly well.

The 0–10 per cent and 10–20 per cent cuts from the five distillations were combined to give 10 liters of material to be distilled a second time. Likewise the 20–40 per cent cuts, the 40–60 per cent cuts, and 60–80 per cent cuts were combined to give 10 liters of material for the second fractionation. The 80–90 per cent cuts combined gave another 5 liters. Thus six more distillations were made. Ten per cent cuts were taken again. These cuts represented 2 per cent of the total amount of wax charged.

Since a fairly close cut wax was desired and since at about 125° F. (51.7° C.) melting point the melting points of the cuts were closer to each other than at the very beginning or at the end of the distillation, a selection of cuts was made from the second fractionation and these were distilled in a 5-liter vacuum still. From these cuts an amount of quite pure 125° F. (51.7° C.) melting point wax was prepared.

A sample of 111° F. (43.9° C.) melting point wax was made by a recrystallization of twice-distilled low melting point cuts from ethylmethyl ketone. A sample of 145° F. (62.8° C.) melting point wax was selected from the higher melting fractions of the second fractionation.

The boiling point range of these fractionated waxes was 5° C. at 5 mm. pressure. Their cooling curves are compared in Plate XII with the cooling curve for the sample of 125° F. (51.7° C.) melting point commercial wax whose solubility was also determined.

Solvents

To study the solubilities of these various waxes it was necessary to obtain oils that were practically free from paraffin wax. It was also desirable to use as solvents oils in which the wax occurs in the plant. The best source for such oils seemed to be a wax-free pressed distillate. Since the ordinary pressed distillate with a chill of 20° F. (−6.67° C). contains an appreciable amount of wax, a quantity of it was repressed to a cold test of −20° F. (−28.89° C.). Ten liters of this oil were charged to the still and distilled at 5 mm. pressure, taking 10 per cent cuts. It was from these cuts that the fractionated oils used in the solubility determinations were obtained. These fractions were clear and fluid at 0° F. (−17.78° C.) and hence were considered to be wax-free. A blend corresponding to a 15 per cent bottom from this distillation had a viscosity of 420 Saybolt seconds at 100° F. (38° C.) and could not be improved in color by claying. It was accordingly redistilled to a small bottom and an oil of good color and 333 viscosity obtained.

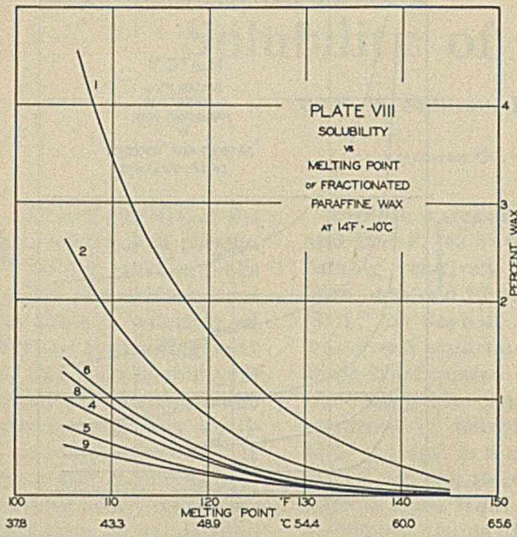
The following solvents were used:

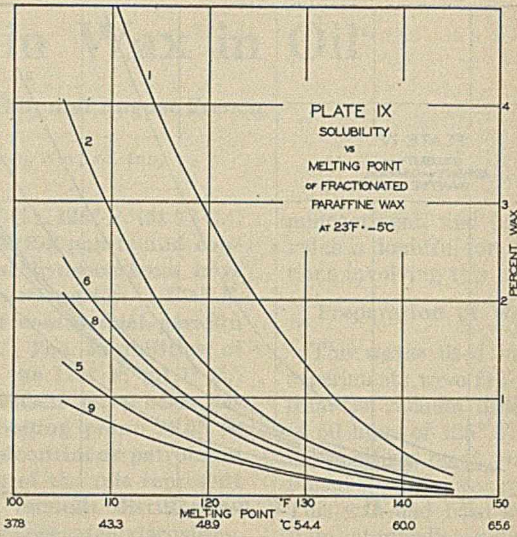
(1) Petroleum ether (b. p., 21.0° to 82.0° C.).

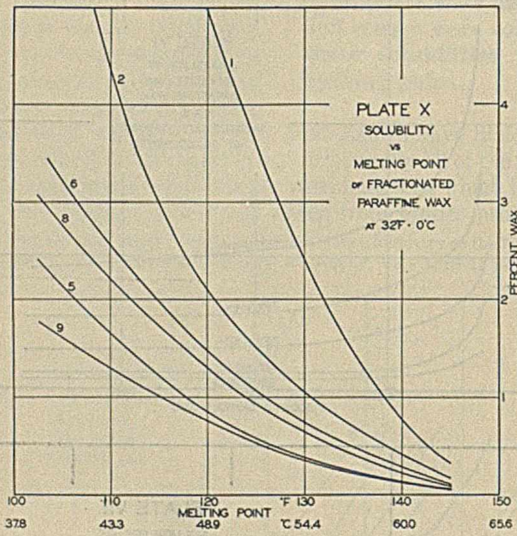
(2) 34-viscosity oil obtained as a bottom in rerunning heavy naphtha.

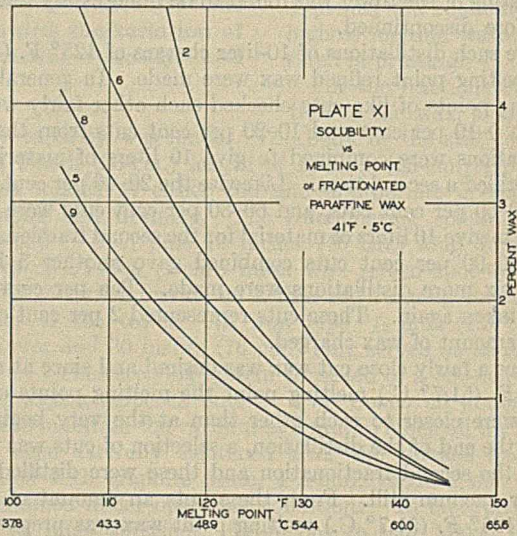
(3) 36-viscosity oil from fractional distillation of a wax-free pressed distillate.

(4) 75-viscosity oil from the same source.









(5) 191-viscosity oil from the same source.

(6) 71-viscosity wax-free pressed distillate, not fractionated.

(7) 45 per cent bottom from pressed distillate diluted to 46 viscosity with 34-viscosity heavy naphtha bottoms.

(8) 65 per cent bottom from pressed distillate diluted with 15 parts of heavy naphtha bottoms; viscosity 71.

(9) 333-viscosity oil obtained by redistillation of a 20 per cent bottom from the fractional distillation of a wax-free pressed distillate.

Solubility Determinations

Since the majority of the waxes used in this work were closely cut fractions—that is, contained relatively few chemical individuals—it was decided that the cloud temperature would indicate the point at which the wax in question saturated the solvent.

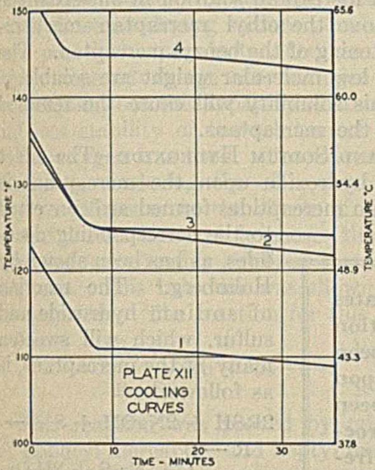
The apparatus used consisted of a 1 by 6-inch (2.5 by 15-cm.) test tube fitted with a chill-test thermometer and a stirrer made of thin glass with a ring at the end. Stirring was effected by a Cenco electric motor geared to produce an up-and-down motion of the glass rod. The wax solution was cooled by immersing the test tube in a beaker of water for cloud points at higher temperatures and by immersing in an ice and salt bath, protecting the glass tube by a metal jacket for cloud points at lower temperatures. For some of the very low cloud points brine at −25° F. (−31.67° C.) was used as the cooling medium.

Twenty-five cubic centimeters of the oil were measured out into the test tubes and the required amount of wax was weighed out into them. The oil was then warmed and stirred until all of the wax was dissolved. The tube was then put into the cooling bath and stirred until the first sign of cloudiness appeared. At this point the temperature was read. In general, the results could be duplicated within less than 1° F. (0.56° C.). The cloud point was more difficult to determine at the lower temperatures, particularly in the case of viscous oils, in the sense that it was not so definite.

Since the primary purpose of the work was to investigate solubilities over a range of pressing temperatures, the cloud points of the maximum concentrations of the solution used were in general below 75° F. (23.89° C.).

Solubility Curves

The curves shown in Plate I were constructed from the data obtained from determinations of the cloud points of various concentrations of 111° F. (43.9° C.) melting point wax in the solvents listed. Plates II, III, and IV show similar curves for two fractionated waxes of higher melting points and a commercial paraffin wax. Most of these curves were based on solubility determinations at eight different concentrations of wax in the respective solvent—between 0.25 approximately and 3.5 per cent, with as high as 6 per cent in a few cases; a few are based on the results of only four or five determinations. The numbers designating the curves correspond to the numbers assigned to the solvents in the list of solvents already given.



From these curves, another set of curves has been constructed showing the effect of viscosity upon solubility at various temperatures, for three fractionated waxes and a commercial wax.

A third set of curves (Plates VIII to XI) utilizes the results shown in Plates I to IV to compare the effect of the melting point of the wax upon its solubility in the various solvents, at different temperatures.

A series of solubility determinations, using as solvent some of the 71-viscosity pressed distillate which had been decolorized with clay, was also made. The results of these proved to be almost identical with those obtained on the pressed distillate before claying and are therefore not included.

Conclusions

1—The solubility of paraffin waxes increases as the melting point of the wax decreases.

2—The solubility of paraffin waxes in petroleum oils decreases with increasing viscosity of solvent.

3—Differences in solubility due to differences in the melting point of the wax or to variations in the viscosity of the solvent decrease with decreasing temperature.

Attempts to develop a useful mathematical expression of the rate of change of solubility with changes in the melting point of the wax or the viscosity of the solvent have not been successful. The rate of change of solubility with temperature is also so variable that any attempt to express it approximately leads to erroneous conclusions.

The curves should be of value in making calculations dealing with the freezing of wax-bearing oils. It is possible that the wax content of an oil whose viscosity and cloud point are known could be predicted from such curves, but the accuracy of such an application remains to be determined.

Note—The use of a similar curve for this purpose has been described by Bjerregard, This Journal, **14,** 215 (1922). No one curve will give acceptable results for distillates from different crudes and made under different conditions of fractionation.

Role of Lead Sulfide in the Sweetening of Petroleum Distillates and Chemistry of the Mercaptans[1]

By J. C. Morrell and W. F. Faragher

Universal Oil Products Company, Chicago, Ill.

For years refiners have known that lead sulfide facilitates the sweetening of petroleum distillates. "Spent doctor" or plumbite sludges containing lead sulfide and sodium hydroxide have been regenerated by blowing with air, and although this operation has not been understood, its value in the reactivation of plumbite sludges has been appreciated. More recently it has been observed that air and lead sulfide are beneficial in the sweetening of refractory distillates. Although the practice of agitating lead sulfide sludges with air in the batch agitator is old, the refiner now introduces specially prepared lead sulfide into the sweetening mixture.

The reaction of sweetening is as follows:

$$2RSH + Na_2PbO_2 + S \longrightarrow \begin{array}{c} R-S \\ | \\ R-S \end{array} + 2NaOH + PbS$$

The action of lead sulfide in the sweetening of petroleum distillates has been generally characterized as catalytic, in the absence of an experimental basis of explanation. Wendt and Diggs[2] assigned to lead sulfide a catalytic action, but offered the explanation that, since the lead sulfide is easily wetted by oil, it adsorbs sulfur compounds, especially the mercaptans, thereby promoting their reaction with the constituents of the sodium plumbite solution. The present writers do not agree with this purely physical explanation, and present the following experiments that prove the function of lead sulfide in sweetening.

Materials

The materials used were pure mercaptans—ethyl, *n*-butyl, isoamyl, heptyl, and benzyl—dissolved in a sulfur-free naphtha made from Pennsylvania crude oil, and a gasoline from Panhandle (Amarillo, Texas) crude oil. The gasoline contained 0.05 per cent of mercaptans and was difficult to sweeten.

The nitrogen and oxygen were taken from standard commercial cylinders. Ozonized air was prepared by passing air through a laboratory ozonizer. The nitrogen contained 4 per cent of oxygen, and when necessary was purified by bubbling through alkaline pyrogallol.

The lead sulfide was obtained from several different sources. In the preparation of lead sulfide great care must be taken to avoid contact with air as it is readily oxidized to lead sulfate. Two samples dried in air showed an average of 22 per cent of lead sulfate. Hence the precipitated and washed lead sulfide was not dried except for special experiments.

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[1] Presented under the title "Role of Lead Sulfide in the Sweetening of Petroleum Distillates" before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] This Journal, **16,** 1114 (1924).

Refiners have long known that lead sulfide facilitates the sweetening of petroleum distillates. Regeneration of plumbite sludges by blowing with air has been adopted in practice. The beneficial effect of air upon refractory distillates treated with lead sulfide has been observed more recently. The chemistry of these processes that have proved useful has been obscure; frequent references to catalytic action are made. A systematic study of pure sulfur compounds and a refractory commercial gasoline with the reagents involved proves that the function of air is the oxidation of lead sulfide to lead sulfate and hence a formation in effect of the usual plumbite reagent. Sweetening consists of two processes—the formation of lead sulfide from hydrogen sulfide and lead mercaptides from mercaptans and the removal from the distillate of the lead mercaptides. The action of other heavy metal sulfides has also been investigated. The reaction of the conversion of mercaptides to disulfides has been shown to be the same for all the metals studied.

Experimental Procedure

For the experiments in which gases were blown through the reaction mixture, a bubbler was inserted in the train of apparatus to control the rate of flow. The gases were then passed through a separatory funnel containing the reaction mixture and into a test tube containing a solution of sodium plumbite to indicate whether mercaptans were being carried from the mixture.

The naphtha solutions of the mercaptans were made from a refined Pennsylvania naphtha by adding approximately 0.10 per cent by weight of a mercaptan. In making an experiment 50 cc. of the naphtha solution of a mercaptan and 2.5 cc. of sodium hydroxide or plumbite solution containing approximately 10 per cent of sodium hydroxide were used. The quantities of sulfur and lead sulfide were 0.025 and 0.05 gram, respectively. Tests were made at regular intervals to determine whether or not the sample was sweet. The experiments were repeated when necessary, and in all cases were duplicated.

The procedure for the tests with the gasoline from Panhandle crude was similar, except that 250 cc. of gasoline were used. Before making a test the gasoline was washed free from hydrogen sulfide with 15 cc. of a 10 per cent solution of sodium hydroxide. The quantities of lead sulfide and sulfur were 0.225 and 0.120 gram, respectively. The experiments were duplicated in all cases.

A maximum reaction period of 40 minutes was allowed for the solutions of the pure mercaptans, and of 60 minutes for the gasoline.

The reactants were used in all possible combinations.

The results are summarized in Table I. Oxygen alone did not sweeten any of the pure mercaptans, and the addition of lead sulfide free from sodium hydroxide did not help. Oxygen and sodium hydroxide sweetened ethyl and benzyl mercaptans. Sulfur substituted for oxygen sweetened all the mercaptans but not the gasoline. Lead sulfide, oxygen, and sodium hydroxide sweetened all the mercaptans except isoamyl mercaptan, as did sodium plumbite; but the gasoline was not sweetened in either case.

The lead mercaptide was always formed when lead sulfide, oxygen, and sodium hydroxide were used. It settled immediately from ethyl and benzyl mercaptans, and upon standing overnight from N-butyl and heptyl mercaptans. The lead mercaptides did not settle from the isoamyl mercaptan or from the gasoline from Panhandle crude.

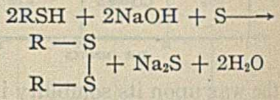
When lead sulfide, sodium hydroxide, oxygen, and sulfur were used, all the mercaptans were sweetened in less than 3 minutes, and the gasoline was sweetened in 10 minutes.

Discussion of Results

Oxygen Alone—Since oxygen alone did not sweeten any of the pure mercaptans, it is concluded that it does not oxidize the mercaptans under the conditions of the test. Ethyl mercaptan was evidently distilled from the solution, as indicated by the heavy precipitate of lead mercaptide in the test tube containing sodium plumbite. Nitrogen had the same effect.

The sodium mercaptides are more readily oxidized by oxygen than the corresponding mercaptans, as shown by the sweetening of the ethyl mercaptan solution in one-sixth the time necessary to remove the ethyl mercaptan mechanically, and by the sweetening of the benzyl mercaptan. The sodium mercaptides of low molecular weight are soluble in sodium hydroxide. This solubility will cause the removal of a small portion of the mercaptans.

Effect of Sulfur and Sodium Hydroxide—The effect of sulfur and sodium hydroxide upon the mercaptans is evidence that the sodium mercaptides formed are converted to the corresponding disulfides, as has been shown by Holmberg.[3] The reaction of sodium hydroxide and sulfur, which will sweeten many of the mercaptans, is as follows:



$$2RSH + 2NaOH + S \longrightarrow \begin{matrix}R-S\\ |\\ R-S\end{matrix} + Na_2S + 2H_2O$$

This reaction is a special case of the general reaction of mercaptides. Sodium mercaptide forms first, followed by the reaction between the mercaptide and sulfur.

Agitation of the mercaptan solution with sodium hydroxide and sulfur was effected by the use of nitrogen in order to avoid any possible side reactions. The use of oxygen for agitation had a marked effect in reducing the time necessary to sweeten isoamyl mercaptan.

Lead sulfide suspended in water or in the oil did not assist in the oxidation, showing that lead sulfide does not function as a catalyst in the oxidation of the mercaptans, as has been believed.

Lead Sulfide, Sodium Hydroxide, and Oxygen—Lead sulfide, sodium hydroxide, and oxygen sweetened all the mercaptans except isoamyl mercaptan and the gasoline from Panhandle crude oil. The lead mercaptides formed in every case, but the N-butyl and the heptyl mercaptides did not settle from the solutions until after standing overnight.

The nitrogen used for agitation contained 4 per cent of oxygen. Even such a small percentage of oxygen caused slow formation of the mercaptides. Ethyl and benzyl mercaptans were sweetened. In all such cases sulfate ion was formed.

The naphtha solution of lead isoamyl mercaptide and the mercaptides of the gasoline from Panhandle crude are very stable, showing no tendency to settle.

The lead sulfide plays a minor role in the stability of the lead mercaptide dispersions, functioning in the same manner, but to a less extent, as chemically inert substances such as fuller's earth and charcoal. When the last-named substances were added to a dispersion of N-butyl or isoamyl lead mercaptides in naphtha both were removed by adsorption. The effect of lead sulfide in this respect was very slow for the butyl lead mercaptide and no effect was observed in the case of the isoamyl lead mercaptide.

A most important conclusion from these experiments is

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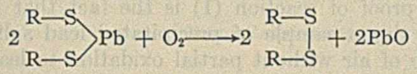
[3] *Ann.*, **359**, 81 (1908).

that both oxygen and sodium hydroxide are necessary to cause lead sulfide to have any effective sweetening reaction.

Sodium Plumbite—A comparison of the experiments in which lead sulfide, oxygen, and sodium hydroxide are used, with those employing sodium plumbite, shows that the two are practical equivalents. Oxygen for agitation seems to have some advantage over nitrogen in the case of *N*-butyl mercaptan, but this apparent advantage resides largely in the inferior stability of the solution of the mercaptide formed when oxygen was used. The mercaptide settled out after standing, rendering the oil sweet.

The difference in the effects of nitrogen and oxygen on *N*-butyl lead mercaptide shows that the lead mercaptides also are more readily oxidized than the corresponding mercaptans. This behavior was shown to be true for sodium mercaptides. The reaction for this oxidation follows:



$$2\,(RS)_2Pb + O_2 \longrightarrow 2\,RS\text{—}SR + 2PbO$$

This reaction was proved by mixing naphtha solutions of isobutyl mercaptan and heptyl mercaptan with a solution of sodium hydroxide containing suspended lead sulfide and agitating for several hours with oxygen. The naphtha solution was separated and filtered, and then extracted with alcoholic sodium plumbite solution to remove unconverted mercaptans. The oil was then reduced with zinc and glacial acetic acid and the mercury derivatives of the mercaptans were made. The melting points of these derivatives were determined. A second set of experiments was conducted by the same procedure, but using molecular proportions of mercaptan and sodium plumbite. The results are given in Table II.

Table I—Sweetening Effect of Various Reagents on Pure Mercaptans and Gasoline from Panhandle Crude Oil

Reagent	Ethyl Mercaptan Doctor[a]	Ethyl Mercaptan Min.	N-Butyl Mercaptan Doctor	N-Butyl Mercaptan Min.	Isoamyl Mercaptan Doctor	Isoamyl Mercaptan Min.	Heptyl Mercaptan Doctor	Heptyl Mercaptan Min.	Benzyl Mercaptan Doctor	Benzyl Mercaptan Min.	Panhandle Gasoline Doctor	Panhandle Gasoline Min.
O_2	−	12	+	30	+	30	+	30	+	30	+	30
N_2	−	12	+	30	+	30	+	30	+	30	+	30
$NaOH + O_2$	−	2	+	30	+	30	+	30	−	25	+	30
$NaOH + S + N_2$	−	2	−	6	−	30	−	30	−	1	+	30
$NaOH + S + O_2$	−	1	−	4	−	12	−	30	−	1	+	30
PbS[b] + $H_2O + O_2$	−	8	+	30	+	30	+	30	+	30	+	30
PbS[b] + $NaOH + O_2$[f]	−	1	+[e]	30	+	30	+[d, e]	30	−	4	+	30
			+	40	+	40						
PbS[b] + $S + NaOH + O_2$	−	1	−	1	−	3	−	2	−	1	−	10
PbS[c] + $NaOH + O_2$	−	1	−	2	+	30	−	6	−	1	+	30
			−	3	+	40	−	5				
PbS[c] + $NaOH + S + O_2$	−	1	−	2	−	4	−	1	−	4	−	8
$Na_2PbO_2 + N_2$[f]	−	1	+	30[d, e]	+	30	−	2	−	1	+	30
$Na_2PbO_2 + O_2$[f]												
Blowing	−	1	−	4	+	30[d]	−	3	−	2	+	30
Shaking	−	1	−	4	+	30[d]	−	3	−	1	+	30

[a] Plus and minus signs indicate presence and absence, respectively, of mercaptan after time shown.
[b] From lead acetate.
[c] From Panhandle gasoline.
[d] Using two portions of reagent.
[e] Lead mercaptide formed and settled out upon standing, rendering sample negative.
[f] Lead mercaptide formed in every case. The positive doctor test in this series indicates that the lead mercaptides remained in solution.

Table II—Properties of Recovered Mercaptans

RSH	RSH	PbS	NaOH	Melting Point of $(RS)_2Hg$ Recovered	Melting Point of $(RS)_2Hg$ From original mercaptan
	Per cent by vol.	*Grams*	*Grams*	*° C.*	*° C.*
Isobutyl	2.0	1.24	0.829	89.5	88.0
Heptyl	2.0	1.24	0.829	74.0	74.0
		Na_2PbO_2			
Heptyl	10.0	9.14		74.0	74.0

A large portion of each mercaptide was not converted to the disulfide, hence the reaction is slow and may be considered as incidental. It is important to remember that this reaction occurs only after the mercaptides are formed, and that plumbite solution or its equivalent, lead sulfide, sodium hydroxide, and oxygen, are necessary to form the mercaptides.

The aqueous sludge from each test was analyzed. Only when lead mercaptide was formed or the oil was sweetened were lead and sulfate ions found. There was an excess of sulfate ions in all cases, showing that the lead was used in forming the mercaptide.

Table III—Analysis of Sludge from Treatment of Panhandle Gasoline with Lead Sulfide, Sodium Hydroxide, Oxygen, and Sulfur

Source of Lead Sulfide	Pb	SO_4	SO_4 Required for $PbSO_4$	Excess SO_4[a]
	Gram	*Gram*	*Gram*	*Per cent*
H_2S from Panhandle gasoline	0.023	0.018	0.012	46
Purchased, contained 22 per cent $PbSO_4$	0.11	0.07	0.05	51

[a] 0.1 gram of sulfur used for converting mercaptide to disulfide; oxidation of sodium sulfide may account for a small part of the excess, but the major cause is removal of the lead as mercaptide.

Chemistry of Sweetening Gasoline Containing Mercaptans

It is concluded from the foregoing facts that the predominant role of lead sulfide in the sweetening of a gasoline containing mercaptans is represented by the following reactions:

$$PbS + 4NaOH + 2O_2 \longrightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O \qquad (1)$$

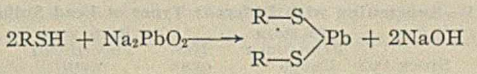
This reaction may be divided as follows:

$$PbS + 2O_2 \longrightarrow PbSO_4 \qquad (2)$$

$$PbSO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O \qquad (3)$$

Reaction (1) also shows what occurs when spent doctor solution is regenerated by blowing it with air.

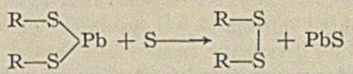
The usual reaction for the formation of lead mercaptides takes place in any system where sodium hydroxide, lead sulfide, and oxygen are present.



(4)

$$2RSH + Na_2PbO_2 \longrightarrow (RS)_2Pb + 2NaOH \qquad (4)$$

The action of added sulfur is indicated by the well-known reaction:



(5)

$$(RS)_2Pb + S \longrightarrow RS\text{—}SR + PbS \qquad (5)$$

As reactions (4) and (5) have been proved for sodium plumbite and the disulfide identified, it was decided to show that reactions (2), (3), and (5) are the equivalent of (4) and (5) with regard to disulfide formation.

The naphtha solutions of ethyl and isobutyl mercaptans were mixed with sodium hydroxide and lead sulfide and blown with oxygen until sweet. The liquids were filtered and the oils separated. An equal volume of glacial acetic acid was added to the oils and the mixture refluxed with zinc dust for one hour. The remaining zinc was filtered off and the oil thoroughly washed with water. The oil was then dried and treated with mercuric oxide. The mercury derivative was dried and the melting point determined (Table IV).

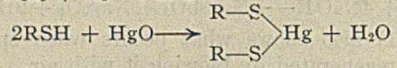
The reactions involving lead sulfide (1 to 3) indicate that lead sulfide and oxygen actually enter into the reaction, forming sodium plumbite in the presence of sodium hydroxide, thus maintaining the concentration of sodium plumbite. This fact is readily proved by the use of the separate components instead of sodium plumbite in sweetening the Panhandle gasoline. This type of gasoline cannot be sweetened unless all these components are present. Further, if a definite quantity of sodium plumbite and gasoline is used, sweetening will not result until lead sulfide is added and oxygen is blown through, because the quantity of sodium plumbite in the solution used does not completely convert the mercaptans to mercaptides. Without the use of oxygen the reaction will not take place for the reasons explained. This fact was established by blowing with an inert gas such as nitrogen. Sulfur functions as usual.

Table IV—Melting Points of Mercury Mercaptides

	From Ethyl Mercaptan	From Isobutyl Mercaptan
	° C.	° C.
Prepared from mercaptan directly	76	88
Prepared from reduced disulfides	76	89
Literature	76	..

The reactions are:

$$R_2S_2 + H_2 \longrightarrow 2RSH$$



$$2RSH + HgO \longrightarrow \begin{matrix} R\text{—}S \\ R\text{—}S \end{matrix}\!\!>\!Hg + H_2O$$

A careful check was made with pure nitrogen, lead sulfide free from lead sulfate, and sodium hydroxide. A 0.1 per cent solution of heptyl mercaptan treated for 60 minutes under these conditions failed to sweeten and the aqueous layer showed no lead or sulfate ions. When the nitrogen contained approximately 5 per cent of oxygen, sweetening resulted in 2 minutes.

Effect of Type of Lead Sulfide

The nature of the lead sulfide is also a factor in the sweetening reaction; and the activity depends principally on its rate of oxidation. One lot sweetened the gasoline in 2.5 minutes (when lead sulfate was removed by sodium hydroxide, 15 minutes were required for sweetening); another required 22 minutes under similar conditions; while galena showed no action even for the pure mercaptans.

Using sodium hydroxide, sulfur, and oxygen the results obtained upon the gasoline from Panhandle crude oil with different types of lead sulfide are shown in Table V.

Table V—Sweetening with Different Types of Lead Sulfide

	Stock PbS (22% $PbSO_4$)	H_2S from Panhandle Crude + Na_2PbO_2	H_2S over PbO_2	Pptd. from $Pb(C_2H_3O_2)_2$ with H_2S	Galena
Reaction to doctor test	–	–	–	–	+
Time of reaction, minutes	2.5	10	10	22	60

The lead sulfides precipitated from aqueous solutions were washed free from adhering reagents and were not dried before using. The sample prepared from lead peroxide and the stock sample were mixed to a paste with water before they were used.

It is noted that galena, which is the naturally occurring form of lead sulfide, did not sweeten the gasoline from Panhandle crude even in the presence of sodium hydroxide, oxygen, and sulfur. The galena was crushed and ground to 50, 100, and 150 mesh and a separate test made with each size. All the lead sulfides with the exception of galena produced sodium plumbite and sodium sulfate when blown with air or oxygen in the presence of sodium hydroxide.

Effect of Concentration of Oxygen

A series of tests was made to determine the effect of the concentration of oxygen upon the time of reaction. The lead sulfide prepared from the Panhandle gasoline was used with sodium hydroxide and sulfur, and the mixture, together with the gasoline, was blown in separate experiments with nitrogen, air, oxygen, and ozonized air. The results are tabulated in Table VI.

Table VI—Effect of Oxygen Concentration

	Nitrogen[a]	Air	Oxygen	Ozonized Air
Reaction to doctor test	+	–	–	–
Time of reaction, minutes	60	25	10	7

[a] Contained 4 per cent oxygen.

These results indicate that concentration of oxygen is a factor in the rate of sweetening. For example, air took twice the time to sweeten required for oxygen, while ozonized air required only one-third the time required for air. Nitrogen showed no sweetening reaction whatever, indicating further that when the lead sulfide is not oxidized to lead sulfate no sweetening will occur.

Further proof of reaction (1) is the fact that it is very difficult to dry a sample of precipitated lead sulfide in an atmosphere of air without partial oxidation to lead sulfate. An experiment was made to show to what extent this oxidation occurred. A sample of lead sulfide precipitated by passing hydrogen sulfide into a solution of lead acetate was carefully washed and the resulting lead sulfide dried in the ordinary manner in a drying oven. The resulting lead sulfide contained 22 per cent of lead sulfate.

In conducting the experiments with lead sulfide it is quite necessary to be assured of the absence of lead sulfate. It is further necessary to wash the lead sulfide thoroughly when it is precipitated from an alkaline solution. One series of experiments showed that when lead sulfide was precipitated from a sodium plumbite solution and filtered, the rate of sweetening for the pure mercaptan solution was practically the same as when the solution of sodium hydroxide was added to the lead sulfide. Determination of the amount of sodium hydroxide remaining in the lead sulfide precipitate on the filter paper showed it to be practically half the total amount used in the experiments with the pure mercaptans.

When samples of lead sulfide (from lead acetate) were suspended in sodium hydroxide and blown with oxygen, the results shown in Table VII were obtained.

Table VII—Effect of Blowing Lead Sulfide

Time of Blowing	Na_2PbO_2	Na_2SO_4
Minutes	*Mol*	*Mol*
10	0.008	0.007
20	0.009	0.008
30	0.01	0.009

These results accord with reaction (1)—i. e., one mol of sodium sulfate is formed for each mol of sodium plumbite.

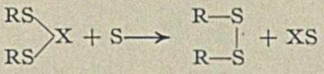
Sweetening Action of Metallic Sulfides

In order to determine whether the sweetening reaction is general, further experiments were conducted with the sulfides of mercury, silver, copper, and nickel.

The solution of benzyl mercaptan was sweetened by all the sulfides when blown with oxygen in the presence of sodium hydroxide. The sulfate ion was strongly present in all cases. The solution of butyl mercaptan was sweetened by nickel sulfide only under the same conditions. The sulfate ion was invariably present. The nickel sulfide was precipitated from a solution of nickel nitrate, washed, and dried. Analysis showed it to contain 17.2 per cent of nickel sulfate. Filtration of the sulfide after precipitation showed the presence of colloidal sulfur formed by the oxidation of hydrogen sulfide by the nitric acid in the nickel nitrate solution. The nitric acid is formed by hydrolysis.

When sulfur was added to the mixture of butyl mercaptan and the suspended sulfides in sodium hydroxide, the mercaptan was sweetened in all cases. The sulfate ion was produced as usual.

In all cases the sulfides are oxidized to sulfates. Even on drying the precipitated sulfides in a drying oven in air the sulfates were formed. Two samples of lead sulfide from different sources showed 23 per cent oxidized to the sulfate; nickel sulfide was oxidized to the extent of 17 per cent; 5 per cent of a copper sulfide was converted to the sulfate. The succeeding reaction, then, depends upon the metal. Lead forms the plumbite; mercury the oxide; silver, copper, and nickel the hydroxide. In all cases, however, the mercaptide of the metal, X, is formed and is subsequently converted to the disulfide in the manner shown for lead sulfide.



$$\begin{matrix}RS\\RS\end{matrix}\!\!>X + S \longrightarrow \begin{matrix}R-S\\|\\R-S\end{matrix} + XS$$

Polishing and Etching Lead, Tin, and Some of Their Alloys for Microscopic Examination[1]

By J. R. Vilella and D. Beregekoff

Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

This work forms part of a series of investigations on improved methods of polishing and etching conducted at the Union Carbide and Carbon Research Laboratories, Inc. In addition to the present contribution, this investigation has resulted in the development of a method of polishing steel which does not drag out the non-metallic inclusions;[2] also in improved methods for polishing and etching iron-chromium alloys, copper and its alloys, and aluminum and its light alloys.[3]

Polishing

The proper development of the structure of lead or any of the lead-base alloys is not a difficult task if the operator, from the very beginning of the process, directs all his efforts toward obtaining a finished surface free from disturbed metal. It is a serious error to base the judgment of satisfactory polishing solely on the absence of scratches, particularly when working with soft metals. Scratches, though very undesirable, seldom obscure the structure beyond recognition and are always easily recognized. On the other hand, disturbed metal often completely covers the prepared surface and the patterns it makes have been frequently accepted as the true structure of the metal.

While the importance of guarding against this error has been frequently stressed in the literature, it cannot be overemphasized when discussing a method for the polishing of lead. Proper polishing is a delicate operation even when working with steel or harder metals, but when working with lead it is to be considered an accomplishment and its success depends as much upon the care and skill of the operator as upon the method of procedure, for it is possible to obtain satisfactory results by more than one method. The procedure to be described has been selected chiefly because it is not complicated and when properly carried out yields finished surfaces quite free from disturbed metal.

Procedure—(1) To minimize distortion of the surface metal, the sample should be cut with a sharp hack saw, taking special care to avoid dragging and pushing. It is well to smear the saw blade with a few drops of oil.

(2) The specimen should then be ground with gentle pressure on a coarse emery paper that has been previously smeared with a concentrated solution of paraffin in kerosene. This prevents the particles of lead from adhering to the paper and forming a glaze which drags and distorts the surface metal. At least $^1/_{64}$ inch of metal should be ground away during this step. The speed of the revolving disks should not exceed 500 r. p. m. at any stage during the entire operation.

(3) The specimen is then ground successively on No. 2, No. 1, No. 0, No. 00, and No. 000 emery papers, all previously smeared with the solution of paraffin in kerosene. Grinding on successive papers should be continued for at least one minute after all the scratches left by the preceding one have disappeared, and care should be taken to exert the minimum pressure needed to secure good cutting action. The scratches left by No. 000 paper are frequently too deep to be easily removed during the next step (wet polishing), and for this reason the specimen should be ground, when necessary, on an old No. 000 paper that has been well worn by previous use. This last paper, as a rule, yields very fine, even scratches which disappear easily during wet polishing. The specimen should now be rid of all traces of paraffin and grit.

(4) Wet polishing is carried out on a perfectly clean broadcloth smeared with an abundant supply of soap. The abrasive to be used is a water suspension of the finest levigated alumina obtainable. At this stage of the operation a black smudge appears on the surface of the specimen. When this happens, polishing should proceed very gently, taking care to maintain the cloth thoroughly wet with alumina and soap, until all traces of smudge have disappeared and the surface appears bright.

(5) The scratches left after polishing on broadcloth are often quite deep and remain visible after etching. They can be removed by finishing the operation by hand on a clean pad of silk velvet well soaked with soap and alumina. The sample is then washed carefully to remove all traces of soap.

The specimen is now ready for its first etching.

Etching

The etching of lead or any soft metal is not a process independent of polishing. Even the best prepared surface is never completely free from a film of distorted metal which must be eliminated in order to reveal the true structure of the metal. This can never be accomplished by the etching reagent alone, no matter how long the specimen is exposed to its action. A prolonged chemical attack will result only in pitting, blackening, and roughing the prepared surface. It is necessary to employ the method of alternate polishing and etching, later described, by means of which the film of distorted metal is gradually removed by the reagent, while the succeeding light polishing prevents the evils of a long-continued chemical attack. Figures 1, 2, and 3 illustrate the gradual development of the true structure of a lead-anti-

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[1] Received April 5, 1927.

[2] Burgess and Vilella, *Trans. Am. Soc. Steel Treating*, **7**, 486 (1925).

[3] Vilella, *Iron Age*, **117**, 761, 834, 903 (1926).

Figure 1—Appearance of the structure after first etch. × 100

Figure 2—Same field after repolishing and re-etching. × 100

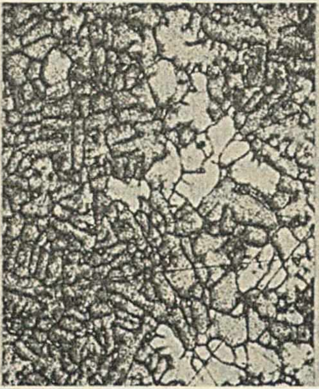

Figure 3—Same field as Figures 1 and 2 after second repolishing and re-etching

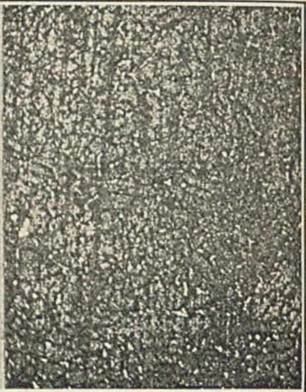

Figure 4—Poor polishing. Same specimen as Figures 1, 2, and 3 after repolishing and re-etching three times. No precautions taken to avoid distortion of surface metal

Figure 5—Rolled lead. × 100

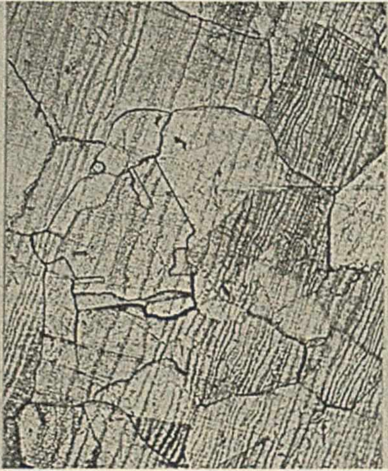

Figure 6—Extrusion bands in hammered lead. × 100

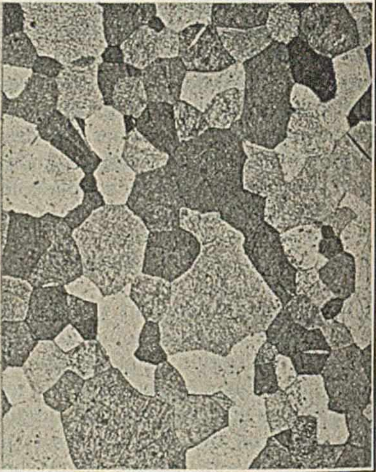

Figure 7—Pure tin. Forged and treated at 150° C. for 2 hours. Air-cooled. × 100

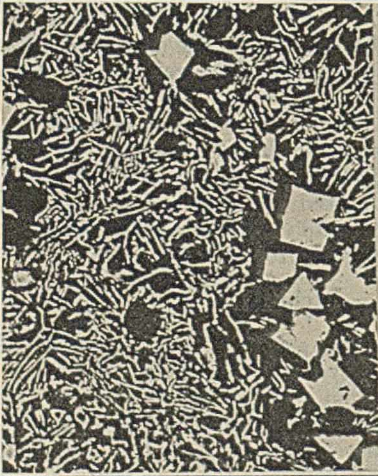

Figure 8—Lead-antimony alloy. 16 per cent antimony as cast. Shows eutectic and primary crystals of antimony. × 250

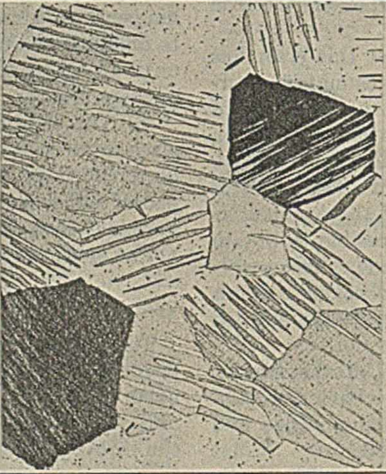

Figure 9—Pure tin. Forged and treated at 175° C. for 12 hours. Air-cooled. × 100

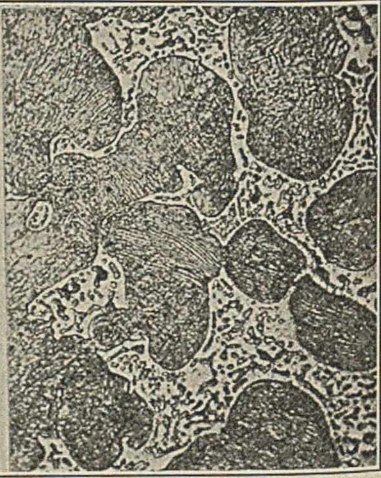

Figure 10—80 per cent lead–20 per cent tin. As cast in hot mold. × 500

mony alloy containing 2.5 per cent antimony by the method of alternate polishing and etching.

Preparation of Reagent—The accompanying structures of lead and lead-antimony alloys have been developed by etching with a reagent of the following composition (by volume): 1 part concentrated nitric acid, 1 part glacial acetic acid, and 4 parts glycerol.

The structures of the lead-tin alloys were developed by a reagent containing twice as much glycerol as the above formula.

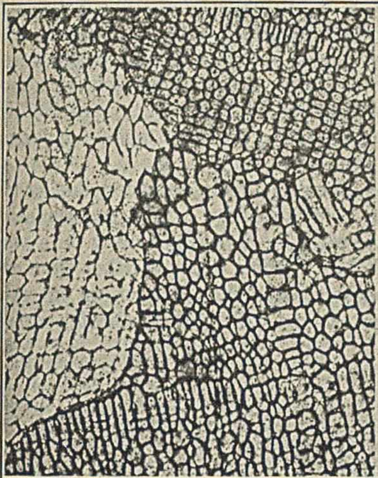

Figure 11—1 Per cent antimony-lead alloy. Cast in a hot mold, cooled slowly. × 100

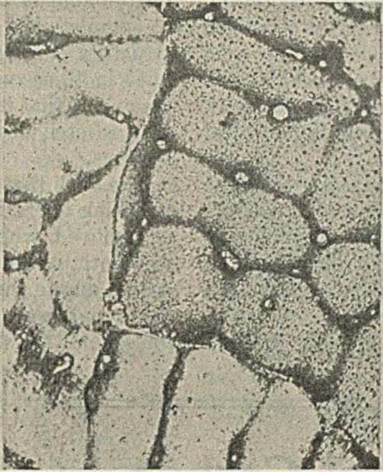

Figure 12—Same as Figure 11. × 500

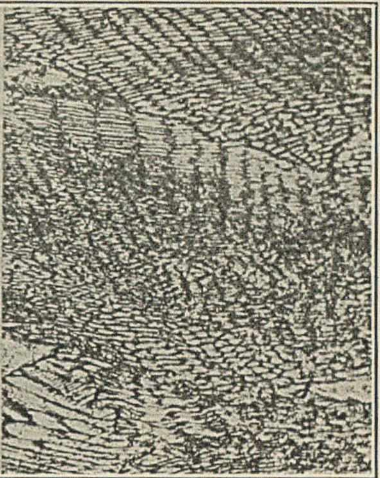

Figure 13—Same alloy as cold-worked. × 100

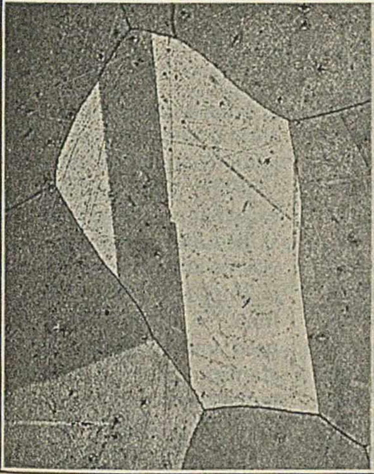

Figure 14—Same alloy, but treated at 225° C. for 1/2 hour and air-cooled. × 100

Figure 15—Lead-tin alloy, 3 per cent tin. Treated at 200° C. for 1/2 hour and quenched. × 100

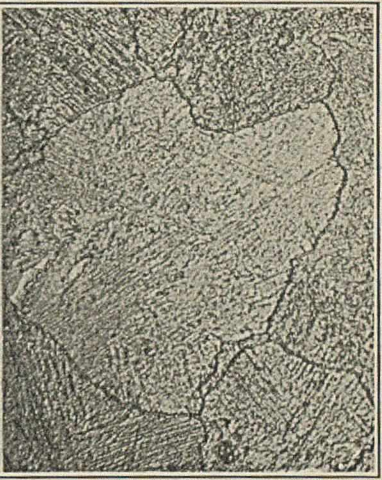

Figure 16—Same alloy at × 500

Pure tin can also be etched with this combination of acids; the ratio must be changed, however, in order to prevent the deposition of metastannic acid on the prepared surface. The accompanying structures (Figures 7 and 9) were developed with a reagent consisting of 1 part by volume of nitric acid, 3 parts of acetic acid, 5 parts of glycerol.

Procedure—Reagents prepared in glycerol are, as a rule, quite slow in starting their action. For this reason it will be found convenient to warm the specimen in a current of hot water before immersing in the reagent. When working with pure lead or lead-antimony alloys the first attack should not exceed 15 seconds in duration. For lead-tin alloys 5 seconds are sufficient. After the first attack the specimen is examined under the microscope and its structure noted. It is next repolished gently on the silk-velvet pad until bright and re-etched for about 10 seconds, if working with lead or lead-antimony alloys, and for 3 seconds in cases of lead-tin alloys. This process of alternate polishing and etching should be repeated as long as the appearance of the structure continues to improve. As a rule, three repolishings suffice, but sometimes more are required. If the method has been carried out carefully the final structure should be rich in detail and free from scratches. (Figures 5, 6, 7, 8, 9, and 10)

The development of the structures of soft metals, and particularly of lead alloys, has been recently discussed by Lucas,[4] who finds after considerable experimentation that the usual methods of polishing are unsatisfactory for the preparation of lead specimens, chiefly because of the difficulty of removing scratches. He finds that in specimens prepared by the usual methods of polishing "one must resort to deep etching to get below the polishing imperfections" and that "the polishing operation also causes the surface of the specimen to blacken." These difficulties coupled with the fact that the polishing of a single sample often required several hours of work, led him to develop the microtome method described in his paper. In view of the results obtained by this method Lucas infers that "from the standpoint of what can be seen with the microscope there is no comparison between the old and the new method of preparation." The photomicrographs illustrating this paper justify the improvement obtained by using the microtome method in preference to the usual practice of polishing in conjunction with deep etching. Unfortunately, however, the microtome is a piece of apparatus not ordinarily found in the equipment of metallographic laboratories and, when available, requires considerable ex-

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[4] "Application of Microtome Methods to the Preparation of Soft Metals for Microscopic Examination." Paper read at the February, 1926, Meeting of American Institute of Mining and Metallurgical Engineers.

perience to sharpen properly and keep the knife in condition. These considerations have led the present writers to publish the result of a study of the polishing methods that has been in progress for some time, and in which has been developed a technic that is rapid, can be successfully carried out with any polishing equipment, and leads to the formation of ideal surfaces for microscopical examination.

Figures 11, 12, 13, and 14 illustrate the appearance of the structures of a 1 per cent antimony-lead alloy after various treatments, as developed by the methods of polishing and etching described here. Figures 15 and 16 illustrate the structure of a 3 per cent tin-lead alloy as developed by the same process.

The time required to prepare a sample depends entirely on the skill of the operator, an experienced one being able to complete the entire operation in less than an hour. The structure of properly prepared samples can be easily developed in 10 seconds, even when employing as slow an acting reagent as that previously described. It is by no means necessary to etch deeply in order to get below polishing imperfections.

The fact that the blackening often observed during the polishing operation can be avoided by careful manipulation or removed, when it appears, by gentle polishing on a very wet cloth, seems to indicate that its cause is other than oxidation due to the polishing operation. It has been observed that a polished specimen of lead will retain its bright surface for several days.

Total Carbon in Coal[1]

Determined by Analysis of Gas from Bomb Calorimeter

By Geo. B. Watkins

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

A mercury-sealed gasometer suitable for measuring the volume of the gaseous products of combustion from heating value determinations of coal and combustible organic compounds is described. The carbon dioxide content of these products is determined and the total carbon calculated.

Five different coal samples and benzoic acid and sucrose were exploded in a bomb and temperature-time readings necessary for heating value calculations recorded. The products of combustion were then released into the gasometer and their volume was measured at about atmospheric pressure. Samples of gas were withdrawn from the gasometer and carbon dioxide was determined by absorption in caustic solution. The total carbon of the coals calculated from these data checks the Bureau of Mines value within one-tenth of one per cent. The time required for the total carbon determination is less than one-half hour after the completion of the heating value test.

A HEAT balance on furnaces using fuel to supply the heat energy requires a material balance. A material balance requires the measurement of either the air or fuel entering the furnace and the analysis of the products of combustion. The analysis of the combustion products is relatively simple. A direct measurement of the air required for combustion is practically impossible since the air usually enters the furnace at many points. The choice of methods for making the material and the heat balance on the furnace is therefore limited to the measurement and analysis of fuel input.

The actual analytical data relative to fuels, and necessary for making a material and heat balance, are the heating value, moisture, ash, and total carbon. While the first three determinations are relatively short and simple, the recognized standard method for total carbon determination is slow and tedious, requiring expensive apparatus and skilful manipulation.

The methods for determining total carbon in organic compounds and fuels all involve the oxidation of the carbon with subsequent determination of the carbon dioxide formed. The methods may be divided roughly into two classes: (1) those using molecular oxygen to complete the oxidation, and (2) those using oxidizing agents other than molecular oxygen to complete the oxidation. An example of the first class is the well-known Liebig method for ultimate analysis, in which the combustion is carried out in a stream of dry and pure oxygen, absorbing the carbon dioxide formed in potassium hydroxide solution. This method is the recognized standard for the determination of carbon and hydrogen in organic compounds and fuels.[2]

While this method gives excellent results when used by skilled and competent chemists in laboratories especially equipped for the study of fuels, it is unreliable when used under adverse circumstances. For this reason numerous attempts have been made to replace it by a simpler and more expeditious method.

Goutal[3] determines the total carbon in coals by exploding the sample in a bomb similar in design to the one proposed by Kroeker.[4] The bomb has a capacity of approximately 100 cc. and is equipped with two needle valves, placed half way up and diametrically opposite. The products of combustion are expanded into a special absorption apparatus containing caustic solution, and the carbon dioxide is determined by titrating the excess alkali with standard acid. This method is said to be accurate within 0.3 per cent.

Parr's[5] method for estimating the total carbon in coal is an example of the second class, in which oxygen other than molecular is used to oxidize the carbon. The method consists in utilizing the residue from the sodium peroxide fusion in which the total carbon of the coal has been oxidized and combined with the chemical to form sodium carbonate. The residue, consisting mainly of sodium peroxide and sodium carbonate, is dissolved in water and treated with acid. The carbon dioxide evolved is estimated by absorption in caustic solution.

The method proposed in this paper consists of exploding

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[1] Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] For detailed directions see *Bur. Mines, Tech. Paper* **8**.

[3] *Fuel Science Practice*, **2**, 344 (1923).

[4] *Z. Ver. Rubenzuckerind.*, **46**, 177 (1896).

[5] "Fuel Gas Water and Lubricants," p. 179, McGraw-Hill Book Co., (1922).

the coal sample in a Mahler type of bomb, using approximately 20 atmospheres pressure of oxygen, and recording the temperature-time readings necessary for heating value computations. The gaseous products of combustion from the heating value determination are expanded into a mercury-sealed gasometer and their volume is measured at about atmospheric pressure. Their carbon dioxide content is then estimated in the usual way and the total carbon of the sample computed.

Apparatus

GASOMETER—The mercury-sealed gasometer shown at the left in Figure 1 was constructed to use as small an amount of mercury as possible by concentrically welding two No. 16 B. W. gage steel tubes, *A* and *C*, to a steel plate, *D*. The outside diameters of the steel tubes *A* and *C* are 10.16 and 8.25 cm. (4 and $3^1/_4$ inches), respectively. A cover plate is welded to the top of the smaller tube, *C*, which is approximately 127 cm. (50 inches) long. The steel plate, *D*, is mounted on a wooden base 40 by 61 cm. (16 by 24 inches) and 5 cm. (2 inches) thick, which in turn is mounted on castors. The float chamber, *B*, was constructed from No. 11 B. W. gage steel tube, by welding a cover plate to the top. A steel nipple connection, *E*, welded to the cover plate serves as an inlet and outlet for the gases. The float chamber has an outside diameter of 95 cm. ($3^3/_4$ inches), giving the gasometer a capacity of approximately 9000 cc. It can be raised or lowered freely in the annular space between the tubes *A* and *C* by means of the windlass, *F*, which is supported on the wooden base of the apparatus. The length of the float chamber is approximately 0.159 cm. ($^1/_{16}$ inch) shorter than tube *C*, giving ample room for the mercury to flow in the annular space when the float chamber is lowered to its zero position.

The mercury reservoir, *G*, was constructed from a sheet steel pan, approximately 24 cm. ($9^1/_2$ inches) in diameter and 12.7 cm. (5 inches) high, by welding a right-angle connection to the bottom. From this connection a rubber tube leads to a steel nipple connection, *H*, welded at right angles to the outside tube, *A*. The reservoir is mounted on a wooden shelf which is supported from the base of the apparatus.

A bowl-shaped collar, *I*, machined from cast iron and fitted to the top of tube *A*, serves as a reservoir to prevent the loss of mercury by overflow in case the float chamber of the gasometer is rapidly forced to its zero position. A level sight, *J*, attached to the collar to facilitate the reading of the instrument was constructed from a piece of sheet steel and extended nearly to the wall of the float chamber.

BOMB—The bomb, *K*, connected to the gasometer and manometer by means of the double needle valve, *M*, and rubber tubing is shown in the upper right-hand corner of Figure 1. The bomb, machined from monel metal, has a capacity of 255 cc. The needle valve (1), which closes the bomb during explosion, was carefully packed so that the gases cannot escape around the connections when the valve is opened. This was accomplished by recessing the packing nut and winding asbestos cord around the valve stem. A detailed drawing of the bomb[6] is shown in the lower right-hand corner of Figure 1.

The double needle valve, *M*, is connected to the oxygen intake in the head of the bomb by means of the brass nipple, *N*. The brass nipple (2) controlled by valve (3) is connected to the float chamber of the gasometer at *E* by a heavy-walled rubber tube. A few centimeters from the nipple (2) a glass bulb, *O*, made from a 25-cc. volumetric pipet, is inserted in the line. The glass bulb is loosely packed with moist cotton gauze, wound on a copper wire and introduced into the bulb in a spiral manner so as to fill the free space completely. This serves to saturate the gases with water vapor as they expand from the bomb into the gasometer. The brass nipple (4) controlled by valve (5) is connected by a rubber tube to a three-way glass stopcock, *P*, which in turn is connected to the water manometer, *L*.

A mercury-filled buret and a bubbling pipet filled with caustic solution are used to estimate the carbon dioxide content of the gaseous products.

Calibration of Gasometer

Before starting the experimental work it was necessary to calibrate the gasometer. This was accomplished by introducing a measured amount of mercury into a gas-tight system through a separatory funnel. The system was connected to the float chamber *E* so that a definite volume of dry air was forced into the gasometer. The system was brought to atmospheric pressure by raising or lowering the float chamber by means of an auxiliary screw attachment, and the calibration mark made on the float chamber. The calibration was continued in this way at 500-cc. intervals up to a volume of 6500 cc. Then, by means of a pair of dividers, the 500-cc. intervals were further divided into 100-cc. intervals.

In the experimental work the gasometer was always read with the level sight, *J*, upon one of the calibration marks and the pressure, either positive or negative, relative to atmospheric was recorded on the water manometer.

Fuels Studied

For the purpose of checking the accuracy of this method for total carbon determination, benzoic acid and sucrose obtained from the Bureau of Standards, Washington, D. C., and five different coals obtained from A. C. Fieldner, of the Bureau of Mines, Pittsburgh, Pa., were used for the experimental work. The coals, whose ultimate analysis had been determined at the Bureau of Mines, included semianthracite, semibituminous, bituminous, and lignite.

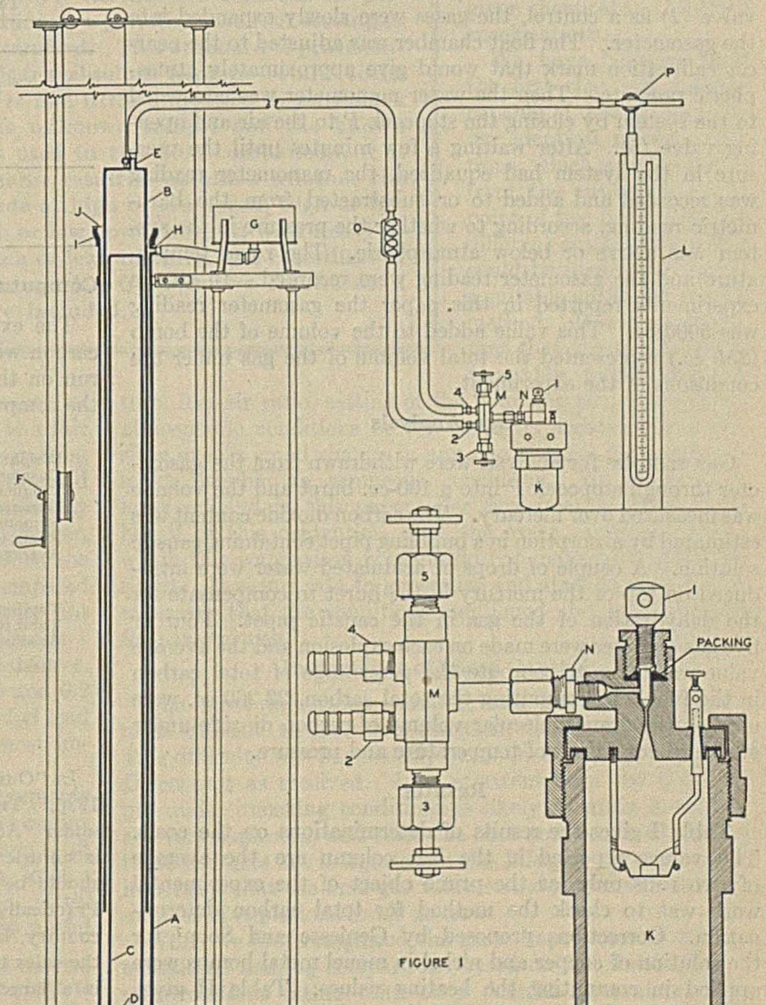

FIGURE 1

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[6] Copied from White's "Gas and Fuel Analysis," p. 260, McGraw-Hill Book Co. (1920).

Experimental Work

A sample of fuel (0.8–1 gram) was exploded as usual in the bomb calorimeter containing approximately 20 atmospheres pressure of oxygen to complete the combustion. The initial temperature of the water in the calorimeter was slightly below that of the room, so that the final temperature of the system would be approximately equal to that of the room. The temperature-time readings necessary for heating value computations were recorded. The bomb was removed from the calorimeter can and connected to the gasometer through the needle valve, *M*, by screwing the brass nipple, *N*, into the head of the bomb. Then with both valves (3) and (4) open and the stopcock *P* open to the air, the gaseous products from the previous run were expelled from the gasometer by lowering the float chamber to its zero point. When the float chamber was in this position the level of the mercury came just to the top of the steel nipple *E* in the float chamber, leaving the rubber tube and connections from the gasometer to the bomb filled with the gases from the previous run. The volume of the rubber tube and connections was about 50 cc. The carbon dioxide content of the gaseous products varied from 1 to 3 per cent with different runs, making it unnecessary to consider the volume of the tube and connections in measuring the total volume, as it canceled out from one run to another introducing a negligible error.

When the mercury in the gasometer and reservoir was at the same level, valves (3) and (5) were closed. The needle valve (1) of the bomb was opened half a turn; then by using valve (2) as a control, the gases were slowly expanded into the gasometer. The float chamber was adjusted to the nearest calibration mark that would give approximately atmospheric pressure. Then the water manometer was connected to the system by closing the stopcock *P* to the air and opening valve (5). After waiting a few minutes until the pressure in the system had equalized, the manometer reading was recorded and added to or substracted from the barometric reading, according to whether the pressure in the system was above or below atmospheric. The room temperature and the gasometer reading were recorded. In all the experiments reported in this paper the gasometer reading was 5000 cc. This value added to the volume of the bomb (255 cc.) represented the total volume of the gas under the conditions of the experiment.

Gas Analysis

Gas samples for analysis were withdrawn from the gasometer through stopcock *P* into a 100-cc. buret and the volume was measured over mercury. The carbon dioxide content was estimated by absorption in a bubbling pipet containing caustic solution. A couple of drops of acidulated water were introduced on top of the mercury in the buret to compensate for the dehydration of the gas in the caustic pipet. Four or five gas analyses were made on each explosion and the average value was taken to compute the percentage of total carbon in the fuel. In computing the total carbon, 22,260 cc. were used as the gram-molecular volume of carbon dioxide under standard conditions of temperature and pressure.

Results

Table I gives the results of determinations on the coals. The values reported in the last column are the average of two runs only, as the prime object of the experimental work was to check the method for total carbon determination. Corrections proposed by Geniesse and Soop[7] for the solution of copper and nickel in monel metal bombs were applied in computing the heating values. Table II gives the results of determinations on the organic compounds.

Table I—Total Carbon and Heating Value of Coals

COAL NO. (B. of M.)	KIND OF COAL	TOTAL CARBON B. of M.	TOTAL CARBON Gasometer	HEATING VALUE B. of M.	HEATING VALUE Monel metal bomb
		Per cent	*Per cent*	*Cal. per gram*	*Cal. per gram*
A.26840	Bituminous		73.4		
			73.4		
			73.5		
			73.6		
			73.6		
		Av. 73.5	73.5	7183	7193
A.26847	Bituminous		76.2		
			76.4		
			75.5		
			76.0		
		Av. 76.1	76.03	7605	7595
A.26839	Semianthracite		63.6		
			62.9		
			62.6		
			62.7		
		Av. 62.7	62.7	5861	5827
A.26566	Semibituminous		83.2		
			83.1		
			83.1		
			83.1		
		Av. 83.1	83.1	8083	8124
A.27336	Lignite		52.6		
			52.8		
			52.4		
			52.9		
		Av. 52.4	52.67	4806	4811

Table II—Total Carbon of Organic Compounds

COMPOUND	THEORETICAL	FOUND
	Per cent	*Per cent*
Benzoic acid		68.7
		68.9
		68.8
	68.8	Av. 68.8
Sucrose		42.2
		42.3
	42.1	Av. 42.25

Computation of Total Carbon from Experimental Data

The experimental data required for computing the total carbon will be easily seen by taking as an example, the first run on the semianthracite coal, No. A. 26839, and making the computation.

DATA

Weight of coal sample	0.9860 gram
Gasometer reading	5000 cc.
Volume of bomb	255 cc.
Barometric pressure	747 mm. Hg
Manometer reading	+173 mm. of water
Room temperature	24.0° C.
Average CO_2 content of gaseous products	23.7 per cent

COMPUTATION

Total gas volume = 5255 cc.
Total pressure on system = 747 + 12.84 = 759.84
Absolute temperature of system = 273 + 24 = 297° K.

$$\text{Total carbon} = 5255 \times \frac{273}{297} \times \frac{759.84}{760} \times \frac{0.237}{986} \times \frac{12}{22{,}260} = 62.6 \text{ per cent}$$

Correction

In "Our Foreign Trade in Chemicals and Allied Products in 1926," THIS JOURNAL, 19, 469 (1927), the statement is made under "Acids and Anhydrides," that "The largest export item is sulfuric acid, which goes entirely to Canada." The reference should be to our imports of sulfuric acid and not our exports. Practically the whole of our large acid imports come from that country, but acid exports are scattered among many countries, the sales to Canada being comparatively small, as that country is a large producer of sulfuric acid. The comparison is, of course, on the basis of quantity rather than value.

OTTO WILSON

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[7] THIS JOURNAL, 17, 1197 (1925).

Quantitative Antiknock Testing[1,2]

By C. K. Reiman

Arthur D. Little, Inc., Cambridge, Mass.

The method of measuring the antiknock quality of motor fuels developed in the laboratories of Arthur D. Little, Inc., where it has been in constant use for more than a year, is explained in detail. The Delco unit, after certain changes in the field wiring, serves as a dynamometer. Speed, a very important factor in determining quantitative results, can be positively controlled electrically. Results are reported in percentage aniline added to a paraffin-base fuel serving as an intermediate standard. This standard is provisionally placed on Edgar's absolute heptane-octane scale.

Provided there is but little difference in antiknock value between the unknown sample and the known aniline standards used in the final comparison, it is shown that the same result is obtained whether the comparison is made at high or low speed, high or low compression, high or low power output, with heavy or light knocking, rich or lean mixture, and regardless of the timing of the spark. Quantitative results on a series of fuels are included.

So MUCH has been said about different methods of antiknock testing, and such expensive equipment has been suggested and used for this work, that it is believed that the story of the excellent results obtained in the laboratories of Arthur D. Little, Inc., with a simple low-priced outfit may be useful to other petroleum groups. During the first three years that we were interested in making antiknock measurements we tried a variety of methods and a number of different types of engines. For more than a year we have obtained reproducible quantitative antiknock measurements using a modified 850-watt Delco unit, and during that period it has not been necessary to change our procedure.

The engine runs regularly 8, and often 16, hours a day, and so far the only repairs besides normal cleanings have been replacements of rings and a new piston and cylinder.

It is assumed that the reader is familiar with the Delco unit and the Midgley bouncing pin, both having been frequently described in recent publications. We have used other methods for indicating knock—for example, the listening method at incipient knocking—but prefer the bouncing pin because it averages with fair accuracy the small variations in knock intensity over a given time interval. It also permits a numerical reading, and the constancy of this reading over a series of tests on the same fuel is a fair indication of the value of the measurement. If the moving parts of this indicator are kept clean and if new pistons and springs are occasionally procured, there will be no difficulty with the instrument. It should be borne in mind, however, that such a device gives quantitative results only when the difference in knock rating between two fuels being compared is small. The volumes of gas produced will certainly not be proportional to the knock ratings over a wide range—as, for example, if the indicator is adjusted to read 2.00 cc. gas per minute with a straight-run paraffin gasoline and 0.2 cc. with the same gasoline containing 3 cc. of tetraethyl lead per gallon (0.8 cc. per liter). This point is of utmost importance and is often overlooked.

No attempt will be made to outline the many arguments in favor of a one-cylinder engine over a multi-cylinder engine or of the need in quantitative antiknock measurements of making comparisons between an unknown and a known fuel, as contrasted with the method sometimes used, of reporting results in terms of spark advance, highest useful compression, volume of gas per unit time produced in the Midgley apparatus, highest engine speed at which knocking occurs, etc. It is becoming generally understood that such data are satisfactory in making comparative and qualitative determinations, but that if the highest useful compression, for example, is to be taken as the absolute measure of the antiknock properties of the given fuel, then all the physical characteristics of the engine must be given, together with blue prints and operating data. By means of a variable compression engine suitable for determining the highest useful compression, it is, of course, possible to arrive at an understandable quantitative result provided a comparison is made between the unknown fuel and a known mixture, and the result expressed in terms of that mixture, which might be, for example, a definite percentage of benzene in a straight-run paraffin gasoline of given chemical and physical specifications.

We have believed from the first that any method capable of determining, under identical motor conditions, which was the better from the antiknock standpoint of two fuels of not too different antiknock quality, could be made the basis of a suitable antiknock testing method. It is very important that the speed, spark, throttle, motor temperature, fuel-air ratio, setting of the bouncing pin, and general atmospheric conditions be the same throughout the series, since even a small change in any one of these factors might make possible an erroneous conclusion. We do believe, however, and in this paper offer experimental evidence in behalf of this contention, that the exact conditions under which this comparison is made do not materially affect the result. It seems safe to generalize and state that it is only necessary that the conditions mentioned above be adjusted for convenience.

Importance of Speed Control

The most important variable, and the one frequently most difficult to maintain constant, is the engine speed. This difficulty was particularly pronounced in the case of the Delco unit as received. It is apparent that the bouncing pin under knocking conditions is likely to make a contact at every explosion, and since the sum and length of time of these contacts are integrated in the Midgley apparatus it is important that the final gas volume read represent the same number of explosions in all cases.

When we first recognized the great importance of this we considered making comparisons based on a definite number of revolutions rather than on a definite interval of time. Another factor is influenced by the speed, however. At higher speeds the piston is running away from the explosion

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[1] Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] These data are published with the kind permission of the Magnolia Petroleum Company.

wave at a higher rate and the maximum pressure developed is less. This might well show up in the results obtained in the Midgley apparatus, which takes into some account, at least, the difference between a hard and a light knock.

Method of Controlling Speed

Our first attempts to maintain constant speed were not successful. It made no difference whether the output from the generator of the Delco unit was used to charge the batteries or to heat an external resistance, or whether variable resistances were put in the field windings of the generator. On taking the generator to pieces it was found that the field was cumulative, compound-wound. The shunt field winding consisted of many turns of relatively fine wire around each of the four poles, and the series coil consisted of a few turns of relatively coarse wire around each of the poles wound in the same direction as the shunt field. This makes an excellent set-up for the farmer as it is foolproof, but it is not a satisfactory dynamometer since, regardless of what the operator may try to do, the unit continues to operate in the manner for which it was designed.

If one of the field windings is disconnected the excitation of the field is not sufficient to hold the speed of the motor at a reasonable level. It tends to run away, since with the 30 volts available at the brushes too small a current, for example, would flow through the high-resistance shunt coil. In order to obtain sufficient field excitation at 30 volts it would have been necessary to rewind the field coil using larger wire. It would then have been possible to put a suitable rheostat in this field circuit and thereby vary the excitation. By this means accurate control of the speed would be possible.

The only other alternative for varying the excitation of the field was to apply a higher voltage to the shunt field windings. Fortunately 110 volts d. c. were available in the laboratory, and with this current through a variable resistance it was possible to excite the field to any degree desired and thereby maintain absolute speed control. The change-over was very simple—the wires of the series field were disconnected and leads were brought out from the shunt field to the external source of current.

Advantages of Dynamometer Method

With this change the generator of the Delco unit becomes an electric dynamometer and offers all the advantages of such an instrument. In antiknock testing this method of applying the load electrically is of great importance, not only in speed control, but also in determining the degree of knocking at which tests are to be made. It is obvious that by increasing the voltage applied to the field winding the load is increased in a way similar to that on an automobile engine when a steep hill is encountered. By varying the applied field voltage and the throttle, within limits, any degree of knocking with any fuel can be obtained with any compression ratio.

The convenience of the dynamometer is evidenced in one more matter of importance in connection with the Delco unit. Using a low-compression head which was designed for use in the outfit, the speed is about 1100 r. p. m. with throttle wide open. Under these conditions the output is 850 watts. With higher compression heads and the throttle wide open, higher speeds and greater power outputs are obtained. The most important result of this increased load is a marked tendency of the motor to overheat. Air cooling becomes inadequate and various cases have been brought to our attention in which unusual efforts were made to keep the engine cool, or at least at constant temperature. If, by varying the applied field voltage, the output of the generator is maintained at a point not far above its rated capacity, no difficulties from overheating will be encountered.

A water-cooled head would make possible constant and controlled running conditions at either a higher power output or a higher knocking level. However, this is not absolutely necessary, since fuel comparisons are readily made at the lower power output and at a modest degree of knocking with identical results.

In connection with such a testing unit a speed indicator of some type is almost essential. We have used satisfactorily an automobile speedometer driven through fiber gears on the generator shaft. The operator watches the speedometer needle and occasionally adjusts the rheostat in the field circuit in order to keep the speed constant. A tachometer having a greater needle movement for a given change of speed would make possible even more accurate speed control.

Standard Fuels

To make quantitative antiknock tests, comparisons must be made with a known standard fuel, preferably blended with known amounts of a knock-suppressing material, such as benzene, aniline, or tetraethyl lead.

We hope that before long all the petroleum laboratories will be reporting results in terms of some absolute standard. In this paper we give some preliminary results comparing the isoöctane-*N*-heptane mixtures suggested by Edgar with our intermediate standard. When more of the normal heptane is available we hope to repeat and improve these data so that we will know exactly where our intermediate standard is on the absolute octane-heptane scale.

We have used as an intermediate standard an especially prepared straight-run gasoline from a midcontinent crude having the following characteristics:

Bé. at 60° F. (15.6° C.), 57.5

Unsaturates, 1.06 per cent

DISTILLATION DATA

	° F.	° C.
Initial	144	62
20%	214	101
50%	266	130
90%	368	187
E. P.	433	223

This material is kept carefully sealed in drums and great care is taken to prevent losses of lights in handling. New batches of this fuel prepared for us at the Magnolia Refinery in Texas are carefully checked against older batches before being put into use.

We have added to the midcontinent intermediate standard benzene, tetraethyl lead, and aniline at different times in order to make the antiknock property of the intermediate standard equal that of the fuel being tested. The amount of such material added becomes a measure of the antiknock quality of the unknown fuel. Of these three materials we prefer the aniline, for the following reasons:

1—The commercial material can be sufficiently purified by making a simple distillation using an air-cooled condenser.

2—Relatively small amounts are required so that the distillation characteristics of the mixture are not changed.

3—Sufficient quantities are used so that they can be measured accurately, whereas in the case of tetraethyl lead they are almost too small.

4—The tetraethyl lead is unpleasant to handle in the laboratory and it is frequently necessary to check the purity of the sample by analysis.

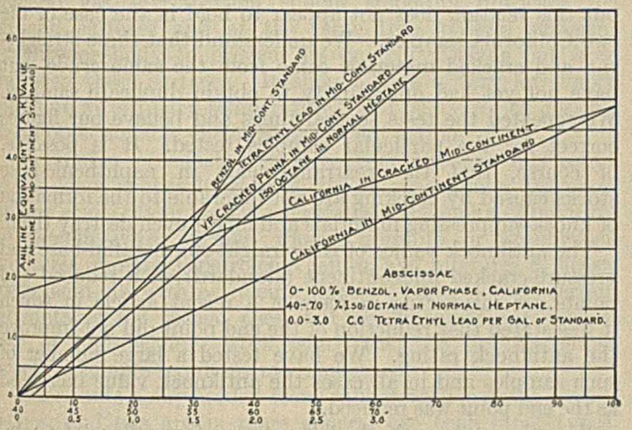
5—Benzene, because of the large quantity required, changes entirely the characteristics of the standard fuel and always tends to enrich the mixture, so that it becomes questionable whether or not the benzene scale is a satisfactory measuring stick for the antiknock property.

6—Aniline additions, like tetraethyl lead up to moderate limits, appear to be almost a straight-line function of the highest useful compression in a given engine.

7—The only serious disadvantage with aniline is that at the higher antiknock levels, about 6 per cent aniline in our standard fuel, the limit of solubility of the aniline is reached. In testing gasolines of high antiknock value it might be well to shift to the tetraethyl lead scale. For the lower range of testing we believe the aniline to be the most convenient. We have found it possible to test high antiknock fuels, with the exception of benzene blends, after diluting with the intermediate standard. Judging from the straight-line plots obtained for mixtures of gasolines, the antiknock value of a 50:50 mixture of a high antiknock unknown fuel and the standard would be half the actual antiknock value of the unknown fuel. This point is further discussed later.

Method of Testing

In determining the antiknock value of an unknown sample of gasoline we first make preliminary tests (to be described later) and then prepare two standard fuels which are blends of the midcontinent standard and aniline so that one will be a somewhat better and one a somewhat worse antiknock fuel than the unknown. On the lower part of the scale we prefer to have no more than from 0.2 to 0.4 per cent aniline difference in the two known samples. At the upper end of the scale when testing fuels of high antiknock value this difference should be made about twice as great in order to get a sufficient difference on the Midgley apparatus between the two standards.



As an example, let us assume that the two standard fuels contain, respectively, 2.8 and 3.2 per cent aniline—the unknown we expect to come between these two. We first adjust the engine as to compression ratio, speed, throttle, and spark so that a modest degree of knocking will be evidenced on the better standard fuel, 3.2 per cent aniline. After running for a few minutes on this fuel we shift to the lower standard fuel, which should knock considerably more. The volume of gas per minute in the Midgley apparatus may be 0.3 and 1.3 cc., respectively, which is a convenient order of difference. Should the knocking be too severe on the poorer fuel or the volume of gas in the two cases not of the order mentioned, changes in the throttle and field voltage, maintaining the speed always constant at about 1100 r. p. m., are made until such is the case.

The motor is then run on each of the two standard fuels for 10 or 20 minutes, making readings of the volume of gas produced in the Midgley apparatus each minute. It is then run for 10 or 15 minutes on the unknown, and finally again on the two standards. The average number of cubic centimeters of gas per minute for the two standard fuels is then plotted against the percentage of aniline in these mixtures. From this plot and the cubic centimeters of gas per minute produced in the Midgley apparatus by the unknown fuel can be read the percentage of aniline in the intermediate standard fuel, which is the equivalent of the unknown in antiknock rating. This percentage of aniline we call the aniline equivalent of the unknown fuel.

In the accompanying tables and curves the antiknock ratings, expressed as aniline equivalent, are given for a series of fuels. The curve showing the relation between our scale and isoöctane-heptane mixtures is provisional, but represents the best values obtainable with the small quantities of these materials available at this time. From this curve, when once it is definitely established, the percentage of isoöctane in normal heptane corresponding to any aniline equivalent can be read, and this figure becomes an absolute value of the antiknock rating.

Preliminary Testing of Unknown Fuels

Before placing an unknown fuel definitely on the antiknock scale it is necessary to know its approximate value in order to choose correctly the two aniline mixtures with which it is to be compared. The dynamometer arrangement has also been found useful here. The operator runs the engine on the unknown fuel and gradually increases the applied field voltage, which slackens the engine speed at a constant power output, until incipient knocking occurs. With a little experience, and of course depending on the throttle opening, compression ratio, etc., he can make a very accurate guess as to the aniline equivalent of the fuel in question by noting the applied field voltage. If a series of unknown fuels is to be tested they are generally run one after the other and given this preliminary test. Each is then definitely placed on the scale by means of the accurate comparison described above. When the accurate comparison is made, if the unknown fuel does not fall between the two standard fuel mixtures and it is necessary to extrapolate, the test is repeated using correctly chosen standards. We have found a much greater divergence in check results when we have accepted values obtained by extrapolation.

Provided no important change has occurred in a sample, such as loss of lights or polymerization and oxidation of unsaturates, we have no difficulty in checking antiknock results on the same sample after a period of months.

Varying Compression Ratio

We have a number of interchangeable heads for the Delco unit which were prepared by the Research Laboratory of the General Motors Company, and which permit us to vary the compression ratio from 5 to 6.4. When we first started testing we were obliged to change these heads frequently in order to make possible the testing of fuels of high and of low antiknock value. By means of the dynamometer device described above, we have found it possible to test high and low antiknock fuels on the same head. As a corollary we can state that the same fuels tested on different heads show identical knock ratings. The results, some of which are given in Table I, indicate that if one fuel is a better antiknock than another when used in an engine of a given compression ratio it will still be a better antiknock fuel if used with a different compression ratio. This seems entirely logical, but for our own information we desired to check this factor and also a number of others.

Effect of Other Factors

We determined on our aniline scale the antiknock value of a cracked gasoline of midcontinent origin in the usual normal manner, and repeated the determination on the same fuel under a number of different conditions, varying such factors as speed, spark, and richness of the mixture, etc. In all cases the unknown and the standard fuel mixtures were compared under identical conditions. As will be seen from Table I, all the results are practically alike, with only such small differences as might be expected in routine testing of this kind. No attempt was made to repeat the tests and make check measurements under each set of conditions to get an average which would be nearer the correct value. Without doubt, had this average been obtained over a series of tests in each case much smaller differences, if any at all, would have been reported. In this connection we have frequently checked results using the bouncing-pin indicator by the listening method, and varying either the applied field voltage or the throttle.

Effect of Benzene

Realizing the effect of the addition of such a low-boiling, high-calorific material as benzene, we repeated this series of tests on a blend of our midcontinent standard gasoline and 25 per cent benzene. The results checked in all cases but one as in the previous tests. As was to be expected, when operating on a richer mixture, the effect was more pronounced with benzene than with the standard fuel plus aniline—in other words, the apparent antiknock value of the benzene blend, when operated at a rich carburetor setting, was high.

This opens up the question as to whether comparative antiknock tests should be made at a given needle valve or jet setting in the carburetor or whether they should be made at a constant fuel-air ratio or held constant in this respect by means of exhaust gas analyses. Benzene, besides being intrinsically a knock suppressor, adds to its intrinsic antiknock effect on two counts: (1) It makes the entire fuel more volatile; and (2) owing to its higher B. t. u. content a benzene blend always runs rich, despite the counter-balancing effect of higher viscosity which permits a smaller amount to pass through a given needle-valve setting. This fact is illustrated in the accompanying chart, where it will be noted that benzene is the only material which does not give a straight-line relation against the standard. Each additional increment of benzene used gives a greater antiknock effect than the preceding increment.

Table I—Effect of Testing under Different Conditions

SPEED	OUTPUT			APPLIED FIELD VOLTAGE	COMPRESSION RATIO	SPARK POSITION	MIXTURE (JET NO.)	ANILINE EQUIVALENT
R. p. m.	*Volts*	*Amps.*	*Watts*					
PRESSURE-CRACKED MIDCONTINENT GASOLINE								
1125	35	× 28.5	= 1000	54	5.6	Normal	Normal 15	1.10
1125	32	× 25.5	= 815	43	6.0	Normal	Normal 15	1.11
1125	40	× 32	= 1280	70	5.2	Normal	Normal 15	1.17
1125	34.5	× 28	= 966	51	5.6	Normal	Normal 15	1.12
1125	33	× 26	= 858	45.5	5.6	Advanced	Normal 15	1.08
900	29	× 24.5	= 710	46	5.6	Normal	Normal 15	1.05
1250	38.5	× 31	= 1175	57	5.6	Normal	Normal 15	1.16
900	31	× 25	= 775	70	5.6	Normal	Normal 15	1.18
900	39	× 28	= 1093	46	5.6	Normal	Lean 13	1.11
25 PER CENT BENZENE IN STRAIGHT-RUN MIDCONTINENT GASOLINE (STANDARD)								
1075	36	× 29	= 1045	59	5.6	Normal	Normal	2.31
1075	38	× 31.5	= 1198	73	5.4	Normal	Normal	2.33
1075	38	× 31.5	= 1198	67	6.0	Normal	Normal	2.35
1200	35	× 28.8	= 1008	58	5.6	Normal	Normal	2.32
950	35	× 28.5	= 1008	73	5.6	Normal	Normal	2.31
1075	39	× 32	= 1248	76	5.6	Normal	Rich	2.62

Unless it is essential that we report antiknock results in terms of benzene blends, the only time when the fuel-air ratio becomes important in antiknock testing is when benzene blends and similar mixtures are tested, which in most laboratories does not happen very frequently. We suggest, therefore, at least until some very simple method is devised for regulating this extra richness of the mixture in the case of benzene blends, that it be disregarded and that the unknown and the standard fuel be run at the same needle-valve setting.

Discussion of Antiknock Values in Table II

We have tested only two authentic straight-run paraffin-base gasolines. They came from Wellsville and Cabin Creek districts, respectively, and had closely similar Engler curves with 437 end points. The antiknock values were −0.48 and −0.50. The pressure-cracked paraffin-base was of Cabin Creek origin.

The pressure-cracked midcontinent is from the same crude as our standard fuel. When midcontinent gasoline is mentioned in this table it refers to this standard.

Table II—Antiknock Values of Gasolines

	ANILINE EQUIVALENT
Straight-run from paraffin-base crude (437)[a]	−0.50
Straight-run midcontinent (437) (intermediate standard)	0.00
41 per cent isoöctane + 59 per cent *N*-heptane (provisional)	0.00
Pressure-cracked paraffin-base (437)	0.93
Pressure-cracked midcontinent (437)	1.45
Vapor phase cracked paraffin-base (437)	(av.) 8.00
Straight-run California (420)	(av.) 4.50
Pressure-cracked California (410)	3.30
3 cc. tetraethyl lead per gallon midcontinent (0.8 cc. per liter)	5.50
Straight-run paraffin-base (400)	0.33
Straight-run paraffin-base (375)	0.63
Pressure-cracked midcontinent (400)	2.15
Pressure-cracked midcontinent (375)	2.43
10 per cent casinghead in midcontinent	0.68
25 per cent casinghead in midcontinent	1.03
50 per cent casinghead in midcontinent	1.98
Commercial premium antiknock gasoline No. 1	3.75
Commercial premium antiknock gasoline No. 2	3.75
Commercial premium antiknock gasoline No. 3	3.42
Commercial non-premium antiknock gasoline No. 1	3.00
Commercial non-premium antiknock gasoline No. 2	1.88
Commercial ethyl gasoline No. 1	4.5 to 7.0
Commercial ethyl gasoline No. 2	4.5 to 5.5

[a] Numbers in parenthesis are end points.

The increase in antiknock value of cracked gasoline over the straight run from the same crude is of the same order of magnitude for paraffin-base and midcontinent base crudes, but this relation does not appear to hold in the case of the two California samples. We understand that these straight-run and cracked materials came from the same crude, but have not yet had opportunity to obtain duplicate samples. We repeated the tests several times and believe our figures correct for the particular samples tested. It is possible, of course, that the rearrangements in naphthenic-base stocks caused by cracking are not favorable to the formation of knock-suppressing materials and might even destroy them.

The antiknock values of the straight-run paraffin-base and pressure-cracked midcontinent (standard) with reduced end points are interesting in view of a recent article in which it was stated that reduction of the end point did not improve the antiknock rating. We have tested a large number of such samples and in all cases the antiknock value increased as the end point was reduced.

We even made up in the laboratory a few gallons of a mixture containing the lights (50 per cent) of Pennsylvania gasoline and the heavy ends (50 per cent) of California gasoline. The mixture was a reasonably good antiknock fuel, the knock-suppressing material obviously being in the heavier half coming from the California gasoline. We then redistilled the mixture cutting at 400 and 375 and, as in all other cases, the antiknock rating increased as the end point was reduced.

The casinghead used in the blends with the standard fuel came from the same midcontinent field. The unsaturates were practically nil. Other recovered gasolines from different sources gave somewhat different results, the increases in antiknock value were of this same order.

The data on the commercial samples are self-explanatory.

Discussion of Chart

All the curves, except that for benzene, are nearly straight lines. We have already suggested that the volatility effect of the low-boiling benzene gives an extra effect, like casinghead additions, which explains this. Curves for isoöctane or diisobutylene in the standard fuel show this effect to a reduced extent, probably because their boiling points (210° and 215° F., or 99° and 101° C., respectively) are higher than that of benzene (176° F. or 80° C.). They do not increase the mean volatility to the extent that the benzene does.

The straight-line relation of the isoöctane and the *N*-heptane is explained on this same basis, since they have nearly the same boiling points; so regardless of the mixture the mean volatility remains nearly constant.

When two gasolines of about the same average volatility are blended the antiknock values on the aniline scale show a straight-line relation to the percentage in the blend.

Rubber Stopcock Lubricants for High Vacuum and Other Uses[1]

By Martin Shepherd and P. G. Ledig

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THE preparation of suitable lubricants for stopcocks has always been a vexing problem. A review of the literature yields little material of real helpfulness, though the general importance of the subject warrants a critical study. While no such attempt has been made in the present instance, there is presented some material resulting from the occasional experiences of several years. The experimental development of a number of suitable lubricants is reported, and the method of preparation is described in detail.

A stopcock grease intended for high-vacuum work or general gas investigation should smoothly lubricate the ground surfaces and at the same time possess sufficient solidity or body to prevent its quickly working out from between these surfaces. It should have a very low vapor pressure at ordinary temperatures, and be as free as possible from objectionable chemical or solvent action.

A number of substances have been used as lubricants. Aside from rubber lubricants, the more common are phosphoric acids, castor or other vegetable oils, lanolin or mixtures of lanolin with paraffin waxes, graphite or graphite-oil mixtures, molasses, petroleum jellies, and mixtures of heavy petroleum oils with petroleum waxes. These possess certain advantages for special uses, but are unsuited for general gas or high-vacuum work, since they do not altogether meet the simple requirements mentioned.

Lubricants compounded from rubber with paraffin waxes, jellies, and oils are in more general use than other types. They have been shown to possess the desirable properties mentioned, with the exception of freedom from certain chemical or solvent action which may occur in specialized work. Their superiority for high-vacuum work is recognized.

The general tendency in preparing this type of lubricant is to use too low a percentage of rubber, too low a temperature, and too short a time of processing. This has resulted in a great many unsatisfactory mixtures. It is very difficult to reproduce a lubricant of given properties. With these considerations in mind, a number of experimental rubber lubricants were prepared in a thermostated electric oven, the mixtures being contained in a large porcelain casserole and continuously stirred by a motor-driven propeller. Considerable resistance is offered the revolving propeller, so it was geared to produce sufficient mechanical advantage.

Development of Suitable Lubricants

The standardized preparation of suitable lubricants was developed from a study of the following variable factors: (1) kind of rubber, (2) kind of vaseline (petroleum jelly), (3) kind of paraffin, (4) percentage composition, (5) temperature of processing, (6) time of processing, (7) method of cooling, and (8) aging.

KIND OF RUBBER—Four kinds of rubber were employed—pale crepe, smoked sheet, pure Para, and sprayed latex. All were obtained freshly milled. In some cases the desired amount of paraffin was milled directly with the rubber.

Lubricants of the same percentage composition, but made from the different rubbers, had markedly different properties. Pale crepe and smoked sheet have so far given the best results. Smoked sheet produced a dark-colored lubricant of greater body than the others, which required no aging period before being entirely suitable for use and retained a satisfactory consistency over a period of 8 to 12 months. The pale-crepe lubricants were of an attractive light color, and possessed less body than the smoked-sheet compound but more than the Para. The lubricants containing a higher percentage of pale crepe had a semifluid consistency when freshly made and required a 10-day period to set to a satisfactory solid grease; but if they were properly prepared, aging over a period of 12 to 18 months did not render them unsuitable for use. Lubricants containing much Para were dark-colored and semifluid. This consistency did not change except over periods as long as 12 months and when the lubricant set it was not a smooth grease, but rubbery and gummy. Sprayed latex showed a marked tendency to oxidize too easily, and lubricants made with it, while of a good consistency, were very dark and had a burnt odor.

KIND OF VASELINE—Several brands of yellow and white vaselines were used. While the chemical composition of the vaseline should play an important part in determining the character of the final product, this is beyond reasonable control. No actual difference in consistency was observed when different samples were employed, except for one type: Some of the petroleum jellies recently placed on the market are apparently more crystalline than the average product of earlier years, and these should be avoided, since they produced granular lubricants. A white vaseline produced a clearer product, and may be desired for this reason.

KIND OF PARAFFIN—Paraffin ranging from 30° to 50° C. melting point was used. Good results were obtained with 36° and 40° C. products. The 50° C. product tended to produce a "caky" lubricant. In some cases a lighter lubricant for special use was obtained by adding small amounts of a heavy liquid petrolatum to a lubricant possessing a heavy body.

PERCENTAGE COMPOSITION—The percentage composition of the lubricant is determined by its intended use. High-vacuum work requires a viscous lubricant containing a high percentage of rubber. General laboratory work, including manipulation of gases at or about atmospheric pressure, calls for a lighter lubricant, yet one possessing sufficient body to prevent its quickly working from between the ground surfaces of the cock. Such a lubricant, if suitable during winter months, may prove too light for summer use. A third lubricant which finds applicability to some work, including volumetric buret cocks, is a light grease permitting easy manipulation of the stopcock. The following compositions for the three general purposes—high vacuum, general, and light—have been developed, although it is hoped to improve the high-vacuum formula:

HIGH-VACUUM	
	Parts
Pale crepe	31
Vaseline (white)	24
Paraffin, m. p. 36° C.	5
GENERAL	
Pale crepe	6
Vaseline	7
Paraffin	1
LIGHT	
Smoked sheet or pale crepe	10
Vaseline (white or yellow)	18
Paraffin, m. p. 30° C.	1

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[1] Received April 25, 1927. Published by permission of the Director of the National Bureau of Standards.

In each case stir continuously for 190 hours at 155° C. Remove to 2-ounce ointment cans, a small portion to each can, and chill on ice immediately. Allow to age for 10 days before use.

If the percentage of rubber exceeds the limit given for the high-vacuum type, the lubricant tends to become a sticky semifluid. The formula recommended by Travers[2] and others—16 parts of pure Para, 8 parts of vaseline, 1 part of paraffin—has this decided objection. In time the rubber gums out of such a solution. Higher temperatures produce a lubricant free from this objection, but one in which the rubber has oxidized considerably. Increasing the percentage of paraffin over that given for the high-vacuum type produces a "caky" lubricant. For special lubricants the percentage of vaseline may be increased above that given in type L (light), or a heavy paraffin oil substituted; but for general use such a formula produces a lubricant without enough body.

A lubricant made several years ago from rubber bands seemed excellent for high-vacuum work. Several attempts to duplicate it failed. The high-vacuum type was then melted and powdered sulfur in varying amounts added in a further attempt to duplicate this lubricant, but the resulting product was quite unsatisfactory.

An effort to make a lubricant by dissolving the rubber in cymene or similar solvent was attempted by others in the rubber laboratory, and some apparently beautiful products were prepared by M. Levin in the remarkably short time of 2 hours. No procedure tried was successful in thoroughly removing the solvent, however, and these lubricants possessed notable vapor pressures. This method has been used by various investigators, but those engaged in high-vacuum work report its failure. The method may possibly yield successful results after further experimentation.

Temperature of Processing—Experience has shown that rubber which appears to be in solution still possesses properties which suggest some sort of structure. It is necessary to heat the solution to a temperature high enough to destroy this structure; yet at too high a temperature the rubber is oxidized. The allowable range proved to be rather narrow—150° to 160° C. In most cases 155° C. was selected. A pale-crepe compound darkened at 160° C. Sprayed latex oxidized badly at 150° C., and a lower temperature (undetermined) would be necessary for this rubber.

Lubricants were not processed in inert atmosphere at elevated temperatures for two reasons: First, since stirring was found essential, the equipment would necessarily become more complicated and it was not deemed worth while in the present instance. Secondly, the dissolved oxygen originally in the rubber comes off very slowly, and there would still remain some possibility of oxidation from this source, even though an inert atmosphere or vacuum were employed in connection with higher temperatures.

Time of Processing—Samples taken during the various stages of processing were held 6 months to observe the changes due to aging. It appears that the rubber does not satisfactorily break down at 155° C., even though actual solution has occurred, much before 170 hours have elapsed. A sample taken between thumb and finger, pressed together, and drawn out by separating thumb and finger to their full extent, should present a single unbroken thread of lubricant. When the rubber is not thoroughly broken down, this procedure results in the production of a multitude of fine threads, which upon rapid repetition of the test will float off into the air. Rubber in such a lubricant has been found to gum out eventually, usually after being in a stopcock 1 or 2 weeks. It also exhibits a tendency to produce rings around the bore of the plug of a stopcock.

The occurrence of an actual chemical reaction involving the rubber, and its importance in determining the suitability of the product, was clearly shown by continuing the processing for 376 hours in the case of the high-vacuum types. Samples of the mix were taken at regular intervals, beginning at 72 hours, when the rubber had been in complete solution for at least 48 hours, and terminating with a 376-hour sample.

The 72-hour samples, when tested by separation between thumb and forefinger, produced fine floating threads. They gummed out in a stopcock, and at the end of 6 months were somewhat hardened and gummy in the storage container. The subsequent samples taken at 24-hour intervals up to 170 hours showed the same characteristic in a uniformly decreasing amount. The 170-hour product was fairly satisfactory. The 190-hour sample did not exhibit this undesirable characteristic. It was smooth and quite satisfactory in every respect when fresh from the oven and after aging. Samples taken at 260 to 360 hours were apparently further improved, but 6 months' aging developed their unsuitability, the rubber gumming out to form a hard, greaseless, elastic mass. This could be redissolved in excess vaseline, but the redissolved product still exhibited the gummy characteristic of the original aged product. The 360-hour sample was taken late in the afternoon. After processing overnight, examination in the morning (376 hours) disclosed that the mix had changed abruptly from a liquid to a solid mass, not unlike a very heavy, sticky art gum. An equal weight of vaseline failed to redissolve this at 155° C., but instead was taken up by the rubbery solid to form a lighter solid more nearly resembling art gum and slightly greasy to the touch. It was possible to redissolve a small portion of this in excess vaseline at an elevated temperature (soft Bunsen flame), but the cooled product still exhibited the gummy characteristic of the original solid.

The apparent physical solution of the rubber is evidently not sufficient. A more fundamental change, probably chemical in its nature, must be brought about in order to produce a satisfactory lubricant. This chemical equilibrium reaches an optimum (for compositions herein given) at temperatures ranging from 155° to 160° C. and reaction times of 180 to 200 hours. The optimum conditions can be overstepped. The exact nature of the changes is not thoroughly understood, although it may be considered to resemble depolymerization.

Cooling—A sample removed from the oven on the thin blade of a steel spatula was perfectly smooth, while larger samples, 2 to 4 ounces, poured from the same mix into an ointment can, cooled slowly and formed a relatively coarse, granular or crystalline compound. This observation led to the adoption of a procedure involving quick cooling. A $^{1}/_{4}$-inch (6-mm.) layer was poured into a 2-ounce tin ointment can and the can capped and immediately placed on ice. A fine smooth grease resulted from this treatment. The apparent explanation of this phenomenon is noted in the work of Carpenter.[3] Using recrystallized waxes possessing narrow ranges of melting point, he was able to produce entirely different crystal forms without change of molecular weight, by the use of different solvents, concentrations, and rates of cooling. In general, rapid cooling from solvents of high boiling point produced small needle-shaped crystals, difficult to find, or interlacing worm-shaped forms. Slow cooling produced large rhomboid plates or foliaceous masses.

It is evident that a satisfactory crystal form for lubrication is attained by the rapid cooling. This form may, on long standing, change over to the larger rhomboid plates, and it then becomes desirable to restore the grease to its

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[2] "Study of Gases," p. 24, Macmillan and Co., Ltd., London, 1901.

[3] *J. Inst. Petroleum Tech.*, **56**, 12, 288 (1926).

preferable crystalline state by reheating and subsequent rapid cooling.

It was subsequently noted that Ardagh and Davidson[4] cooled a lubricant on an aluminum sheet and that this practice is established in other laboratories.

AGING—As indicated above, aging plays an important part in determining the final quality of a lubricant. Some compositions set from a sticky semifluid to a smooth grease in 10 days. Others, suitable at first, caked out in periods ranging from 6 to 12 months. In general, the smoked sheet lubricants possessed sufficient body when fresh from the oven, and retained a desirable consistency until used up—say, 12 to 24 months. In the lubricants containing much rubber (high-vacuum type), though not in the case of the lighter lubricants, pale crepe requires a definite aging period. Para requires a long aging period. Latex more nearly resembles Para.

Lubrication of Stopcocks

There are many methods of lubricating a stopcock, and not all are entirely efficacious. A method familiar to many acquainted with high-vacuum technic may be recommended. The lubricant is applied in two parallel longitudinal streaks, one on either side of the plug and away from the bore. The streaks should be as thin as possible, and contain only enough lubricant to flow entirely around the plug. The lubricant so placed, the plug is held above a soft Bunsen flame, so that the grease just melts to form a smooth ridge of semicircular cross section. The key is allowed to cool and then carefully inserted into the barrel so that the bores of plug and barrel coincide. The plug is pressed downward into place, with little, if any, turning, the lubricant forming V's on either side of bore and pressing out all air films until it has flowed smoothly around the entire grinding.

A stopcock lubricated with a high-vacuum or heavy grease should be turned slowly and smoothly with a very slight pressure of the plug into the barrel. A good high-vacuum lubricant presents enough resistance to turning to require the use of two hands for nice manipulation, one to support the bottom of the cock against strain and the other to press slightly and turn.

If a stopcock is finely ground and carefully lubricated with a type of lubricant suitable for high vacua, it will occasion the worker in high vacua no difficulty because of stopcock leaks. This laboratory has had several systems of such cocks hold a vacuum for 2 years, as indicated by a barometric manometer (accurate to 0.2 mm.) which showed no pressure change. An apparatus in constant use, containing paraffin hydrocarbon gases whose vapor pressures were 0.0001 mm. or less at $-210°$ C., and involving seventeen plain stopcocks without mercury seals, consistently failed to show pressure increases greater than 0.0001 to 0.0005 mm. over 2 to 4 weeks time, as measured by a McLeod gage.

Well-ground, well-lubricated stopcocks do not stick. Such stopcocks have been known to stand idle over periods of several years without exhibiting any tendency to "freeze."

It is believed that the disfavor with which stopcocks are held by many investigators is not warranted, since varied experience has clearly shown that a well-ground cock properly lubricated is an entirely satisfactory and extremely handy unit of apparatus in the great majority of gas investigations.

[4] *Can. Chem. Met.*, **9**, 137 (1925).

Determination of Isopropyl Alcohol in Presence of Acetone, and of Methylethylketone in Presence of Secondary Butyl Alcohol[1]

By H. A. Cassar

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IN INVESTIGATING the oxidation of isopropyl alcohol to acetone, analytical methods were lacking which would quickly and accurately determine isopropyl alcohol in a mixture of the alcohol plus its oxidation product, acetone. It was finally found that by oxidizing the alcohol quantitatively to acetone by means of chromic acid solutions and titrating back the excess chromic acid the isopropyl alcohol could be readily determined in less than an hour.

A similar method, at slightly different concentrations, was found to hold for secondary butyl alcohol in the presence of methylethylketone; but whereas acetone could be determined in the presence of isopropyl alcohol by Messinger's well-known method,[2] applying a correction of 1 to 2 per cent for the isopropyl alcohol present, it was not possible to determine methylethylketone in the presence of secondary butyl alcohol without a considerable modification of the method.

This method when applied directly to methylethylketone under certain conditions gives results that are constantly 10.5 per cent too high, over a wide range of alkali and ketone concentrations, and hence methylethylketone can be easily and quickly determined by the iodine method. This method is not quite independent of the presence of secondary butyl alcohol; and a mixture of 50 per cent methylethylketone and 50 per cent secondary butyl alcohol gives results which are 2.5 per cent too high, over and above the 10.5 per cent. The procedure will therefore be to determine the secondary butyl alcohol content by means of the dichromate oxidation method and correct the final methylethylketone value found by a quantity which will not exceed 3 per cent (Figure 1).

The probable reason for the high value found by the iodine method of determining methylethylketone is that the two following reactions occur simultaneously:

$$CH_3CH_2COCH_3 + 3I_2 + 3NaOH \leftrightarrows CHI_3 + CH_3CH_2COOH + 3NaI + 2H_2O$$

$$CH_3CH_2COCH_3 + 5I_2 + 4NaOH \leftrightarrows 2CHI_3 + CH_3COOH + 4NaI + 3H_2O$$

In one case six atoms of iodine are used up, and in the other case ten.

The methods herein described have been used on commercial samples for more than a year, and the results have always checked with the results of careful fractional distillation.

Isopropyl Alcohol and Acetone Mixture

A quantity of the isopropyl alcohol and acetone mixture containing about 15 grams of isopropyl alcohol is accurately

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[1] Received May 4, 1927.

[2] *Ber.*, **21**, 3366 (1888); Goodwin, *J. Am. Chem. Soc.*, **42**, 39 (1920).

weighed out and made up to 500 cc. Twenty-five cubic centimeters are pipetted out into 100 cc. of 45 per cent (by weight) sulfuric acid contained in a glass-stoppered 250-cc. Erlenmeyer flask and 50 cc. of 1 *N* sodium dichromate solution are added from a buret, a few drops at a time at first, with careful shaking until the solution turns green before adding more. The addition of dichromate should take about 10 minutes, and the temperature should not go above 25° C. The stoppered flask is then put aside for a half hour, and then the contents are made up to exactly 500 cc. Twenty-five cubic centimeters are pipetted out and added to 200 cc. of water, to which are finally added 25 cc. of a 12 per cent potassium iodide solution. The flask is stoppered and put aside for 10 minutes and then titrated by means of 0.1 *N* sodium thiosulfate. It is very useful at this point to use activated starch, as the end point is very perplexing and elusive with ordinary starch. Activated starch is made by treating ordinary starch with a very dilute solution of hydrochloric acid for 24 hours, washing on a Büchner funnel free from acid, and heating for 3 days at 100° C.[3]

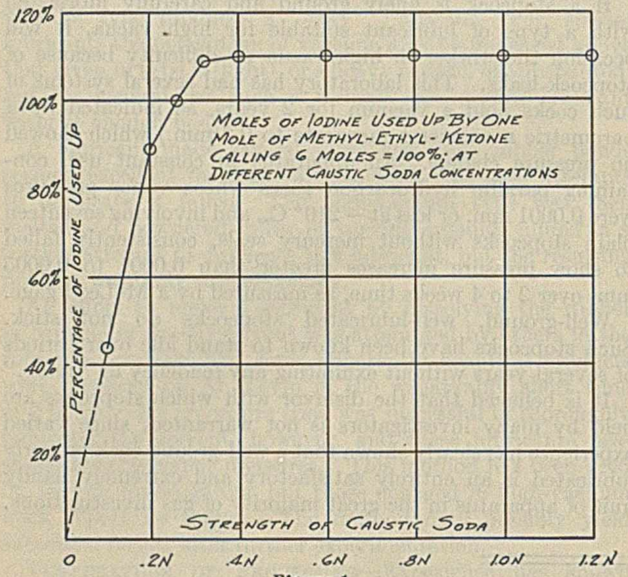

Figure 1

Samples of pure isopropyl alcohol, taken from several liters that had been carefully dried and fractionated to 0.1° C., were analyzed and found to be in error to the following extent: −0.1, −0.47, +0.32, and +0.48 per cent. Addition of 40 per cent of acetone did not cause variations in the final results beyond the experimental error. A sample of Kahlbaum's isopropyl alcohol, whose strength had been previously determined by a specific gravity determination as 99.1 per cent, was also used as a check.

CALCULATION—

$$CH_3CHOHCH_3 + O \longrightarrow CH_3COCH_3 + H_2O$$

One cubic centimeter of 1*N* dichromate gives 0.001 equivalent of oxygen, which corresponds to 60.214 × 0.001 × 0.5 = 0.03003 gram of isopropyl alcohol.

Methylethylketone in Presence of Secondary Butyl Alcohol

PRELIMINARY DETERMINATION OF METHYLETHYLKETONE ALONE—Ten cubic centimeters of a methylethylketone solution, strength 1.1835 grams per 500 cc., were pipetted into 50 cc. of caustic soda ranging from 0.1 to 1.2 *N*. The various mixtures were treated with 25 cc. of 0.1 *N* iodine solution, put aside for 10 minutes, neutralized with sulfuric acid, 0.5 cc. extra of 2 *N* sulfuric acid added, and excess iodine titrated back.

The quantity of iodine solution used up, reckoning on six atoms as 100 per cent, rises from 44 per cent for the weak caustic soda solution to a maximum of 110.6 per cent, and remains constant at that figure.

The sharp break in the quantity of iodine taken up by the methylethylketone solutions is shown in Figure 1. A sample of Kahlbaum's methylethylketone, dried over potassium carbonate and redistilled, was used for this experiment.

In the series described above the iodine added in excess of that used up was about 15 per cent. A similar series was found to behave in the same manner when the quantity of iodine added in excess of that used up was about 35 per cent. There is therefore quite a respectable working margin.

ANALYTICAL PROCEDURE—Ten cubic centimeters of the secondary butyl alcohol and methylethylketone mixture containing about 24 mg. of methylethylketone are pipetted into a glass-stoppered 250-cc. Erlenmeyer flask containing 50 cc. of 1 *N* caustic soda; and 25 cc. of 0.1 *N* iodine solution are added from a buret with constant shaking. The flask is stoppered and allowed to stand for 10 minutes and 25.5 cc. of 2 *N* sulfuric acid are added, and the iodine thus set free is titrated with 0.1 *N* sodium thiosulfate, using starch as an indicator. One cubic centimeter of 0.1 *N* iodine solution is equal to 0.001089 gram methylethylketone.

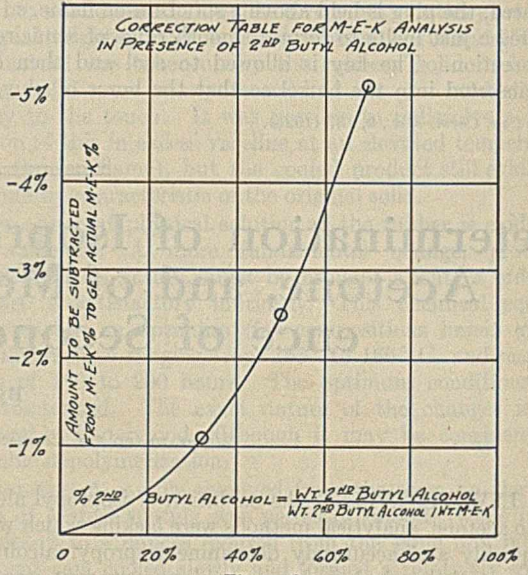

Figure 2

CALCULATION—Reckoning on six atoms of iodine per mol of methylethylketone; and on the empirical factor being 10.2 per cent too high, we get 1 cc. of 0.1 *N* iodine equivalent to 72.08 × 0.0001 × 1/6 × 100/110.6 or 0.001089 gram methylethylketone.

Also deduct 2.6 per cent from the result for every gram of secondary butyl alcohol present with 1 gram of methylethylketone. This is shown in Figure 2, where the circles show the actual variations that were found on adding Kahlbaum's C. P. secondary butyl alcohol, redistilled, to methylethylketone solutions in the proportions stated. Thus, if the mixture to be analyzed is found to contain 10 per cent of secondary butyl alcohol and 20 per cent of methylethylketone, the actual quantity of methylethylketone present will be 20 − 1.2 per cent, that is, 18.8 per cent.

ANALYSIS OF SECONDARY BUTYL ALCOHOL—The secondary butyl alcohol present is analyzed in the same way as isopropyl alcohol, except that the solution after the addition of the sodium dichromate is allowed to stand for 15 minutes instead of 30.

One cubic centimeter of 1 *N* dichromate is equivalent to 0.03705 gram of secondary butyl alcohol.

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[3] Lord and Demorest, "Metallurgical Analysis," 4th ed., p. 225.

Earliest History of the Friedel-Crafts Reaction[1]

By Avery A. Ashdown

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INTEREST in the use of aluminum chloride as a reagent for bringing about chemical reactions on a commercial scale has been growing rapidly during the past ten years. New methods for manufacturing the chloride have led to a product at a figure attractive to industry. In 1923 a little over 5000 tons were manufactured in the United States, while during 1926 the quantity produced reached 16,750 short tons and at a marked decrease in price per ton over that for 1925. Success in the commercial production of aluminum chloride has stimulated a number of industrial processes. The formation of toluene from xylene has been shown to be feasible by Moore and Egloff.[2] Cheaper aluminum chloride has made possible the manufacture of anthraquinone, which is better for vat dyes than that recovered from coal tar.[3] Probably the most outstanding commercial application has been in the cracking of petroleum for gasoline.[4]

The advent of the summer of 1927 marks the fiftieth anniversary of the announcement of the Friedel-Crafts reaction, which has now become of so much interest to the industrial world. It has been one of the most fruitful and far-reaching reactions known to organic chemistry. Indeed, Elbs said: "The Friedel-Crafts synthesis is the one most commonly used. It serves for the preparation of hydrocarbons, ketones, acids, keto acids, and phenols, especially phenol ethers."[5] Had Elbs been writing at a somewhat later date, just so certainly would he have included in his praises the action of aluminum chloride as an agent for cracking hydrocarbons.

To American chemists the discovery of the reaction possesses peculiar interest for, contrary to the belief of many, James Mason Crafts was one of our own fellow citizens. He was born of American parents in the city of Boston in 1839 and there received his early education. He pursued graduate studies in chemistry under Bunsen in Heidelberg and under Wurtz in Paris. After returning home he became the first professor of chemistry at Cornell University. Three years later he went to the Massachusetts Institute of Technology, where he remained until impaired health made him resign active teaching in 1874. He then returned to the laboratory of Wurtz and there he worked for the next seventeen years, much of the time in collaboration with Prof. Charles Friedel. When he came back to America in 1891, he was again associated with the Massachusetts Institute of Technology, serving in turn as a member of the corporation, professor of organic chemistry, head of the department of chemistry, and finally as president of the Institute. In 1900 he resigned the presidency, devoting the rest of his years and strength to scientific work. He died in June, 1917.

The discovery of the Friedel-Crafts synthesis "sprang from an accidental observation on the action of metallic aluminum on chloride of amyl."[6] It is very interesting to note that the commonly accepted statement that an attempt was being made to convert amyl chloride into the iodide by means of aluminum and iodine made its first appearance seven years after the original paper.[7] In spite of the great handicap under which the work was done, the early development of the reaction proceeded with dramatic speed. "The discoverers had at that time only a very small laboratory, with no place for students, and not even provided with the convenience of running water."[6] The first paper was presented to L'Academie des Sciences on June 11, 1877. Peligot was president and the papers were sponsored by Wurtz.[8] "The experiments which demonstrated the wide scope of the reaction were so easy of execution that those described in the first three papers were carried out in the course of five or six weeks."[6] The first paper is a classic for clearness and simplicity in presenting an account of an important discovery. In honor of the fiftieth anniversary of its presentation to L' Academie des Sciences and for the value it may have for readers of English, it is presented here translated from the original French.

The First Observations

In a research which we undertook together we were led to study the action of metallic aluminum in thin plates or leaves on various organic chlorides. We observed that the reaction, slow at first and initiated only by the aid of heat, afterwards accelerated to the point of becoming tumultuous when it was necessary to control it by cooling. The addition of a very small quantity of iodine provoked the reaction, which was always accompanied by an abundant evolution of hydrogen chloride. In the case of certain chlorides, such as amyl chloride, it was accompanied by the formation of numerous gaseous and liquid hydrocarbons, certain of which boiled at a very high temperature. The reaction seemed the more active if a considerable proportion of aluminum chloride was formed.

Aluminum Chloride the Activating Agent

This last circumstance led us to find out if the principal reaction ought not be attributed to the metallic chloride instead of to the metal, as we supposed at first.

It was easy to assure ourselves that such was indeed the case. For example, when a little aluminum chloride was added to amyl chloride we saw at once a vigorous evolution of gas, even in the cold. The gas was composed of hydrogen chloride accompanied by gaseous hydrocarbons not absorbed by bromine. In the midst of the amyl chloride in which the first portions of the aluminum chloride dissolved small droplets were formed. Shortly a layer of dense brown liquid developed and the reaction appeared to pass principally to the interface between the two liquids. We had noticed a similar circumstance in the reaction with aluminum, when a similar brown liquid was produced.

When the reaction had continued long enough, with the aid of a gentle heat to complete it at the end, a quantity of hydrogen chloride could be recovered which corresponded to nearly all the chlorine originally contained in the amyl chloride. An extremely varied series of hydrocarbons, from gases to products boiling above the boiling point of mercury, was also recovered. The residue consisted of aluminum chloride, which sublimed in hexagonal plates or in a crystalline crust when sufficiently heated in a current of an inert gas.

First Conclusions

We have not yet completed the study of the numerous products, the first members of which appear to be in the series of hydrocarbons C_nH_{2n+2} and the higher members of which are much poorer in hydrogen. For the present we wish to make the following observations: First, organic chlorides are attacked by aluminum chloride; second, the greater part of the products formed, which contain a large proportion of saturated hydrocarbons, could not be produced by a simple polymerization of amylene resulting from the subtraction of hydrogen chloride from amyl chloride; third, it seems much more likely that the hydrogen chloride which disengages itself is formed at the expense of two molecules, of which one furnishes the chlorine and the other the hydrogen, and the two parts then unite.

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[1] Adapted from a paper under the title "James Mason Crafts" presented before the Section of History of Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Chem. Met. Eng.*, **17**, 61, 128 (1917).

[3] Phillips, *Ibid.*, **33**, 173 (1926).

[4] McAfee, THIS JOURNAL, **7**, 737 (1915); Egloff, *Ibid.*, **15**, 581 (1923).

[5] "Synthetischen Darstellungs Methoden," Vol. II, p. 144 (1891).

[6] Crafts, *J. Chem. Soc. (London)*, **77**, 1006 (1900).

[7] Friedel and Crafts, *Ann. chim. phys.*, [VI], **1**, 449 (1884).

[8] Friedel and Crafts, *Compt. rend.*, **84**, 1392, 1450 (1877); **85**, 74 (1877).

Synthetical Applications

These observations led us to attempt the application of aluminum chloride under conditions which offered a much larger interest—namely, the possibility of a general synthetical method for furnishing an infinite number of hydrocarbons and even of oxygenated compounds. It occurred to us that on mixing a hydrocarbon with an organic chloride and adding aluminum chloride we might be successful in obtaining a reaction having for its result the combination of the radical which was linked to the chlorine, with the hydrocarbon, minus an atom of hydrogen.

In fact, the method worked with great facility. Amyl chloride was mixed with a considerable excess of benzene. When aluminum chloride was added in small portions we saw the production of a regular reaction, in the cold, accompanied by the evolution of hydrogen chloride. Soon two layers were formed, the lower one being colored brown. As soon as the hydrogen chloride was being evolved, but slowly and only with the aid of heat, the two layers were separated and each was treated with water. After drying and distilling they both gave almost the same products. The difference was that the upper, limpid layer contained a much larger proportion of benzene and of hydrocarbons boiling at relatively low temperature. The lower layer, which contained almost all the aluminum chloride, gave principally products boiling at an elevated temperature. By but few fractionations there was extracted from both a liquid boiling between 185° and 190° C. and having the composition and properties of amyl benzene. This compound could be formed by a reaction expressed empirically by the following equation:

$$C_6H_6 + C_5H_{11}Cl = C_6H_5.C_5H_{11} + HCl$$

Synthesis a General Method

We assured ourselves immediately that the method of synthesis was general and that it was applicable, not only to organic chlorides, but equally to the bromides and the iodides.

Ethyl iodide and benzene were mixed and aluminum chloride was added. We observed the disengagement of thick acid fumes containing hydrogen iodide. After treatment with water and distillation, we were able to isolate ethylbenzene, boiling between 133° and 137° C. The reaction seemed, nevertheless, to proceed a little less cleanly with the iodide than with chlorides and gave a much larger proportion of products boiling at a high temperature. The high-boiling fractions probably contained benzene derivatives in which several atoms of hydrogen were replaced by ethyl groups, but they have not yet been completely studied.

On working with methyl bromide and benzene, under the pressure of a column of 30 cm. of mercury, we observed the same evolution of fuming acid and the production of hydrocarbons boiling at a temperature higher than benzene and containing toluene or methylbenzene.

Furthermore, we obtained toluene and other methyl derivatives of benzene in a very convenient manner by simply passing a current of methyl chloride into benzene mixed with aluminum chloride and heating very gently. Under these conditions hydrogen chloride was disengaged as before and the methyl radical attached itself to the benzene. On fractionating the product, after treating it with water, considerable quantities of toluene were obtained, passing over near 111° C., then products boiling much higher—close to the boiling point of xylene (137° C.), of mesitylene (163° C.), of durene or tetramethylbenzene (190° C.), and above. It appeared that there were formed even pentamethyl and hexamethylbenzenes, products not yet known. At least it seemed clear that the substitution of a methyl group was not affected by one or more methyl groups already fixed on the benzene ring. Had the case been otherwise we should have obtained ethylbenzenes, or even derivatives of benzene containing more complex radicals of the aliphatic series.

We have further ascertained that aluminum bromide and iodide act on organic chlorides or iodides in the same manner as the chloride, forming analogous products.

In the next communication, we shall have the honor of making known to the Academy several other syntheses of complex hydrocarbons and ketones which we have already realized, and we shall endeavor to give an explanation of this reaction so general and so unexpected.

In the second paper, presented just a week after the first, the following preparations were described: diphenylmethane from benzyl chloride and benzene, triphenylmethane from chloroform and benzene, benzophenone from benzoyl chloride and benzene, acetophenone from acetyl chloride and benzene, and *o*-dibenzoyl benzene and anthraquinone from phthalyl chloride and benzene. It was shown, too, that chlorobenzene and dichlorobenzene would not react in the same manner as the alkyl chlorides. An effort to synthesize benzoic acid from benzene and chloro-carbonic ester yielded only carbon dioxide and ethyl benzene. Acidic and alcoholic hydroxyl-bearing compounds were shown not to exhibit analogous syntheses, probably on account of their action on aluminum chloride. The erroneous claim put forward that tetraphenylmethane was formed from carbon tetrachloride and benzene was later explained.

The mistake in the first papers, which announced the formation of tetraphenylmethane, was due to an error in Watt's Dictionary, 2nd Suppl., p. 948, which gives 335° for the boiling point of triphenylmethane. The product isolated boiled 24° higher, namely, at 359°, and was therefore assumed to be a tetraphenyl compound, the percentage composition of the two compounds being not far different. Subsequent determinations made by Crafts with a hydrogen thermometer showed 359° to be the boiling point of pure triphenylmethane.[9]

Triphenylmethane	93.01% C	6.99% H
Tetraphenylmethane	93.41% C	6.59% H

The third paper was presented on July 9, 1877, only five weeks after the first. The use of chlorides other than aluminum was studied. The reaction of Zincke,[10] in which diphenylmethane and phenyltolyl methane were formed from benzyl chloride and benzene and toluene, respectively, by the use of zinc dust, was shown to be due to zinc chloride. Ferrous and ferric chlorides were also found to be useful. On the other hand, magnesium chloride, cobalt chloride, anhydrous cupric chloride, and antimony trichloride gave no reaction under the conditions which they used. The double salt, sodium-aluminum chloride, was found to be reactive, only much less so than pure aluminum chloride.

It was also pointed out that chlorides other than organic could undergo a similar reaction in the presence of aluminum chloride. For example, phosphorus trichloride heated with an excess of benzene in the presence of aluminum chloride gave a product in which phosphorus was combined with the organic radical.

The paper closed with a proposed mechanism "of the curious reaction which had already given so many diverse products and would certainly give a great many more." The hypothesis was proposed that a compound was formed between the hydrocarbon and the aluminum chloride, as indicated by the formula $C_6H_5.Al_2Cl_5$.

In spite of numerous experiments, however, but little could be concluded on this point. "We still have no decisive proof to contribute in favor of the hypothesis we have fashioned for the mechanism of the reaction."[11]

So end the first accounts of a far-reaching discovery. In six weeks of the summer of 1877, Friedel and Crafts had shown its dependence upon certain metallic chlorides, particularly aluminum chloride, its wide applicability, and something of its limitations. They had also proposed an interesting hypothesis to explain its mechanism. From the beginning they were aware of its commercial possibilities. In the Friedel Memorial Lecture Mr. Crafts stated: "Triphenylmethane and its homologs were prepared on a large scale, and these seemed to offer a new method of making aniline dye stuffs commercially."[6] Probably the first patent was granted to Charles Denton Abel,[12] "of No. 20 Southampton Building, in the County of Middlesex, for the invention of 'Improvements in the Treatment of Hydrocarbons for Their Purification and Conversion into Other Products.' (A communication from abroad by Charles Friedel and James Mason Crafts, both of Paris, in the Republic of France.)" So much

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[9] Crafts, *J. Chem. Soc. (London)*, **77**, 993 (1900).

[10] *Ber.*, **2**, 737 (1869); **4**, 298 (1871).

[11] Friedel and Crafts, *Compt. rend.*, **85**, 77 (1877).

[12] British Patent 4769 (December 15, 1877).

was claimed in the patent that it reads like a prophetic vision of our own day. Unquestionably, the great significance of the earliest studies on the reaction lay in the secure foundation which had been built for an enormous development in synthetical, theoretical, and industrial organic chemistry. The fiftieth anniversary of the discovery witnesses great and vigorous growth in the importance and use of the Friedel-Crafts reaction.

Nitrogen as a Catalyst in the Determination of Sulfur in Coal by the Bomb-Washing Method[1]

By J. F. Kohout

Commercial Testing and Engineering Co., Chicago, Ill.

At the meeting of Committee D-5 of the American Society for Testing Materials held in Pittsburgh, Pa., in November, 1926, three methods for the determination of sulfur in coal were presented—namely, the Eschka, the sodium peroxide fusion, and the bomb-washing method.[2] The Eschka and sodium peroxide methods give results which are very slightly higher than the bomb-washing method as ordinarily used. This paper deals with the bomb-washing method alone, and shows how the bomb-washing method may be brought into agreement with the other two methods.

Some form of catalytic agent is required for the complete oxidation of sulfur to sulfuric acid by combustion processes. This is true whether the sulfur is being burned in a large commercial sulfuric acid plant or in an oxygen bomb calorimeter. The catalysts usually employed in the acid plants are platinum or platinized asbestos or oxides of nitrogen. In the oxygen bomb the oxides of nitrogen are the agents used. This function of the oxides of nitrogen was shown by Regester.[3] This nitrogen ordinarily comes from the coal and from the air in the bomb. Part of it is oxidized when the coal or coke burns in the bomb charged with oxygen under pressure. The oxides of nitrogen form the catalytic agent required for the conversion of the sulfur.

The American Society for Testing Materials in its method for calorimetric determination on coal[4] specifies that at least 5 per cent of nitrogen be present in the bomb atmosphere. Since a small part of the nitrogen is oxidized in the bomb, it was thought that by increasing the total amount of nitrogen in the atmosphere in the bomb to 10 or 15 per cent the amount of oxides of nitrogen formed would be increased. This increased quantity of mixed oxides insures the complete oxidation of the sulfur in the coal or coke to sulfuric acid in 5 minutes. This is the average length of the combustion period in a heat value determination as made by any standard oxygen bomb calorimeter.

Sulfur Determinations

A Parr illium bomb of 370 cc. capacity was used, 0.5 cc. of water being placed in the bomb to absorb the acids formed when the 1-gram sample was burned.

When oxygen alone was used the pressure in the bomb was 22 atmospheres. When the nitrogen-oxygen mixture was used the nitrogen was run into the bomb to a pressure of 3 atmospheres, and the total pressure in the bomb was then increased to 25 atmospheres with oxygen.

The nitrogen and oxygen cylinders were connected to the pressure gage and bomb union with a T connection, so that either oxygen or nitrogen could be introduced into the bomb without disconnecting it.

After ignition the bomb was allowed to stand in water for 5 minutes. At the end of this time the gases were slowly released from the interior, so that the pressure in the bomb fell to atmospheric in about 2 to 3 minutes. The interior of the bomb, including the valve, was thoroughly washed with distilled water containing 1 cc. of saturated methyl orange solution to 1 liter of water, until the indicator gave no test for acid. The washings were neutralized with sodium carbonate solution, 2 cc. of ammonia water were added, and the solution was boiled and filtered. The filtrate was acidified with hydrochloric acid, 3 cc. of bromine water were added, and the solution was boiled to expel the bromine. Ammonia was added to neutrality and then 1 cc. of concentrated hydrochloric acid was added, and the solution heated to boiling. The sulfur was precipitated in the boiling solution with hot 10 per cent barium chloride solution. The barium sulfate was allowed to settle in the hot solution for about 2 hours, and was then filtered out, ignited, and weighed.

Table I—Per Cent Sulfur in Coal
(Figures on dry basis)

Sample[a]	Oxygen	Oxygen and Nitrogen	Diff.	Sample[a]	Oxygen	Oxygen and Nitrogen	Diff.
1	1.17	1.17	0.00	21	0.68	0.67	−0.01
2	0.58	0.56	−0.02	22	1.70	1.71	+0.01
3	0.60	0.61	+0.01	23	2.23	2.25	+0.02
4	8.01	8.08	+0.07	24	3.65	3.69	+0.04
5	4.47	4.55	+0.08	25	4.49	4.62	+0.13
6	5.55	5.63	+0.08	26	5.20	5.36	+0.16
7	2.59	2.61	+0.02	27	6.64	6.64	0.00
8	1.36	1.38	+0.02	28	6.65	6.83	+0.18
9	1.89	1.88	−0.01	29	6.64	6.71	+0.07
10	6.32	6.31	−0.01	30	3.77	3.87	+0.10
11	3.11	3.19	+0.08	31	1.88	1.92	+0.04
12	5.12	5.35	+0.23	32	3.12	3.14	+0.02
13	6.47	6.62	+0.15	33	0.78	0.74	−0.04
14	6.19	6.29	+0.10	34	2.58	2.64	+0.06
15	0.97	0.96	−0.01	35	1.85	1.85	0.00
16	0.55	0.54	−0.01	36	1.41	1.55	+0.14
17	3.46	3.46	0.00	37	0.97	0.97	0.00
18	3.69	3.76	+0.07	38	0.78	0.77	−0.01
19	1.16	1.16	0.00	39	5.02	5.22	+0.20
20	0.79	0.79	0.00	40	0.80	0.80	0.00

[a] All coals were bituminous except 1, 2, 16, and 40, which were semi-bituminous, and 3, which was coke.

It will be noted from Table I that in most cases the effect of the added nitrogen was to increase slightly the amount of sulfur obtained. The exceptions where a decrease is shown are low-sulfur coals, and the differences are so small that either value could be taken as the true percentage of sulfur. The increase is generally most marked in the coals of high sulfur content. The values in the table are the averages of two or more determinations.

Determination of Heat Values

The heat values of the last five coals (36 to 40, inclusive) were determined to see if the added nitrogen interfered in any way with the B. t. u. determination. The results (Table

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[1] Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Selvig and Fieldner, This Journal, **19**, 729 (1927).

[3] *Ibid.*, **6**, 812 (1914).

[4] Am. Soc. Testing Materials, Standards, p. 1008 (1924).

II) indicate that no complication is introduced, and check as closely as could be desired.

Table II—Heat Values

(Figures on dry basis)

	British Thermal Units, Using:			Titer, cc. Na_2CO_3 Soln.		
Sample	Oxygen	Oxygen and Nitrogen	Diff.	Oxygen	Oxygen and Nitrogen	Increase
36	13,015	13,011	4	26.0	39.0	13.0
37	13,285	13,276	9	23.0	37.0	14.0
38	13,801	13,814	13	21.0	35.0	14.0
39	12,136	12,120	16	50.5	64.5	14.0
40	14,914	14,903	11	22.0	39.0	17.0

The total heat liberated in the calorimeter was greater when the nitrogen was used, but the washings from the bomb were more strongly acid, so that the correction for acid and sulfur overcame the effect of the greater rise in temperature. The washings were titrated with a sodium carbonate solution (3.658 grams per liter of water) to determine the acidity correction. From 13 to 17 cc. more solution were required to neutralize the bomb washings when the nitrogen was used.

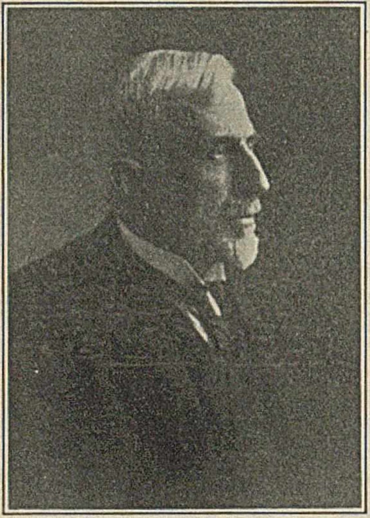
Conclusions

The effect of added nitrogen in the oxygen bomb calorimeter is to increase slightly the amount of sulfur obtained by the bomb-washing method for the determination of the sulfur in coal and to bring the results obtained by the three methods generally used for the determination into substantial agreement. No complication in the heat value determination is introduced thereby.

F. J. Moore—Historian of Chemistry[1]

By Tenney L. Davis

Massachusetts Institute of Technology, Cambridge, Mass.



F. J. Moore

All American students of the history of chemistry are familiar with Moore's book upon the subject. Many owe to it their first interest in the history of their science. But only a few of us have had the privilege of a personal acquaintance with its genial author. Prof. Forris Jewett Moore died suddenly on November 20, 1926, at his home in Cambridge, Mass. The accompanying portrait is reproduced from a photograph taken ten days before that date.

F. J. Moore was born at Pittsfield, Mass., June 9, 1867. He graduated from the Stevens High School of Claremont, N. H., in 1884, and received the degree of bachelor of arts from Amherst College in 1889. At Amherst he studied chemistry with Prof. William P. Harris, and after graduation continued at that college for another year as a teacher in the laboratory. He then went to the University of Heidelberg, where he studied with Victor Meyer and with Gattermann, carried out under the direction of the latter his doctor's research on the isolation of the aromatic sulfonic acids, and was awarded the degree of doctor of philosophy in 1893. In 1892 he married Miss Emma Tod of Edinburgh, Scotland. After returning to the United States he served for one year as instructor of chemistry at Cornell University. In the autumn of 1894 he came to the Massachusetts Institute of Technology. Here he first taught analytical chemistry, but soon transferred to the organic chemistry section of the chemistry department, where for many years he was in charge of undergraduate instruction in that subject. The condition of his health caused him to retire from active teaching in 1925, but he retained his research assistants and visited the laboratory frequently for conference with students who were working under his direction for the doctor's degree.

Professor Moore considered himself to be an alchemist sort of a chemist, for he preferred to examine new territory and to study new permutations and combinations of atoms. His published researches deal with the sulfocinnamic acids, with colored salts of Schiff's bases, with the constitution of xanthogallol, and with the oxidation of uric acid by means of hydrogen peroxide. They show throughout that mastery of innumerable detail which is necessary for pioneer work in structural organic chemistry. He published "Outlines of Organic Chemistry" (1910), "Experiments in Organic Chemistry" (1911), and "A History of Chemistry" (1918). The last book shows the character of the man—widely read, witty, and lucid. It is entertainingly written and can be recommended to chemist and non-chemist alike. The writer has found it excellent medicine for the student who thinks that organic chemistry is difficult, for it gives him an interest which removes difficulties and makes intricacies appealing.

As an undergraduate at Amherst, F. J. Moore was interested in chemistry and in philosophy—to such an extent that he found it difficult to choose between the two. Although he decided to pursue the chemistry, his "History of Chemistry" makes it clear that he never abandoned the philosophy.

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[1] Presented under the title "Two Portraits of F. J. Moore, Historian of Chemistry" before the Section of History of Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

Kjeldahl Digestion Apparatus

Editor of Industrial and Engineering Chemistry:

We feel that it would be undesirable to go into a discussion concerning the patentable features of the Kjeldahl apparatus described by us [E. G. Hastings, E. B. Fred, and W. H. Peterson, This Journal, 19, 397 (1927)] and referred to by W. H. Scott [This Journal, 19, 761 (1927)]. Apart from the sliding lead stopper, our apparatus does not possess any new or novel feature. The idea of a fume tube with side arms is old and well known. See Merkle [This Journal, 8, 521 (1916)]. The absorption of the fumes and their discharge into a sewer is also old and well known. See Sy [This Journal, 4, 680 (1912)].

The University of Wisconsin
College of Agriculture
Madison, Wis.
April 4, 1927

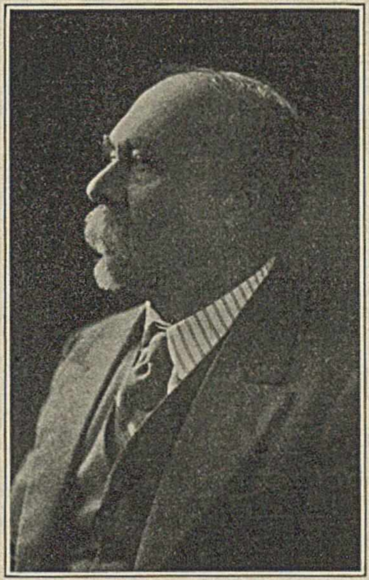
E. B. Fred

Correction—In the article on "By-Product Hydrochloric Acid" by E. J. Fox and C. W. Whittaker, This Journal, 19, 349 (1927), the patent number in footnote 3 should be 1,235,025.

AMERICAN CONTEMPORARIES

Alfred Meredith Peter

IT IS only once in a great while that the mantle of an illustrious father falls upon a son; however, that this does happen is to be gleaned from the life and labors of Dr. Alfred Meredith Peter, who not only shared heavily in the voluminous work during the last twenty years of his father's busy career, but has continued to carry on in a quiet and unassuming way the chemical work relating to geology, soils, and crops at the Kentucky Agricultural Experiment Station for more than forty years.



Alfred M. Peter

Alfred Meredith Peter was born May 25, 1857, within a stone's throw of the famous old Transylvania University at Lexington, Ky. His early boyhood was spent, he says, in learning the rules of the three R's at his mother's knee and tagging along at his father's heels as he went about his work at Transylvania University, and he often sat in the lecture room and watched with unusual interest the experimental demonstrations which his father performed in connection with his lectures in chemistry and physics. Later he attended the Academy and College of Arts of the old Kentucky University, and during this time he rendered material service in his father's laboratory in the preparation of samples for analysis and such other odd jobs as spare moments of leisure permitted. During his undergraduate period he was assistant instructor in chemistry from 1876 to 1878. He graduated from the Department of Chemistry of the Agricultural and Mechanical College in 1880 with the degree of bachelor of science. He was then appointed assistant professor of chemistry in the State Agricultural and Mechanical College and also assistant chemist to the Kentucky Geological Survey. In 1885 he obtained his master's degree from the Agricultural and Mechanical College. In 1887 he married Miss Mary B. McCauley, of Lexington, Ky., and their home was, until Mrs. Peter's death in 1925, famed in this community for its charming and gracious hospitality.

Since June, 1886, he has been connected with the Kentucky Agricultural Experiment Station in the capacity of chemist, and chief chemist, to the present time. Since 1904 he has had general supervision and control of the chemical work of the Kentucky Geological Survey. In 1910 he was made professor of soil technology in the State University of Kentucky and in 1913 his Alma Mater conferred upon him the degree of doctor of science in recognition of his scholarly and distinguished scientific attainments. Even though his Alma Mater may have been tardy in thus honoring a son, that much larger institution, the general public, which he has served long and faithfully, was in no way derelict in this matter, for from his early youth he had been familiarly known as "Little Doc." During the latter part of Professor Scovell's term of office as director of the Kentucky Agricultural Experiment Station, Doctor Peter served as vice director. After the death of Doctor Scovell, Doctor Peter was made acting director and served in this capacity until Doctor Kastle was elected director. Upon the death of Doctor Kastle, Doctor Peter was again appointed acting director and served in that capacity until the present incumbent, Dean Thomas Cooper, was appointed director.

Doctor Peter is the author, joint author, and collaborator in a large number of the Station's publications. The manuscript and proof of practically everything that has been published by the Kentucky Agricultural Experiment Station in the little more than forty years of its existence was carefully scrutinized by him before publication. He has always manifested a deep interest in the work and progress of the Association of Official Agricultural Chemists, and in the early days of its existence, when new methods were being tried and tested, he rendered much valuable assistance in this connection because, like his father before him, he has long held the enviable reputation of a careful and painstaking analyst, of the order of the old school. Doctor Peter has long evidenced an abiding interest in the progress of chemistry both locally and nationally. He has been an active member of the American Chemical Society since 1894, a member of the American Association for the Advancement of Science since 1886, and a fellow since 1890. He was for many years a member of the German Chemical Society. He is a member of the Society of Chemical Industry, a fellow of the American Institute of Chemists, a member of the National Geographic Society and of the Kentucky Historical Society. He was instrumental in the formation of the first section of the American Chemical Society in Kentucky, with headquarters at Louisville. Later he assisted in organizing the Lexington Section of the Society and served as its first president. He is a member of the Masonic Order, Lexington Lodge, No. 1, F. and A. M., of Alpha Chi Sigma, Sigma Xi, and Phi Beta Kappa fraternities. He assisted in the organization of the Kentucky Academy of Science and has served as its secretary since 1915.

Dr. Joseph H. Kastle, a life-long friend, pupil, and fellow chemist who has passed to the great beyond, paid Doctor Peter this very sincere tribute:

> Our present knowledge of the soils of the state and of their fertilizer requirements is due in a very large measure to Doctor Peter, and more than any other man he has assisted the Commonwealth in attaining the ends of justice by numerous toxicological examinations requiring the highest degree of patience and chemical skill. He has at his immediate command a greater store of really helpful chemical information than anyone I have ever known. I always think of him as one of the dependable men of this community, one whose good judgment and helpful advice are beyond all questions of immediate compensation. I have never seen him in a hurry, never angry; on the other hand, he is always busy, always helpful, always ready to render to others the most valuable expert service in his chosen field of work.

J. S. McHargue

BOOK REVIEWS

Allen's Commercial Organic Analysis. Volume V—Tannins, Writing Inks, Stamping, Typing and Marking Inks, Printing Inks, Amines and Ammonium Bases, Analysis of Leather, Colouring Matters of Natural Origin, Colouring Substances in Foods, Benzene and Its Homologues, Aniline and Its Allies, Naphthylamines, Pyridine, Quinoline and Acridine Bases. Edited by SAMUEL S. SADTLER, ELBERT C. LATHROP, AND C. AINSWORTH MITCHELL. xii + 700 pages. P. Blakiston's Son & Company, Philadelphia, 1927. Price, $7.50.

The book is divided into nine sections, each contributed by a specialist. The plan followed by each is to give general information regarding the composition and methods of preparation of the materials under consideration, outline methods of identification, and give detailed instruction for analysis. For certain products, such as ink, government specifications are added. Many data from widely different works have been brought together, and references to original sources have often been given. A bibliography of general works has been placed at the end of each chapter.

Although the work is, in general, well done, a number of irregularities have crept in. Thus, on page 269, it is proposed to designate by the term "true aromatic amines" those derivatives which, like benzylamine, have the amino radical attached to a side chain. Nevertheless, on page 278 it is stated that nitrous acid converts "tertiary aromatic amines into nitroso derivatives which contain the nitroso-group in the benzene nucleus." The author probably refers to compounds of the type of dimethylaniline, though his definition of aromatic amine on page 269 would lead one to suppose that he had in mind such products as dimethylbenzylamine, tribenzylamine, etc. The reviewer has been unable to find any evidence that the nitroso products thus suggested are formed in the way indicated. Further, in speaking of the action of nitrous acid on aliphatic primary amines, the author disregards the fact that the alcohol obtained is often an isomer of what one would expect [Henry, *Compt. rend.*, **145**, 899, 1247 (1907)].

Some of the descriptions could have been made more accurate. On page 191, in giving directions for the estimation of glucose by Fehling's solution, it is stated that "the tube is then gently ignited with a slight current of air through it to destroy possible traces of organic matter and the copper reduced in a stream of pure dry hydrogen." On page 539 Börnstein's work on the oxidation of aniline and homologs is mentioned, but it is called the "reduction of aniline." There is also lack of uniformity in the structural representation of certain radicals, and in the designation of reagents. Several errors in formulas are also noted. The formula for the product obtained by the action of chlorine water on benzidine, recorded on page 603, is that found by Claus and Risler [*Ber.*, **14**, 85 (1881)]. Later work by Schlenk [*Ann.*, **363**, 318 (1908)] on purer material, which does not support the first, is not noted in the present work.

Apparently much time has been given to the preparation of a subject index, which contains some authors' names. The work seems well done, but it is to be regretted that a separate author index was not prepared.

L. CHAS. RAIFORD

Leim und Gelatine. BY E. SAUER. A monograph reprinted from *Kolloidchemischen Technologie*, edited by R. E. LEISEGANG, Dresden and Leipzig, 1927. 57 pages; 40 illustrations. Price, paper, 3 marks.

The monograph is divided into two parts: the first half presents a discussion of the theoretical physical and chemical properties of glue and gelatin solutions; the second half describes the manufacturing process.

The theoretical part is a brief compilation of the results of different investigators and is not a description of original work. Very few opinions are given on the validity of the various ideas expressed. The main points of the research of each investigator are summarized in a very brief paragraph with a few diagrammatic illustrations.

The whole treatment seems to be disconnected and written perhaps for the manufacturer who is somewhat concerned over the possible advantages or accomplishments of research and wishes to have the complete story of the theory of gelatin solutions in a sentence or two. There is very little attempt at applying the theory to the actual manufacturing process.

The description of the manufacturing process seems to have been given a little more attention.

R. H. BOGUE

The Relation of Motor Fuel Characteristics to Engine Performance. BY GEORGE G. BROWN. *Engineering Research Bulletin* 7, May, 1927, University of Michigan, Ann Arbor, Mich. 129 pages. Price, $1.00.

This bulletin gives a thorough discussion of the two major characteristics of motor fuels (gasolines)—volatility and knock tendency. It is based on all the best data available from the literature, as well as those obtained by the Department of Engineering Research of the University of Michigan.

It is hard to define volatility quantitatively in the case of a complex mixture like gasoline. Professor Brown presents and discusses the various methods of measuring and expressing it, and then studies systematically the behavior in the engine of a series of fuels of widely different volatilities, in reference to the four most important factors of satisfactory operation—ease of starting, acceleration, power, and economy. The second part of the opuscule treats of knocking tendency. It makes clear the importance of using fuels which have a reasonably low tendency to detonate. A discussion of the various theories of detonation, the methods of measuring it, and of expressing the results, follows.

The author takes a highly commendable stand in insisting that volatility and knocking tendency are the outstanding characteristics of gasoline. He considers volatility to be the more important of the two, and also draws his own very definite conclusions regarding optimum volatility and the mechanism of detonation. The reader is, however, not forced, nor even invited, to share these views. The data on which these opinions are based are clearly presented, so that the attentive reader may draw his own conclusions. The author has obviously given thorough consideration to his subject, and so much information and ideas are condensed into the bulletin as to make it a valuable contribution to a field which is attracting a great deal of attention from those interested in the development of gasoline and gasoline engines.

GEORGE CALINGAERT

Soil Mineralogy: A Discussion of Mineralogy in Its Application to Soil Studies. BY FREDERICK A. BURT. vii + 82 pages. 6 illustrations. D. Van Nostrand Company, New York, 1927. Price, $1.50.

According to the preface this book is written for the students and scientific workers in our agricultural colleges and related organizations. It is a mineralogy enlarged with geology and chemistry.

The topics discussed are the physical properties of minerals; the various compounds in the soil considered under the heading of the elements; the weathering of minerals; determinative mineralogy applied only to those minerals found in soils; descriptions of mineral species; and supplementary tables showing the relative occurrence, resisting power, and volume changes of minerals.

The chapter on weathering, disintegration, and decomposition of minerals in the soil brings geology to bear on the formation of new mineral species from old, and the "mass law" from chemistry to help explain the process. This is the high spot in the book.

The determinative table, which may have been compiled for this work, has a specific gravity as the main distinguishing property. How effective this method may be for class separation the reviewer cannot state, but the author points to thirteen years' teaching which would lead one to think it a workable procedure.

To a chemist some expressions are unfortunate and do not lead to clear thinking. For example: "Hydrogen sulphide and sulphuric acid are two forms of sulphur***" (p. 18); and "Chloridation, or the addition of chlorine,***" (p. 35) when, obviously, it is substitution that is being discussed. The index has too many references to the same subject, and thereby loses its usefulness.

This book is the outcome, evidently, of that school of agricultural education which would develop students in agriculture by giving them a bite of every subject that touches the farm. From that viewpoint the author is successful and is to be commended for his book. The reviewer, however, doubts if this educational procedure will produce men of the same breadth in the agricultural field as have come from the old-time institutions. If the agricultural student is to stand with his Greek and Latin brother he must have the same breadth in any subject he touches, and this is not obtained by a little of this and a little of that.

On the whole, the book contains much to make it of value to agricultural workers.

C. A. Peters

Aluminum Bronze Powder and Aluminum Paint. By Junius D. Edwards. The Chemical Catalog Company, Inc., New York, 1927. 104 pages. Price, $3.00.

This volume can be considered as a milestone on the road to progress in the protective-coating industries. The author has succeeded in collecting into a limited space a vast amount of valuable information. Using the words of the author, "The major part of this monograph has been devoted to the use of aluminum bronze powder in paint because of the widespread interest in the subject." Many pages are quotations from the results of other investigators in the same field. The arrangement of the methods of testing, especially of the liquids for the aluminum paint, is very satisfactory. The difficulties of aluminum paint when the wrong liquid is used are ably discussed, as well as the correct combinations to obtain good results.

The discussion and data on moisture-proofing of wood contain considerable new information, although the underlying principles have been known for some time. The paragraphs on prevention of "bleeding" and painting "knots" might have been discussed in a manner that would throw more light on these difficulties. Some detailed methods of testing could have been omitted, for instance, the "kauri test" is described in the majority of varnish specifications.

The headings of chapters indicate the following lines of discussion: Composition, Specifications and Testing, Uses and Applications, and Special Properties. The discussion of manufacturing and testing of aluminum bronze occupies 25 pages. The eighteen illustrations of apparatus, test panels, and films add interest to the discussions. Approximately only one page is given to pyroxylin lacquer. The several pages on application discuss Inks, Pyrotechnic Uses, Thermit, Aërated Concrete, and Aircraft Applications.

The book is easy to read, being printed on excellent paper in clear type. The index appears to be very complete, and adds considerable value to the volume as a reference book. The author has succeeded in so arranging the data and investigations that by the time the reading is completed one has the idea that aluminum bronze paint is a valuable product.

P. E. Marling

Die Wärmeübertragung. Ein Lehr- und Nachschlagebuch. By M. ten Bosch. 2nd enlarged edition. 304 pages. 169 figures. 69 tables. Julius Springer, Berlin, 1927. Price, 22.50 marks.

The author presents his subject matter in the conventional way, considering radiation, conduction, and convection in the order named. In addition, electrical heating and the diffusion of heat through surface films are considered. In each case a thorough theoretical discussion precedes the analysis of existing data and the presentation of technically useful information.

That part of the book dealing with radiation concerns itself with radiation from non-luminous gases as well as from solids. Fourier's diffusion law is developed for the case of conduction of heat through solids. Extensive tables of data regarding the thermal properties of engineering materials are presented.

Approximately 60 per cent of the subject matter is devoted to that very important phase of heat transmission, the heating and cooling of fluids in pipes. After a broad survey of the factors affecting heat transfer, and the relation between resistance to flow of fluids and heat transmission, the author derives a general formula for all cases of the transfer of heat to moving fluids in pipes. This relationship, and the method of its derivation, is similar to one published in a series of anonymous articles in *Engineering* (*London*) in 1923. However, the ideas there presented are greatly extended in this book, with consequent increase in utility of the resulting formula. This equation accomplishes something heretofore not done—viz., the coördination of experimental data for water, air, and superheated steam. As given, the equation is involved, but with the aid of several graphs its use is greatly facilitated. In applying this relationship to actual technical cases the author defines a so-called "normal case" which involves standard fluid characteristics and pipe dimensions. If the case in hand varies from these standards, the coefficient of heat transfer computed for the normal case is corrected by the use of ratios. This, of course, implies a knowledge of the functional relationships between the heat transfer coefficient and the variable in question. Graphs covering the different variables are provided.

Over fifty numerical examples are given, more than thirty of these having to do with the design of tubular heat exchangers.

Although the book has a detailed table of contents, its usefulness would be enhanced by an index.

R. E. Turner

Les Etablissements Kuhlmann 1825–1925. Cent Ans d'Industrie Chimique. Compagnie Nationale de Matières Colorantes et Manufactures de Products Chimique du Nord Réunies. 137 pages. Etablissements Kuhlmann, Paris, 1926.

Probably the best known and the largest of the French corporations, Les Etablissements Kuhlmann, has recently issued an interesting book which is, at least, a marvel of the printer's art. This trade monograph gives a history of this corporation from the time when, in 1825, Frédérick Kuhlmann established the first company under the name at Lille, France, for the manufacture of sulfuric acid. The frontispiece, in colors, of Frédérick Kuhlmann, is itself impressive. The work describes the development of the organization and the parts of the present huge corporation. It gives descriptions of the various works, photogravures of the men responsible for their developments, illustrations of the works themselves and of the destruction wrought during the German occupation. The reconstructed plants are also shown and graphs drawn indicating production and progressive development.

The work well deserves its title, "Livre d'Or des Etablissements Kuhlmann."

C. L. Parsons

Die Rohstoffe des Pflanzenreiches. By Julius von Wiesner. **Band I—Alkaloide bis Hefen.** 4th edition. By Paul Krais and Wilhelm von Brehmer. 1122 pages. Verlag von Wilhelm Engelmann, Leipzig, 1927. Price, paper, 46 marks; bound, 49 marks; half-leather, 52 marks.

This encyclopedic work is designed to supply information concerning the technically used products obtained from the plant kingdom. As such it summarizes available data about such diverse classes of substances as fibers, drugs, gums, fats and oils, etc. The botany, pharmacognosy, morphology, microscopy, etc., of the various classes of raw plant materials have been considered in order to provide the necessary classifications.

The various types of products derived from plants are classified by chapters, each class being described according to its characteristics, occurrence, tests, and chemical reactions. Similar descriptions are given for the individual members of each class. The classes of products included in this first volume are: alkaloids, ethereal oils and camphor, bitter substances, albumins, enzymes, dyes, fibers, fats and oils, tannins, rubber and allied substances, and resins and balsams. Many of the chapters are excellently illustrated by photographs.

To the chemist, such a work is invaluable. It supplies information concerning the botany, sources, and distribution of the plant products, together with sufficient information concerning the properties of the products to meet the ordinary need. The books are well edited, printed, and bound. The lack of a general index may be felt, although it is hoped that one will be provided when the last volume has been issued.

E. H. Volwiler

New Books

Manuel du Parfumeur. Askinson. 4th French edition, revised and corrected by R. Sornet. 141 pp. Gauthier-Villars et Cie., Paris. Price, 18 francs.

Report of the Fuel Research Board for the Year 1926, with Report of the Director of Fuel Research. Department of Scientific and Industrial Research. 62 pp. H. M. Stationery Office, London. Price, 1s. 3d. net.

Studi e Ricerche sui Combustibili. Vol. I (1922–1926). M. G. Levi. 307 pp. Associazione Italiana di Chimica Generale ed Applicata, Rome.

Thermometric Conversion Chart. Percy L. Marks. Crosby Lockwood & Son, London. Price, 3 s. 6 d. net.

Transactions of the Institution of Chemical Engineers. Vol. 4—1926. 209 pp. Institution of Chemical Engineers, London.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Possibilities for Para Rubber Production in Northern Tropical America. J. C. Treadwell, C. R. Hill, and H. H. Bennett. Prepared under the direction of H. N. Whitford and P. L. Palmerton as part of the Survey of Essential Raw Materials Authorized by the Sixty-seventh Congress. *Trade Promotion Series,* No. **40.** 375 pp. Paper, 65 cents.

Bureau of Mines

Apparatus for Vacuum Distillation of Lubricating and Heavy Petroleum Oils. M. J. Gavin and A. L. Foster. *Reports of Investigations* **2819.** 5 pp. Issued July, 1927.

Carbon Black Produced from Natural Gas in 1926. G. R. Hopkins. *Mineral Resources of the United States, 1926.* Part II, 16 pp. Paper, 5 cents.

Carbon Monoxide Self-Rescuer. A. C. Fieldner, S. H. Katz, and D. A. Reynolds. *Serial* **2591.** 13 pp. Paper, 5 cents.

Chromite in 1926. J. W. Furness. *Mineral Resources of the United States, 1926.* Part I, 8 pp. Paper, 5 cents.

Coal-Mine Fatalities in June, 1927. W. W. Adams. *Reports of Investigations* **2821.** 6 pp. Issued July, 1927.

Consumption of Explosives in June, 1927. W. W. Adams. *Reports of Investigations* **2823.** 9 pp. Issued July, 1927.

Copper Mines and Mining. Drilling and Blasting in Open-Cut Copper Mines. E. D. Gardner. *Bulletin* **273.** 98 pp. Paper, 30 cents.

Desulfurizing Action of Manganese in Iron. C. H. Herty, Jr., and J. M. Gaines, Jr. *Reports of Investigations* **2817.** 8 pp. Issued July, 1927.

Ferric Sulfate-Sulfuric Acid Process. O. C. Ralston. **With a Chapter on Producing Small Bubbles of Gas in Liquids by Submerged Orifices.** Chas. G. Maier. *Bulletin* **260.** 122 pp. Paper, 30 cents.

Fuller's Earth in 1926. Jefferson Middleton. *Mineral Resources of the United States, 1926.* Part II, 12 pp. Paper, 5 cents.

Permissible Explosives Approved Prior to June 30, 1927. G. St. J. Perrott and S. P. Howell. *Reports of Investigations* **2818.** 6 pp. Issued July, 1927.

Pyrotannic Acid Method for Quantitative Determination of Carbon Monoxide in Blood and in Air: Its Use in Diagnosis and Investigation of Cases of Carbon Monoxide Poisoning. R. R. Sayers and W. P. Yant. *Technical Paper* **373.** Reprinted with slight changes. 18 pp. Paper, 10 cents.

Quarry Accidents in the United States during the Calendar Year 1925. W. W. Adams. *Bulletin* **286.** 98 pp. Paper, 20 cents.

The Use of Solvents for Dewaxing Paraffin-Base Crude Oil. H. M. Smith. *Reports of Investigations* **2822.** 4 pp. Issued July, 1927.

Bureau of Standards

Absorption Spectra of Iron, Cobalt, and Nickel. W. F. Meggers and F. M. Walters, Jr. *Scientific Paper* **551.** 22 pp. Paper, 10 cents.

Aging of Soft Rubber Goods. R. F. Tener, W. H. Smith, and W. L. Holt. *Technologic Paper* **342.** 32 pp. Paper, 15 cents.

Caroá Fiber as a Paper-Making Material. M. B. Shaw and G. W. Bicking. *Technologic Paper* **340.** 24 pp. Paper, 25 cents.

Determination of Sulfur Trioxide in the Presence of Sulfur Dioxide, Together with Some Analyses of Commercial Liquid Sulfur Dioxide. J. R. Eckman. *Scientific Paper* **554.** 9 pp. Paper, 5 cents.

Determination of Weight per Gallon of Blackstrap Molasses. C. F. Snyder and L. D. Hammond. *Technologic Paper* **345.** 4 pp. Paper, 5 cents.

Federal and State Laws Relating to Weights and Measures. Revised by William Parry under the direction of F. S. Holbrook. 3rd ed. 976 pp. Cloth, $2.30.

Standard Samples. General Information. *Circular* **25.** 9th ed. 31 pp. Issued July, 1927.

Wave-Length Measurements in Arc Spectrum of Scandium. W. F. Meggers. *Scientific Paper* **549.** 13 pp. Paper, 5 cents.

Bureau of the Census

Forest Products, 1926. Pulpwood Consumption and Wood-Pulp Production. Compiled in coöperation with the Forest Service, Department of Agriculture. 13 pp. Paper, 5 cents.

Manufactured Ice. *Census of Manufactures, 1925.* 13 pp. Paper, 5 cents.

Paper and Wood Pulp. *Census of Manufactures, 1925.* 19 pp. Paper, 5 cents.

Petroleum Refining. *Census of Manufactures, 1925.* 10 pp. Paper, 5 cents.

Smelting and Refining (Nonferrous Metals). *Census of Manufactures, 1925.* 12 pp. Paper, 5 cents.

Tanning Materials, Natural Dyestuffs, Mordants, and Assistants, etc. 8 pp. Paper, 5 cents.

Department of Agriculture

A Study of the Toxicity of Acid Lead Arsenate on the Japanese Beetle (*Popollia japonica Newm.*). E. R. Van Leeuwen. *Journal of Agricultural Research,* **34** (June 1, 1927), 1043–7.

Commercial Dehydration of Fruits and Vegetables. P. F. Nichols, Ray Powers, C. R. Gross, and W. A. Noel. *Department Bulletin* **1335.** 40 pp. Paper, 10 cents.

Grouping of Soils on Basis of Mechanical Analysis. R. O. E. Davis and H. H. Bennett. *Department Circular* **419.** 15 pp. Paper, 5 cents.

Relation of Size of Oil Drops to Toxicity of Petroleum-Oil Emulsions to Aphids. E. L. Griffin, C. H. Richardson, and R. C. Burdette. Reprinted from *Journal of Agricultural Research.* 12 pp.

Selection for Quality of Oil in Soy Beans. L. J. Cole, E. W. Lindstrom, and C. M. Woodworth. *Journal of Agricultural Research,* **35** (July 1, 1927), 75–95.

Sulfuric Acid as a Weed Spray. Alfred Aslander. *Journal of Agricultural Research,* **34** (June 1, 1927), 1065–91.

The Discoloration of Canned Cranberries. F. W. Morse. Reprinted from *Journal of Agricultural Research.* 4 pp.

Department of Commerce

Commerce Yearbook 1926. Volume I—United States. Cloth, $1.00.

Geological Survey

Correlation of Geologic Formation between East-Central Colorado, Central Wyoming, and Southern Montana. W. T. Lee. *Professional Paper* **149.** 80 pp. Paper, 50 cents.

Geology and Ore Deposits of the Mogollon Mining District, New Mexico. H. G. Ferguson. *Bulletin* **787.** 100 pp. Paper, 65 cents.

Mines and Mineral Resources. Operating Regulations to Govern Methods of Mining and Safety and Welfare of Employees on Leased Lands on Public Domain under Mineral Leasing Acts, Potash, October 2, 1917 (40 Stat., 297) and February 7, 1927 (44 Stat., 1057), Oil Shale, Sodium Phosphate, February 25, 1920 (40 Stat., 437) Sulfur, April 17, 1926 (44 Stat., 301), Gold, Silver, and Quicksilver, June 8, 1926 (44 Stat., 710); approved June 2, 1927. 8 pp. Paper, 5 cents.

Surface Water Supply of the United States 1923. Part XII—North Pacific Slope Drainage Basins. C. Lower Columbia River Basin and Pacific Slope Drainage Basins in Oregon. N. C. Grover, F. F. Henshaw, and G. L. Parker. *Water-Supply Paper* **574.** 194 pp. Paper, 35 cents.

The Toklat-Tonzona Region. By Stephen R. Capps. **Geologic Investigations in Northern Alaska.** Philip S. Smith. *Bulletin* **792-C.** 50 pp.

President of the United States

Cresylic Acid. *Proclamation* authorizing certain decrease in duty on Cresylic Acid in order to equalize differences in costs of production in the United States and Great Britain. No. **1809.** 2 pp. July 20, 1927.

Public Health Service

A Distinctive Test for Cysteine. M. X. Sullivan. Reprint **1084** from *Public Health Reports.* 27 pp. Paper, 5 cents.

Experimental Bacterial and Chemical Pollution of Wells via Ground Water, and Factors Involved. C. W. Stiles, H. R. Crohurst, and G. E. Thompson. **Report on Geology and Ground Water Hydrology of Experimental Area of United States Public Health Service at Fort Caswell, N. C.** N. D. Stearns. *Bulletin* **147,** Hygienic Laboratory. 168 pp. Paper, 30 cents.

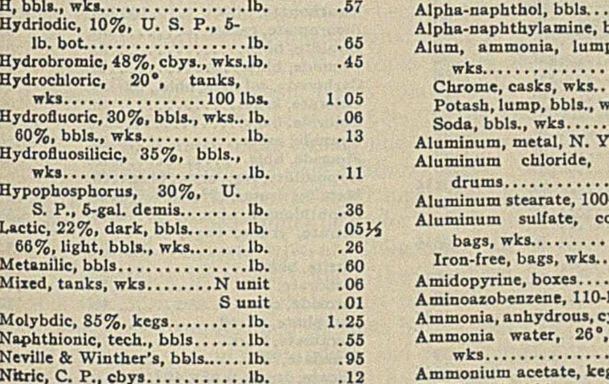
Experimental Studies of Water Purification. III—Discussion of *B. coli* Results Obtained from Primary Series of Experiments. H. W. Streeter. *Public Health Reports,* **42** (July 15, 1927), 1841–59.

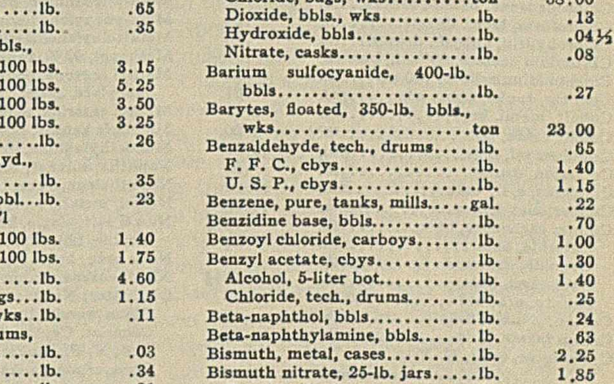
Sickness among Industrial Employees. Incidence and Duration of Disabilities from Important Causes Lasting Longer than One Week among 133,000 Persons in Industry in 1924, and a Summary of the Experience for 1920–1924. Reprint **1060** from *Public Health Reports.* 19 pp.

MARKET REPORT—AUGUST, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON AUGUST 15

Acetanilide, tech., bbls	lb.	.21
U. S. P., bbls	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks	lb.	.12
Acetophenetidine, bbls	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.38
56%, c/1. bbls	100 lbs.	6.34
Glacial, c/1. bbls	100 lbs.	11.92
Acetylsalicylic, bbls	lb.	.85
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls	lb.	.58
Boric, bbls	lb.	.08½
Butyric, 60%, pure, 5-lb. bot	lb.	.55
Chloroacetic, mono-, bbls., wks	lb.	.25
Di-, cbys	lb.	1.00
Tri-, bbls	lb.	2.50
Chlorosulfonic, drums, wks	lb.	.15
Chromic, pure, 98%, drums	lb.	.37
Chromotropic, bbls	lb.	1.00
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls	lb.	.44
Cresylic, pale, drums	gal.	.62
Formic, 85%, cbys., N. Y	lb.	.11
Gallic, U. S. P., bbls	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.40
H, bbls., wks	lb.	.57
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks	100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks	lb.	.06
60%, bbls., wks	lb.	.13
Hydrofluosilicic, 35%, bbls., wks	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.36
Lactic, 22%, dark, bbls	lb.	.05½
66%, light, bbls., wks	lb.	.26
Metanilic, bbls	lb.	.60
Mixed, tanks, wks	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls	lb.	.55
Neville & Winther's, bbls	lb.	.95
Nitric, C. P., cbys	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys	lb.	.07
Picramic, bbls	lb.	.50
Picric, bbls. c/l	lb.	.30
Pyrogallic, tech., bbls	lb.	.86
Salicylic, tech., bbls	lb.	.37
Stearic, d. p., bbls. c/l	lb.	.11¼
Sulfanilic, 250-lb. bbls	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks	ton	15.00
60°, tanks, wks	ton	10.50
Oleum, 20%, tanks, wks	ton	18.00
40%, tanks, wks	ton	42.00
Sulfurous, U. S. P., 6%, cbys	lb.	.05
Tannic, tech., bbls	lb.	.30
Tartaric, U. S. P., cryst., bbls	lb.	.37
Tobias, bbls	lb.	.85
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls	gal.	3.70
Amyl, 10%, Imp. drums	gal.	1.40
Butyl, drums, c/l. wks	lb.	.19
Cologne Spirit, bbls	gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs	gal.	.44
No. 1, Comp. denat., drs	gal.	.46½
Isobutyl, ref., drums	lb.	...
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls	lb.	.65
Alpha-naphthylamine, bbls	lb.	.35
Alum, ammonia, lump, bbls., wks	100 lbs.	3.15
Chrome, casks, wks	100 lbs.	5.25
Potash, lump, bbls., wks	100 lbs.	3.50
Soda, bbls., wks	100 lbs.	3.25
Aluminum, metal, N. Y	lb.	.26
Aluminum chloride, anhyd., drums	lb.	.35
Aluminum stearate, 100-lb. bbl	lb.	.23
Aluminum sulfate, comm'l bags, wks	100 lbs.	1.40
Iron-free, bags, wks	100 lbs.	1.75
Amidopyrine, boxes	lb.	4.60
Aminoazobenzene, 110-lb. kgs	lb.	1.15
Ammonia, anhydrous, cyl., wks	lb.	.11
Ammonia water, 26°, drums, wks	lb.	.03
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls	lb.	.05¼
Lump, casks	lb.	.12
White, bbls	lb.	.05¼
Iodide, 25-lb. jars	lb.	5.20
Lactate, bbls	lb.	.15
Nitrate, tech., cryst., bbls	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.27½
Phosphate, dibasic, tech., bbls	lb.	.18
Sulfate, bulk, wks	100 lbs.	2.40
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	lb.	1.90
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks	lb.	.60
Anthraquinone, subl., bbls	lb.	.90
Antimony, metal	lb.	.11¾
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls	lb.	.16¼
Salt, Dom., bbls	lb.	.18
Sulfide, crimson, bbls	lb.	.25
Golden, bbls	lb.	.15
Vermilion, bbls	lb.	.37½
Tartrolactate, bbls	lb.	.45
Argols, red powder, bbls	lb.	.08
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.10½
White, c/l. kegs	lb.	.04
Asbestine, bulk, c/l	ton	16.00
Barium carbonate, bbls., bags, wks	ton	47.50
Chloride, bags, wks	ton	58.00
Dioxide, bbls., wks	lb.	.13
Hydroxide, bbls	lb.	.04½
Nitrate, casks	lb.	.08
Barium sulfocyanide, 400-lb. bbls	lb.	.27
Barytes, floated, 350-lb. bbls., wks	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzene, pure, tanks, mills	gal.	.22
Benzidine base, bbls	lb.	.70
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys	lb.	1.30
Alcohol, 5-liter bot	lb.	1.40
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls	lb.	.24
Beta-naphthylamine, bbls	lb.	.63
Bismuth, metal, cases	lb.	2.25
Bismuth nitrate, 25-lb. jars	lb.	1.85
Oxychloride, boxes	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	2.20
Blanc fixe, dry, bbls	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, powd., bbls	lb.	.04½





Bordeaux mixture, bbls	lb.	.11
British gum, com., c/l	100 lbs.	4.37
Bromine, bot	lb.	.47
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.55
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.05
Calcium acetate, bags	100 lbs.	3.50
Arsenate, bbls	lb.	.07½
Carbide, drums	lb.	.05½
Chloride, drums, wks	ton	21.00
Lactate, tech., bbls	lb.	.35
Nitrate, bbls	ton	52.00
Phosphate, monobas., bbls	lb.	.07
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Amer., bbls	lb.	.62
Jap., cases	lb.	.64
Crude, cases	lb.	.64
Camphor, monobrom, cs	lb.	1.85
Caramel, bbls	gal.	.63
Carbazole, bbls	lb.	.15
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls	lb.	.18
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Chalk, pptd., casks	lb.	.04¼
Charcoal, willow, powd., bbls	lb.	.06
China clay, imp., bgs	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine U. S. P., 5-lb. bot	lb.	1.75
Chlorcosane, 5-lb. bot	lb.	.55
Chlorine, liq., c/l., cyl	lb.	.05½
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.20
Chlorohydrin, anhyd., drums	lb.	.75
Chromium acetate, 20° sol., bbls	lb.	.05½
Cinchonidine sulfate, 100 oz	oz.	.35
Coal tar, tanks, bbls., wks	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	2.00
Cod-liver oil, bbls	bbl.	45.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec	100 lb.	12.90
Copper carbonate, bbls	lb.	.16¼
Chloride, bbls	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls	lb.	.16½
Sulfate, c/l., bbls	100 lb.	5.00
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.27
Cyanamide, bulk, N. Y.	Ammon. unit	1.80
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.25
Dichlorobenzene, drums	lb.	.06
Diethylaniline, drums	lb.	.55
Diethylphthalate, drums	lb.	.25
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.15
Dinitronaphthalene, bbls	lb.	.32
Dinitrophenol, bbls	lb.	.31
Diphenylamine, bbls	lb.	.45
Diphenylguanidine, bbls	lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.10
Ether, nitrous, bot	lb.	.90
Ether, U. S. P., drums	lb.	.14
Ethyl acetate, 99%, drums	gal.	1.10
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.30
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls	lb.	.07½
Ferrous chloride, cryst., bbls	lb.	.05
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls	lb.	.10
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drs., c/l	lb.	.17½
Glauber's salt, bbls	100 lbs.	1.05
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.21
G salt, bbls	lb.	.50
Hexamethylenetetramine, U. S. P., drums	lb.	.65
Hydrogen peroxide, 25 vol., bbls	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls	lb.	.14
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	110.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lb.	6.50
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls	lb.	.14
Oxide, litharge, bbls	lb.	.09
Red, bbls	lb.	.10
Peroxide, drums	lb.	.25
White, basic carb., bbls	lb.	.09
Sulfate, bbls	lb.	.08¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithium carbonate, 100-lb. kgs	lb.	1.45
Lithopone, bbls	lb.	.06⅛
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks	ton	48.00
Magnesium, metal sticks, wks	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	37.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.58
Mercury, flasks, 75 lbs	flask	121.00
Meta-nitroaniline, bbls	lb.	.72
Meta-phenylenediamine, bbls	lb.	.90
Meta-toluylenediamine, bbls	lb.	.72
Methanol, 97%, tanks	gal.	.52
Methyl acetone, drums	gal.	.88
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls	lb.	.04½
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.08
Double, bbls	lb.	.08½
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.13
China wood, bbls	lb.	.17¾
Coconut, Ceylon, tanks	lb.	.09½
Cod, N. F., tanks	gal.	.59
Corn, crude, tanks, mills	lb.	.08½
Cottonseed, crude, tanks	lb.	.08½
Lard, edible, bbls	lb.	.15¼
Linseed, bbls	lb.	.108
Menhaden, crude, tanks	gal.	.47½
Neat's-foot, pure, bbls	lb.	.14¾
Oleo, No. 1, bbls	lb.	.14
Olive oil, denat., bbls	gal.	1.64
Foots, bbls	lb.	.08¾
Palm, Lagos, casks	lb.	.07½
Peanut, crude, tanks	lb.	.12
Perilla, bbls	lb.	.16¼
Rapeseed, bbls., English	gal.	.80
Red, bbls	lb.	.09¼
Soy bean, crude, bbls	lb.	.09¼
Sperm, 38°, bbls	gal.	.85
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.35
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.13
Ortho-toluidine, bbls	lb.	.29
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.15
Paraldehyde, tech., drums	lb.	.27
Para-formaldehyde, cases	lb.	.45
Para-nitroaniline, drums	lb.	.52
Para-nitrochlorobenzene, drums	lb.	.32
Para-nitrophenol, bbls	lb.	.50
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.30
Para-phenylenediamine, bbls	lb.	1.20
Para-toluidine, bbls	lb.	.38
Paris Green, 500-lb. kgs	lb.	.19
Phenol, drums	lb.	.20
Phenolphthalein, drums	lb.	1.30
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl	lb.	.45
Phthalic anhydride, bbls	lb.	.18
Platinum, metal	oz.	95.00
Potash, caustic, drums	lb.	.07⅞
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls	lb.	.16
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅝
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.14½
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.25
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.30
Rochelle salt, bbls., U. S. P.	lb.	.23
R salt, bbls	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot	oz.	.40⅞
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	3.10
Sodium acetate, bbls	lb.	.04½
Benzoate, bbls	lb.	.50
Bicarbonate, bbls	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls	lb.	.08½
Bromide, bbls	lb.	.42
Carbonate, sal soda, bbls.,	100 lbs.	1.30
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls	lb.	.08¼
Hyposulfite, reg., crys., bbls	lb.	.02½
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.35
Nitrite, bbls	lb.	.08½
Perborate, bbls	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.12
Silicate, drums, tanks, 40°,	100 lbs.	.75
Silicofluoride, bbls	lb.	.04¼
Stannate, drums	lb.	.48½
Sulfate, anhyd., bbls	lb.	.02¼
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.40
Tungstate, kegs	lb.	.85
Strontium carbonate, bbls	lb.	.08
Nitrate, bbls	lb.	.08
Strychnine alkaloid, 100 oz., powd	oz.	.56
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks	ton	19.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, commercial, cyl	lb.	.08½
Sulfuryl chloride, drums	lb.	.65
Thiocarbanilid, bbls	lb.	.22
Tin, Amer., stand	lb.	.65
Tin bichloride, 50% sol., bbls	lb.	.18½
Oxide, bbls	lb.	.72
Titanium oxide, bbls., wks	lb.	.40
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls	lb.	.75
Tungsten	WO_3 unit	10.50
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.50
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	100 lbs.	6.75
Zinc ammonium chloride, bbls	lb.	.06¼
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls	lb.	.07⅜
Stearate, bbls	lb.	.19
Zinc dust, bbls., kegs, c/l	lb.	.09