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EDITORIALS

On to Birmingham

Leading men in any activity agree that one of the best investments in their experience and a most potent factor in their success has been attendance at meetings of their fellows. Chemistry is no exception. You owe it to yourself to obtain that advantage which comes only from frequent contact with those in your own field. The benefits are cumulative. He profits most who attends with regularity.

It has been seven years since the Society has enjoyed the hospitality of the South. Birmingham is preparing for us, and the industrial region is attractive. Your especial attention is called to the announcement on page 238 in this issue, and we urge you to plan definitely to be among those present.

The Dye Lobby Investigation

Several months have passed since Senator King demanded an immediate investigation of what he described as a wicked dye lobby. Two months have passed since the probe was ordered, after being widened to include the importers of coal-tar chemicals and dyes. After much difficulty the subcommittee has been completed, comprising Senators Shortridge, *Chairman*, Sterling, and Ashurst. Delays, varied with postponements, followed, until we began to wonder whether the Senator had not found vital weaknesses in his case after his charges were stripped of verbose generalities. We understand he has urged that the Committee be empowered to employ counsel to prepare a case against American dye makers. We suspect the Senator wishes he might be given a place on the Committee and allowed to pass upon the case based upon his own charges.

Meanwhile, both the American Dyes Institute and the Synthetic Organic Chemical Manufacturers Association of the United States have stated their willingness to aid in the investigation and to put their facilities at the disposal of the Committee. It does seem that if things were as bad as stated by the Senator the Committee should be well along with its work. As it is, industrial development is being retarded because the thought of executives is now directed away from business by the impending call to appear at the hearing which began on February 20.

Delay may be a part of the plan to harass our industry continually and give time for foreign penetration while we await decisive action.

Speed the investigation!

Popularity versus Security

Those who really understand something of chemical warfare service were pleased when a committee of technical men, of which the President of this Society was chairman, was formed to bring in a well-considered report on the possibility of controlling chemical warfare by resolutions. An Advisory Committee composed of people who are not chemists and who have given no special thought to the science was also appointed. It has been much to the disappointment of many people that the report of the latter committee, not of the former, has been given publicity. From our present information, it appears that the conference made up its mind in advance and without expert advice that chemical warfare should be made the scapegoat, and that such a report as the Advisory Committee made was the kind it would publish. We have been unable to learn just what the technical report recommended, and we call upon the officials of the conference to give it publication.

In discussing the resolutions pertaining to the abolition of chemical warfare, the Secretary of State declared that the proposed action would be a *popular* thing. We cannot help wondering whether in the minds of the delegates popularity may not at times have taken precedence over security. No one would have felt secure in conferring upon the limitation of navies unless the leading naval powers had been parties to the conference. How can we feel secure in cheerfully passing resolutions on the most humane, efficient, and latest development of warfare without those who first used it, and who are best prepared to develop it further, being parties to the action? And if every nation in the world should sign the treaty, what defense could be made if the treaty were broken unless we had continued research? Quoting Mr. Balfour, "No nation, therefore, can forego the duty of examining how such attacks could be properly dealt with and effectively met."

Chemists in particular and thousands of others want to read the report of the technical committee.

An Invitation

The Woman's Department of The National Civic Federation, of which Mrs. Warren G. Harding is the Honorary Chairman, Miss Maude Wetmore, Chairman, Mrs. Rogers H. Bacon, Secretary, Miss Anne Morgan, Treasurer, and Mrs. Coffin Van Rensselaer, Executive Secretary, passed a resolution at their Thirteenth Annual Meeting which is essentially an invitation to the chemists of the country to appear before the various groups of interested women and tell them something of what chemistry in its various phases means to them and to the country. The resolution follows:

> WHEREAS, The science of chemistry and its applications to industry bear directly upon the welfare of the home, the betterment of agriculture, the efficiency of manufacture, the progress of medicine, the surety of national defense, and
>
> WHEREAS, Advance in chemistry is conditioned by facilities for research both as to personnel and equipment, and
>
> WHEREAS, In a democracy an intelligently informed public understanding of chemistry and the chemical industries is a prerequisite for stimulation of the study of the science of chemistry, advancement in research and stabilization and preservation of the chemical industries,
>
> *Therefore be it resolved,* That the Woman's Department of The National Civic Federation approves and urges the immediate and effective presentation of this subject to the women of America, convinced that through such an educational movement the life of the nation will be bettered and made more secure.

For some time chemists have been complaining of the fact that their work is not understood and appreciated, that too few people know what research in chemistry means to industrial progress and national welfare. Some months ago President Smith urged members to speak upon chemical subjects wherever an audience could be found. Here is an invitation. For your own sake, speak!

Our Viewpoint

Let us suppose there is a community where all buy their supplies by mail. Surely they have a right to do so. But suppose the community encourages one of its members to engage in the general store business? They wish to avoid uncertainties, to have better accommodations, establish a line of credit, obtain specialties upon short notice, and enjoy personal contact in their transactions. It seems to us their action morally binds them to give the support implied in their invitation to the local enterprise so long as it deals fairly with them.

In a time of actual need, a large group of scientists, industrialists, and even government officials insisted that Americans must establish a domestic laboratory apparatus and supply industry, advised that investments necessary for development be made, and assured each other that not only did they desire to make America reasonably independent in essentials, but that they were determined never again to be left without an American source of apparatus. Many of these scientists now seem willing to forget the moral responsibility which they assumed at that time, a responsibility which if fulfilled would guarantee the future of the industry. We highly commend the many consumers of scientific and chemical apparatus and chemicals who have actually made sacrifices in order to do their bit in support of American-made goods. If this support is to continue, certain manufacturers must do their part by careful adherence to specifications. We do regret that so large a number of educational institutions (which buy about 70 per cent of the apparatus used and are alone able to purchase standard items in quantity) are tempted to place abroad the quantity orders which would enable any American manufacturer to reduce his costs. Quality is no longer debated, for America has made good. It is merely a matter of price, in which American costs, always higher than European costs, are still further boosted by the exchange situation.

In commercial graveyards one often finds an epitaph relating how the deceased died because he had a single source of supply which failed, or one single customer whom he lost. The present purchasing policy of some institutions seems certain to leave our laboratories in the hands of a European monopoly, and when Europe ceases to work for nothing and board herself, as she must very soon, we shall have the pleasure of paying through increased prices for all her economic blunders, unless we have a competing industry. Our industry is still very much alive and fighting hard to stay. There is ample American competition. We have seen so many instances in which low prices were used temporarily to crush competition and the losses were later retrieved quickly by advanced prices, that the truth requires no emphasis. To-day importation is at an uncertain price, quality in many cases is below pre-war, and adjustments for breakage and errors are unsatisfactory.

We will admit that there is justification for the importation of some specialties, but we urge that these be purchased through reputable established dealers—the dealers who to-day are importing some things only because their customers demand them, dealers who urge American-made materials but who are being required to import for self-preservation. Is your dealer responsible? Do you investigate your source of supply? Cases have come to our notice where the importer, unfamiliar with the requirements of the trade, has guessed at prices, later found himself unable to deliver at the quotation made, and has then simply quit, leaving the laboratory six to nine months behind its own schedule. Some of these importers live in the catalog of others and content themselves with blanket quotations five per cent below any bid, or send out sheets based upon the convenient catalog of an American dealer. They carry no stock, give no service, and often supply worthless material.

American colleges depend for support upon American industries. If the policy of importation of apparatus were followed to a logical conclusion few domestic industries could grow to philanthropic proportions. We often wonder how a college trustee or university regent can clamor for a protective tariff for his business interests and yet sanction wholesale importation of supplies for the school he helps govern. We urge the abandonment of any purchasing policy which seems so certain to kill our apparatus and chemical industry, founded at such cost, and which is equally certain to weaken our established dealers. There are those ready to spend large sums to improve their product. Competition is sufficiently keen to assure fair dealing, reasonable prices, and real service. Why are so many willing to give up the well-tried principle of the square deal?

A Victory

On February 14, the Senate, without discussion or dissent, passes the Lambert Patent Bill in the form previously approved by the House. The American Chemical Society deserves a large measure of credit for this action, which will make possible such a reorganization of the Patent Office as all industry must have. The coöperation of the Society, led by its patent committee and its untiring chairman, E. J. Prindle, has been most effective.

Let Congress now take prompt and favorable action on tariff so that industry may get under way, and on reclassification of Federal scientific employees, in the interest of public welfare.

Our Personal Loss

We first had the privilege of making the acquaintance of Dr. Charles Baskerville at the Annual Meeting of the Society in Boston in 1909, where his ability to work when there was work to be done and play when the time came for recreation made a strong appeal. From time to time afterward we had occasion to discuss many problems with him, some of which were of personal interest and many related to the activities of the Society. We soon came to know that he could be depended upon to work enthusiastically for what he believed was right, and that he was pretty generally on the right side of things. We came to know of his unusual devotion to the interests of the American Chemical Society, and to know that he devoted many hours of tedious labor to the interests of the Society for which no proper acknowledgment was ever made. Only last autumn he devoted himself to the international phase of the New York Meeting. Previously he discharged the duties of Chairman of our Committees on Occupational Diseases and on Business Management with great credit to himself and great profit to the Society. He never seemed too busy to take up any task which he believed to be for the good of chemists, chemistry, and the American Chemical Society, and it was a comfortable feeling to know that we could go to him, discuss our problems fully, and receive a perfectly frank reply to our questions. Dr. Baskerville was one of those whom one comes to love as a result of much work in common. Without him the going will be made a little more difficult.

Authoritative Information

Many difficulties arise from the use of incorrect information, and serious false impressions are sometimes created. To aid in supplying authoritative information, the A. C. S. News Service was established and has done much toward giving the public a better conception of what chemistry really is. The News Service strives to supply authentic stories of chemical achievements that are newsy and thus to crowd out the sensational accounts usually written by those who know nothing of the real facts.

The daily press, however, is not the only offender, and it is even more important that books be written by those who are authorities upon the subjects treated. There are enough good books to read without taking time for the uncertain ones, but popular subjects are frequently seized upon by those who appreciate a business opportunity but lack the requisite first-hand knowledge. Just now vitamins are everywhere before us, and we would call attention to the review in this issue of Professor Sherman's monograph on the subject. It is an authoritative work, where the writer not only is entirely able to stand upon his own reputation, but has the distinct advantage of having been chosen by our Committee on Scientific Monographs for this contribution to American scientific literature.

It is not difficult to learn whether or not a given writer is a leader in his specialty, and the fact that chemistry is becoming of wider interest makes it more necessary for those who are informed to aid in guiding readers generally in their selection of reference books. It becomes our duty not only to use authoritative sources of information ourselves, but to recommend them to others.

The Earning Power of Research

A few years ago the X-ray tube was an erratic apparatus not in any very general use. The research laboratory of the General Electric Company realized that there was a possibility of utilizing pure electronic emission from a hot filament to produce controllable X-rays in a perfect vacuum. They conducted extensive research upon such devices as then existed, and as a result the tungsten target took the place of platinum in the standard gas tube of that day. Research had also to be applied before the laboratory learned positively that available electrons already existed and that there was a possibility of controlling them, as, for example, focusing them on a target. The research has been continued, until to-day practically all the X-ray tubes of the country are made by the company in accordance with the discoveries of the man whose name the tubes bear. The Coolidge tube is also used abroad almost to the exclusion of other types. These remarkable results have been achieved through very careful, accurate, and often discouraging studies of electric phenomena in high vacua, with very pure materials. The perfection of the tube is the nucleus of an annual business, including accessories and generating apparatus used in X-ray work, of from five to ten million dollars a year. The benefit cannot be measured wholly in monetary return, for everyone is familiar with the humanitarian benefits.

Our oldest industries have been the most reluctant in establishing research laboratories. But the experience of a leader may guide the entire industry. Some years ago the Ward Baking Company established a fellowship at the Mellon Institute. The research soon brought results and the application of a more balanced yeast nutrient to the dough gave better fermentation and better bread. It was discovered that the baker can grow yeast in the dough and control fermentation wastes. This conservation amounts to 2 per cent of the flour, 15 per cent of the sugar, and sufficient yeast to make the total saving 45 cents net per barrel of flour used. It is estimated that this process saves American, Canadian, and British bakers not less than $40,000 per day, without detriment to the quality of the bread.

In 1915 a control laboratory was installed with one chemist. To-day there are a variety of control laboratories with twenty-five technical workers. A chemist has frequently saved two months' salary for his employer with a report on samples from a single carload of butter. The control which has been established as a result of research upon the raw materials makes possible uniformity in the finished product. Time, temperature, and other factors which influence fermentation have been established, and since no two carloads of flour are alike the data are vital in determining how fermentation must be varied to secure uniformity. The study of enzymes, proteins, colloids, yeasts, bacteria, and nutrient value is pointing the way to still better bread, higher nutritive values, economy in production, and the elevation of the entire industry. It is no wonder that during these days of industrial depression this pioneer in research as applied to baking has increased the number of its scientific workers. Results continue to justify the increase.

A Request to Authors

We are indeed anxious to make the JOURNAL still more useful to busy men, and to pack into its pages a maximum of information. We bespeak the coöperation of authors.

Hereafter we plan to print a synopsis of the longer articles, preceding the discussion. We want our summaries really to summarize the articles, to save the time of the busy reader, so that he need not read them in their entirety unless he is truly interested. At the same time he can easily obtain a general idea of the work going on in fields not his own. We feel that these synopses should be prepared by the authors themselves. Please make them a part of the manuscript you send in.

Our office has always tried to have literature references complete. This often imposes an unreasonable burden upon our manuscript editor, of work which in all fairness belongs to the author. Most of our authors are careful about this important detail. Be sure never to overlook it yourself.

Our readers are also interested in knowing the official connections of the authors of articles. Unless there is some strong reason why yours cannot be given, include it on the manuscript.

Another small matter is our desire for double-spaced typewritten manuscripts, not carbon copies. By the time single-spaced or carbon copies reach the printer they may be almost illegible. We also wish more and better illustrations. Read the instructions which we printed at the beginning of "Original Papers" last year.

In order that publication may be given to as large a number of papers as possible, we venture to suggest that authors practice condensation wherever it is possible without weakening the article. It seems to us, for instance, that when most papers on methods of analysis have given enough detail to permit another to duplicate the work, have noted applications, and given conclusions, they have fulfilled their mission. We wish to give important articles ample space, and we also wish to have space available to allow a very broad field to be covered. We feel certain of your coöperation.

Hydrogen Peroxide: Its Manufacture and Preservation[1]

By Paul Poetschke[2]

The L. D. Caulk Co., Milford, Delaware

A detailed account is given of the various stages in the manufacture of hydrogen peroxide from barium peroxide.

The most difficult problem confronting the manufacturer is to secure a product of reasonable stability, so that it will retain its effectiveness until used by the consumer. Experiments in which peroxide was stored in the dark and in varicolored light showed that the solutions keep infinitely better in the dark; orange and red light afford some protection; blue light causes the greatest deterioration.

Manufacturers have not given sufficient attention to the selection of glass bottles of suitable quality for bottling hydrogen peroxide. Carefully conducted experiments confirm the fact that traces of alkali dissolved from the bottle cause rapid deterioration of the peroxide. The interesting fact is that the quality of the glass has a remarkable influence, some bottles causing rapid deterioration while others show but little effect.

Preservatives such as acetanilide retard decomposition but are not uniformly effective. Other factors, such as the character of the glass, exposure to light, acidity, and traces of organic matter often overbalance the restraining effect of the preservatives. Quinine sulfate has many advantages over acetanilide, particularly in that only one-tenth as much is required, and no foreign odor or discoloration results. A mixture of benzoic and salicylic acids is also effective.

Storage in glass bottles of suitable quality and exclusion of light are far more effective in restraining decomposition than are any of the preservatives studied.

Hydrogen peroxide was discovered in 1818 by P. Thenard, who produced it by the action of dilute acids upon barium peroxide in the presence of water. With certain modifications, adapted to production on a commercial scale, this process is commonly employed at the present time for making medicinal and technical hydrogen peroxide.

The methods of preparation of medicinal and technical hydrogen peroxide are similar, except that phosphoric and sulfuric acids are used for the former, and hydrochloric acid is used in place of phosphoric acid for the technical grades. A further distinction is that materials of greater purity and much greater care and refinement in processes are necessary in preparingthe medicinal product. A knowledge of the process used for making the medicinal article, because it requires greater care and skill, will enable one readily to adapt the process to the manufacture of the technical product.

As actually carried out in practice the manufacture of hydrogen peroxide is perhaps as troublesome as many other industrial processes which appear simple enough when carried out on a laboratory scale. If we had a stable substance to deal with there would be little occasion for presenting this paper, but the fact is that hydrogen peroxide has the peculiar property of decomposing upon the slightest provocation during manufacture and after it is bottled.

Chemicals Required

The chemicals required for the manufacture of medicinal hydrogen peroxide are: barium peroxide containing approximately 90 per cent BaO_2 and as little chloride as possible, phosphoric acid 85 per cent, U. S. P., a good grade of concentrated sulfuric acid, pure barium hydroxide, and distilled water.

Equipment Required

A considerable amount of equipment is required for a hydrogen peroxide plant and the type used depends largely upon the volume produced and the amount of money available for the purpose. The plants that have been in existence for many years often continue to use old-fashioned equipment merely because it is producing and replacement for more up-to-date appliances involves expense. The following general statement of the principal equipment required is all that is necessary:

1—A bin, hopper, and chute for holding and discharging the barium peroxide, all of which may be constructed of wood.

2—Mixers for washing and hydrating barium peroxide, consisting merely of iron tanks provided with heavy mixing blades.

3—A chute leading from the mixers to a small mixing tank.

4—A small mixing tank to keep the hydrated barium peroxide stirred before adding it to the reaction tank.

5—A reaction tank constructed of wood, having a wood mixing paddle or stirrer and lead cooling coils arranged around the sides of the tank. The coils are arranged so that cold water may circulate through as many coils as may be desired.

6—A lead-lined tank for dilute sulfuric acid.

7—A stoneware tank for phosphoric acid.

8—Large filter press for filtering out the barium sulfate by-product.

9—A tank for treatment of the filtered reaction product with barium hydroxide and a small stoneware tank for dissolving barium hydroxide.

10—Small filter press for filtering out precipitated hydrates and phosphates.

11—A lead-lined tank for precipitation of dissolved barium salts with sulfuric acid.

12—Block tin tank for washings from large and small filter press.

13—Receiving and storage tanks.

14—Bottling and packing plant.

In addition to the above equipment, of which there may be one or more units, the plant may have tanks for treating the by-product for recovery of phosphoric acid and a dryer for drying the barium sulfate. As a rule the by-product barium sulfate containing barium phosphate is washed and the wet material packed directly into barrels and sold to dealers in mineral pigments. For this purpose it should be washed free from acid. There are probably some plants where this valuable pigment is still discharged into the sewer. The possibilities of recovering phosphoric acid and producing a fine wet or dry barium sulfate would certainly warrant attention.

Process

WASHING OF BaO_2—The material should be tested for available oxygen. It usually contains 90 per cent of BaO_2 when fresh. The powder is sifted through a 30-mesh sieve and 3000 lbs. are fed into 720 gal. of clear filtered water, which is stirred while the powder is being added and for 10 min. longer. The stirrer is then stopped and the heavy powder allowed to settle for 5 min., the supernatant liquid being siphoned off. The washing is repeated from three to five times, the last washing being made with distilled water. A mark is made on the mixer and water added to this mark each time after siphoning off. Finally the tank is filled up to this mark with distilled water.

HYDRATION OF BaO_2—The barium peroxide is partly hydrated during the washing. In order to complete the hy-

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[1] Presented before the Division of Chemistry of Medicinal Products at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Director, Department of Chemistry.

dration to $BaO_2.8H_2O$ and $BaO_2.10H_2O$ the mixer is allowed to run slowly for 18 to 24 hrs., depending upon the temperature. The hydration requires from 307 to 383 gal. of water, the excess of water being sufficient to reduce the mixture to a heavy creamy fluid. It is very important to hydrate the barium peroxide thoroughly so as to reduce all hard lumps. Gritty particles of unhydrated BaO_2 must be avoided because they cause decomposition to take place during the saturation process.

SATURATION—The washings from a previous batch, amounting to 300 or 400 gal. and containing from one to two volumes of oxygen, are run into the reaction tank, and 160 lbs. of pure phosphoric acid (85 per cent) are added. The stirrer is started and cold water allowed to circulate through the cooling coils (from one to three coils depending upon the temperature of the water). The stirrer is allowed to run continuously during the saturation; otherwise losses will take place. The $BaO_2.xH_2O$ cream is then run into the mixing tank through the chute and the mixing tank kept filled and contents continuously stirred. About three-eighths of the quantity required to neutralize the phosphoric acid is now run in a stream into the diluted phosphoric acid and the reaction allowed to proceed for 10 min. Another charge of like amount is then added with another interval of 10 min. for the reaction to take place. A sample of the mixture is then tested for any gritty particles of barium peroxide; if they are present, a further quantity of $BaO_2.xH_2O$ must not be added until they are reduced, after which the liquid is tested for acidity and if strongly acid small amounts of $BaO_2.xH_2O$ are added at a time until the acidity is mild. At this stage of the process substantially three-fourths of the phosphoric acid will be neutralized.

An interval of 10 min. is now allowed to complete the reaction and 28° Bé. sulfuric acid added, which should be cooled to room temperature. Sufficient sulfuric acid is added to regenerate 85 per cent of the phosphoric acid.

A further quantity of $BaO_2.xH_2O$ is again added, followed by sulfuric acid, and the operation is continued as outlined for the first stage, with all the precautions previously mentioned. The phosphoric acid is used repeatedly to decompose the $BaO_2.xH_2O$, whereas the sulfuric acid is used to regenerate the phosphoric acid.

During the saturation the temperature is maintained at from 90° to 110° F. by running water through the cooling coils. The batch is not allowed to cool below 90° F. because the reaction is too sluggish, or to heat above 110° F. because excessive loss of hydrogen peroxide will then take place.

A quantity of about 75 lbs. of $BaO_2.xH_2O$ is reserved for finishing the reaction, the rest being added in stages as outlined. When all but 75 lbs. of $BaO_2.xH_2O$ have been added the mixture in the reaction tank will be slightly acid and it must be free from any gritty particles because if the latter are present the entire batch may decompose in a few minutes during the finishing of the saturation. The batch should now test about 18 volumes of oxygen. The 75 lbs. of $BaO_2.xH_2O$ are sufficient to convert all of the acid barium phosphates, $BaH_4(PO_4)_2$ and $BaHPO_4$, into the tribarium phosphate, $Ba_3(PO_4)_2$, which is insoluble in water.

About 5 gal. of distilled water are added to the 75 lbs. of $BaO_2.xH_2O$ so as to render it more fluid, and the mixture in the reaction tank is cooled to 95° to 100 ° F. The diluted $BaO_2.xH_2O$ is fed slowly into the mixture through a 30-mesh sieve, made of brass or bronze wire cloth, until the reaction is neutral. This part of the process must be most carefully conducted because if the reaction is allowed to become alkaline even for a few minutes, considerable loss in hydrogen peroxide will result. If the reaction should go over to the alkaline side a small amount of sulfuric acid must be promptly added. The end reaction must be neutral or very faintly acid. If too acid the mixture will be difficult to filter.

FILTRATION—As soon as the reaction has been properly adjusted the mixture is run through the filter press and collected in the tank. The filter press must be in perfect working order in advance of sending the mixture through because there must be no delay at this stage.

If the process has been carefully conducted about 750 gal. of filtrate will be obtained, testing around 18 volumes of oxygen. The reaction tank and press are then washed with 300 gal. of distilled water, this first washing being collected in the same tank (9). This will yield about 1000 gal. and reduce the strength to about 16 volumes of oxygen.

NEUTRALIZATION—Barium hydrate is dissolved in distilled water in a small stoneware tank by injecting steam into it, yielding a saturated hot solution. This solution (while hot) is added to the hydrogen peroxide solution in tank (9) until the reaction is alkaline, so that litmus paper is turned a purple-violet when dipped into the solution. The precipitate of tribarium phosphate, iron hydroxide, and other impurities is filtered off through the small filter press (10) into tank (11), the filtrate being perfectly clear and bright.

ACIDIFICATION—The stirrer is started in tank (11) and 28° Bé. sulfuric acid added in small amounts at a time which will precipitate all of the soluble barium salts as sulfate. From time to time a sample of the fluid is tested by filtering, adding sulfuric acid to the filtrate, and boiling. Addition of sulfuric acid is continued until the barium salts have been completely precipitated and only a slight excess of sulfuric acid remains.

SETTLING—The precipitated barium sulfate is allowed to settle over night and the clear hydrogen peroxide solution siphoned off through a block tin siphon into a receiving tank. After settling in the tank for a day it is drawn off into a clean storage tank and is then ready for preservation, standardization, and bottling if absolutely clear and bright.

WASHINGS—The large and small filter presses are washed with from 300 to 400 gal. of distilled water immediately after being used for filtering the hydrogen peroxide solution, and the washings are run into the tank (12).

PRESERVATION—Acetanilide is the most commonly used preservative for hydrogen peroxide. The U. S. Pharmacopeia limits the amount added to not more than 0.04 g. per 100 cc., corresponding to the customary three-sixteenths of a grain per fluid ounce, which is the amount usually declared on the label as required by the U. S. Pure Food and Drug Law. As a rule from one-eighth to three-sixteenths of a grain is used for each fluid ounce and the desired amount is added to the solution after precipitating the barium salts or to the solution in the storage tank.

Preservatives are not used in all cases and in some instances unusual preservatives, the presence of which need not be declared on the label, such as caffein and quinine, are used. An analysis of one product revealed the presence of a mixture of benzoic acid, salicylic acid, and acetanilide.

STANDARDIZATION—It is necessary to standardize the solution of medicinal hydrogen peroxide so that it will correspond to the requirements of the U. S. Pharmacopeia. As a rule, there is no difficulty in meeting the requirements, the acidity, strength, and nonvolatile matter requiring the most careful attention. All tests are made in accordance with the U. S. Pharmacopeia methods.

If the hydrogen peroxide is sold under the designation "U. S. P." it is necessary to standardize the solution so as to comply with the requirements. Distilled water is added to adjust the strength to somewhat above 3 per cent H_2O_2 by weight or 10 volumes of oxygen, and the liquid is examined in accordance with the U. S. P. tests.

SPECIAL STRENGTH HYDROGEN PEROXIDE—Stronger solutions of hydrogen peroxide are sometimes sold containing 15 volumes or 30 volumes of available oxygen. The former can be obtained directly by the aforementioned process by avoiding dilution. To make the 30-volume product, the process is "doubled up," so to speak, by using 18-volume hydrogen peroxide instead of washings in the reaction tank and diverting the filter press washings, using only the concentrated filtrate as it leaves the filter press.

BOTTLING—The important point in connection with bottling is to use a sound cork of the best quality and to select a good grade of glass bottle. Packing in cartons is advisable. The corks should be wired.

Effect of Light on Deterioration of Hydrogen Peroxide

STORAGE IN DARK—Hydrogen peroxide solutions deteriorate much more rapidly when exposed to the action of light. The extent to which light influences decomposition is clearly indicated by the results shown in Table I.

Table I

Sample	Original Volume	Per cent Loss in Volume in 7 Wks. Dark	White Light
1	15.07	19.9	83.6
2	16.42	5.4	84.1

In these experiments, glass bottles of the same kind were used and the conditions of exposure were identical except as to exclusion of light.

STORAGE IN VARICOLORED LIGHT—The following experiments were conducted to determine the effect of orange, red, white, and blue light. Incidentally, the influence of glass bottles of different composition of glass and the effect of filtration through paper as compared with settling was determined. All of the test bottles were stored in a specially constructed closet, provided with compartments each having windows of orange, red, plain, and blue glass. The results are given in Table II.

Table II

F = Filtered, original volume 16.08
S = Siphoned, original volume 16.28

Time of Exposure, Days		14		36		56		67	
Method of Clarification		F	S	F	S	F	S	F	S
Bottle A: Color of light	Orange	12.94	14.63	6.03	9.09	3.35	6.86	2.06	5.77
	Red	12.51	14.04	5.93	6.92	3.93	4.08	2.75	2.85
	White	12.04	13.99	5.93	7.58	3.99	5.40	2.71	4.22
	Blue	11.09	12.79	5.16	6.48	3.03	4.41	2.10	3.46
Bottle B: Color of light	Orange	14.63	15.26	10.89	14.63	6.08	12.88	3.17	11.38
	Red	14.61	15.30	10.15	13.71	5.36	11.67	2.71	11.41
	White	12.85	14.55	7.48	10.51	3.18	7.36	1.44	5.17
	Blue	12.38	14.71	7.00	10.02	1.84	7.08	1.15	4.97
Bottle C: Color of light	Orange	14.95	15.24	13.65	14.54	12.52	13.87	11.55	13.27
	Red	14.71	15.26	13.02	14.57	11.34	13.79	10.10	13.23
	White	14.97	15.30	14.00	14.50	12.48	13.51	11.65	12.95
	Blue	14.83	15.16	13.81	14.27	12.60	13.40	11.76	12.73

The results in Table II show very conclusively that hydrogen peroxide filtered through paper deteriorates very much more rapidly than hydrogen peroxide which has been clarified by settling. The hydrogen peroxide lost only 0.20 volume upon filtration, showing that the deterioration is due to dissolved organic matter from the paper acting as a catalyst. This proves definitely that hydrogen peroxide should not be clarified by filtration after it is "sulfated," but should be allowed to clarify by settling. Experience has shown that a worn filter cloth used to filter hydrogen peroxide through a filter press will often introduce enough organic matter to result in a seemingly inexplicable tendency of the hydrogen peroxide to decompose.

If the results in varicolored light are examined collectively, it will be noted that orange light affords the best protection and red next. Blue light causes a more rapid deterioration than white light. There are a few results that are apparently contradictory, but the general results plainly show the above relationship.

The composition of the glass bottle evidently has a pronounced effect on deterioration of hydrogen peroxide. A remarkable difference was obtained with the three kinds of glass bottles tested. The A bottle causes the greatest deterioration, B bottle next, and the C bottle has but little influence. In fact, the hydrogen peroxide in C bottle stood up so well that it might be stated definitely that the glass bottle has more effect on the deterioration of hydrogen peroxide than light or conditions of clarification.

Effect of Glass Bottles on Deterioration of Hydrogen Peroxide

It is well known that alkalies, even the traces dissolved from the glass of the bottle, favor deterioration. However, manufacturers have considered this in the light of an unavoidable difficulty and have not given the matter serious consideration from the standpoint of studying the glass so as to secure glass bottles which would insure the greatest permanency. The experiments on the three bottles, the results of which are given in Table II, clearly indicate that a wide difference exists in the quality of the glass actually used in bottling hydrogen peroxide.

In order to verify these results two bottles made of a borosilicate glass, which was known to be more soluble than ordinary glass, were compared with two bottles regularly employed for bottling hydrogen peroxide. All bottles were filled with the same hydrogen peroxide, made by the barium process and free from any preservative, all of the samples being stored in white light under identical conditions. Table III gives the results of these experiments.

Table III

	Bottle	Original Volume	Per cent Loss in Volume, 7 Days
Borosilicate glass...	A	12.85	29.1
	B	12.88	38.4
Regular glass......	A	12.88	8.2
	B	12.88	9.4

An average of the results on the two bottles of the same kind shows that the more soluble borosilicate glass resulted in deterioration approximately four times as rapid as the regular glass used in the trade. Moreover, the evolution of gas bubbles plainly showed that the decomposition was more rapid in the case of the borosilicate glass. The hydrogen peroxide was titrated in the cold, using methyl orange indicator, with the results given in Table IV.

Table IV

	Bottle	Original Cc. 0.1 *N* NaOH	After 7 Days' Storage Cc. 0.1 *N* NaOH
Borosilicate glass...	A	1.75	Neutral
	B	1.75	Neutral
Regular glass......	A	1.75	1.77
	B	1.75	1.77

These results show that there is a marked difference in the solubility of the glass and that the solution of alkali from the glass resulted in the greater deterioration observed to take place with the borosilicate glass.

Influence of Alkali from Glass on Deterioration of Hydrogen Peroxide and the Effect of Acetanilide

In order to study the effect of the alkali from the glass bottle still more thoroughly, four samples of medicinal hydrogen peroxide, representing the product of four manufacturers, were obtained. Samples supposed to be free from acetanilide or other preservatives were selected. The real object of this was to ascertain, if possible, the reason for the difference in keeping qualities of various brands of hydrogen peroxide and particularly whether the kind and quality of acid or impurities contained in the different brands were responsible for the difference in keeping quality or whether the glass bottles had more to do with the deterioration.

Incidentally, the effect of acetanilide as a preservative was determined, particularly as to whether the restraining effect of acetanilide was similar for different brands or whether the quantity and kind of acid or impurities would alter or influence its effect. Table V gives an analysis of the four brands.

TABLE V

Sample	A	B	C	
Hydrogen dioxide: Absolute	2.828	2.615	2.620	2.622
Volumes	9.304	8.603	8.619	8.626
Total acidity, cc. of 0.1 *N* alkali required for 25 cc	2.36	2.36	1.28	2.89
Residue on evaporation, g. per 100 cc	0.054	0.082	0.064	0.153
Hydrochloric acid, g. per 100 cc	0.011	0.007	0.015	0.034
Sulfuric acid, g. per 100 cc	0.005	0.012	0.014	0.017
Phosphoric acid, g. per 100 cc	0.029	0.034	0.006	0.060
Silica (SiO_2), g. per 100 cc	0.009	0.023	0.023	0.023

The above samples were tested for relative stability both in the original form and after adding three-sixteenths of a grain of acetanilide per fluid ounce, all conditions of storage in white light being identical. Table VI gives the result of these observations.

TABLE VI

Sample		Volumes Oxygen Original	Per cent Loss in Volume in Wks. 1	2	3	7	11
A	Original	9.304	0.15	10.68	11.21	25.08	39.04
	With acetanilide	9.389	0.30	0.87	0.94	2.23	6.79
B	Original	8.603	15.11	25.58	36.80	67.10	82.68
	With acetanilide	9.001	1.98	3.00	5.23	27.34	63.09
C	Original	8.619	6.45	19.79	29.45	63.45	79.24
	With acetanilide	8.938	1.43	3.33	5.12	15.98	47.07
D	Original	8.626	5.28	14.80	18.15	42.49	57.97
	With acetanilide	8.731	0.64	1.84	2.87	8.03	21.47

The acidity of the different samples was carefully determined by titration in the cold, with 0.1 *N* NaOH, titrating first to methyl orange, and then adding phenolphthalein and completing the titration. The samples were titrated after storage for 1 and 13 wks., with the results given in Table VII.

TABLE VII

Sample		Time of Storage Wks.	Acidity Cc. 0.1 *N* NaOH Required for 25 Cc.			Reduction or Increase in Acidity after 12 Wks.		
			Total	Methyl Orange	Phenolphthalein	Total	Methyl Orange	Phenolphthalein
A	Original	1	2.36	1.07	1.29	−0.16	+0.09	−0.25
		13	2.20	1.16	1.04			
	With acetanilide	1	2.89	1.18	1.71	+0.99	+0.57	+0.42
		13	3.88	1.75	2.13			
B	Original	1	2.36	0.77	1.59	−0.61	−0.12	−0.49
		13	1.75	0.65	1.10			
	With acetanilide	1	2.80	0.98	1.82	−1.01	−0.49	−0.52
		13	1.79	0.49	1.30			
C	Original	1	1.28	0.53	0.75	−0.41	+0.01	−0.42
		13	0.87	0.54	0.33			
	With acetanilide	1	1.71	0.86	0.85	−0.62	−0.49	−0.13
		13	1.09	0.37	0.72			
D	Original	1	2.89	1.18	1.71	−0.08	−0.06	−0.02
		13	2.81	1.12	1.69			
	With acetanilide	1	2.89	1.18	1.71	+0.36	−0.06	+0.42
		13	3.25	1.12	2.13			

The analyses given in Table V show that the samples are all quite pure; at least no explanation for the remarkable difference in stability is possible from the standpoint of purity or acidity.

Acetanilide (see Table V) has a restraining influence on the rate of decomposition which varies with the different samples. Sample A, which is a widely advertised product, is generally understood to have unusual stability and to be free from preservatives. The fact that the sample gave the best results in the original condition and after the addition of acetanilide naturally led to a question as to the possible presence of a preservative. A liter of the sample was extracted with ether in acid solution and then again after addition of sodium hydroxide solution to render it alkaline. The two extracts were evaporated spontaneously and examined for any ether-soluble preservatives. The alkaline ether extract was found to contain quinine equivalent to 60 mg. quinine sulfate per liter. Owing to the presence of hydrochloric, sulfuric, and phosphoric acids in the product it is impossible to state what salt of quinine was originally used. The presence of quinine in the product was verified recently by examining a sealed sample purchased in the open market in July 1921, and an examination made as far back as November 1912 showed quinine to be present.

A study of the results given in Table VII shows that those products which show an increase or the least decrease in acidity upon storage are the more stable, whereas those which show the greatest reduction in acidity deteriorate more rapidly. This relation is shown in Table VIII.

TABLE VIII

Sample		Per cent Loss in Volume 11 Wks.	Per cent Increase or Decrease in Total Acidity 12 Wks.
A	Original	39.04	− 6.8
	With acetanilide	6.79	+34.2
B	Original	82.68	−25.8
	With acetanilide	63.09	−36.0
C	Original	79.24	−32.0
	With acetanilide	47.07	−36.2
D	Original	57.97	− 2.7
	With acetanilide	21.47	+12.4

It must be remembered that Sample A contained quinine, the presence of which was not suspected when the experiment was started. This explains why the original Sample D which contained no preservative showed a greater loss although the decrease in acidity was less. In other respects the results show that samples containing acetanilide, which are the most stable, show an increase in acidity on storage, whereas unpreserved samples show the greatest deterioration with the largest decrease in acidity.

Acetanilide has a tendency to increase the acidity initially and to increase the acidity continually in the more stable products, while in those products which show the greater losses acetanilide appears to lose this property and actually show a decrease in acidity. This explains the variable results obtained in the effectiveness of acetanilide as a preservative and indicates that the alkali derived from the glass acts as a catalyst and has a greater effect in accelerating decomposition than acetanilide has in restraining it.

The remarkable difference in the rate of deterioration observed in the same sample of hydrogen peroxide stored in bottles of different composition, taken in conjunction with the relation of deterioration to decrease in acidity upon storage as determined in these experiments, shows conclusively that the resistance of the glass to attack by the hydrogen peroxide solution is the most prominent cause of deterioration of hydrogen peroxide. Manufacturers have neglected this important phase of the glass problem, evidently upon the assumption that all glass has a similar effect in causing deterioration, little realizing that a remarkable difference in stability may be secured by careful selection of glass of suitable resistance. A proper selection is best made by studying the resistance of the glass to water and weak acids in conjunction with observations on the rate of deterioration of the hydrogen peroxide upon storage. This is a problem well worth the attention of the bottle manufacturer. As a matter of fact, entirely too little attention is given to the suitability of glass bottles as containers for manufactured products and it is the author's experience that defective glass bottles in many instances have been responsible for the deterioration of manufactured products, particularly solutions of various chemicals, pharmaceutical preparations, and beverages.

PRESERVATIVE EFFECT OF CERTAIN ORGANIC SUBSTANCES UPON HYDROGEN PEROXIDE SOLUTIONS

QUININE SULFATE—The U. S. P. salt was added to hydrogen peroxide solutions of two different strengths made by the process already described. In both cases, 3.5 grains of quinine sulfate were added to 1 gal. of the solution. Three different bottles were used in these tests, the bottles containing the original and treated hydrogen peroxide solutions being exposed to white light under identical conditions. Table IX gives the result of these experiments.

TABLE IX

SAMPLE		Bottle	VOLUMES OF OXYGEN Original	After 11 Days	Per cent Loss in Volume
A	Original.........	1	16.44	15.60	5.1
		2	16.44	15.16	7.8
	With quinine sulfate...........	1	16.67	16.59	0.5
		2	16.67	16.68	0.0
		3	16.67	16.54	0.8
B	Original.........	1	25.68	24.44	4.8
		2	25.68	24.21	5.7
		3	25.68	24.28	5.4
	With quinine sulfate...........	1	26.10	26.14	0.0
		2	26.10	26.21	0.0
		3	26.10	26.18	0.0

These results show that quinine sulfate restrains decomposition of hydrogen peroxide solutions of high strength. It was considered interesting to determine whether a solution of pure hydrogen peroxide which had been stored until considerably reduced in H_2O_2 content would show a similar result and also whether a reduced amount of quinine sulfate would be effective. This constitutes a more rigorous test of its effectiveness than when added to a fresh solution because solutions of hydrogen peroxide which have undergone decomposition are more susceptible to decomposition. These results are given in Table X.

TABLE X

SAMPLE	Description Grs. per Gal.	VOLUMES OF OXYGEN Original	After 16 Days	Per cent Loss in Volume
1	$+{}^{7}/_{12}$	5.50	3.39	38.3
2	$+1^{1}/_{6}$	5.53	4.22	23.7
3	$+1^{3}/_{4}$	5.50	4.62	16.0
4	$+2^{1}/_{3}$	5.50	4.72	14.1
5	No addition	5.50	2.28	58.5

The results given in Table X show that addition of quinine sulfate restrains the decomposition of hydrogen peroxide solutions which have already lost considerable oxygen and that the restraining effect is dependent upon the amount added. Moreover, it appears that $2^{1}/_{3}$ grains per gallon are as much as need be added for preservation.

It was thought interesting to determine whether quinine sulfate added in the various amounts used in all of these experiments would cause a bitter taste in the product. Organoleptic tests made by seven observers, all of whom were asked to determine whether any of the samples had a perceptible bitter taste, gave results which established the fact that quantities up to the limit tested ($3^{1}/_{2}$ grains per gallon) did not contribute any bitter taste to the original quinine-free solutions.

VARIOUS PRESERVATIVES—A sample of hydrogen peroxide made by a prominent pharmaceutical manufacturer was found to contain 11.75 grains of benzoic acid, 0.93 grain of salicylic acid, and 1.28 grains of acetanilide in each gallon of the product. Tests were made to determine the effect of this mixture of substances as compared to the same quantity of benzoic and salicylic acids without any acetanilide.

In connection with the organoleptic tests, it was found that some observers reported that plain hydrogen peroxide solutions had a slightly bitter taste. In fact, this is a property of pure hydrogen peroxide. Addition of 1 grain of saccharin per gallon of hydrogen peroxide solution was found to improve the taste. An experiment was, therefore, made to determine the effect of a mixture of $2^{1}/_{3}$ grains of quinine sulfate and 1 grain of saccharin on the stability of hydrogen peroxide (Table XI).

A mixture of benzoic acid and salicylic acid in the quantity used exerts a preservative action, which is not appreciably enhanced by the amount of acetanilide added.

Quinine sulfate and saccharin in the quantities used also show a preservative action, although the results with quinine sulfate alone appear to be better.

TABLE XI

SAMPLE	VOLUMES OF OXYGEN Original	After 1 Wk.	After 4 Wks.	PER CENT LOSS IN VOLUME 1 Wk.	4 Wks.
A + 11.88 grs. benzoic acid 0.92 gr. salicylic acid 1.23 grs. acetanilide per gal.	16.16	15.81	13.95	2.1	13.6
B + 11.88 grs. benzoic acid 0.92 gr. salicylic acid 1.23 grs. acetanilide per gal.	25.45	24.98	21.96	1.8	13.7
A + 11.98 grs. benzoic acid 0.92 gr. salicylic acid per gal.	16.08	15.66	13.69	2.6	14.8
B + 11.88 grs. benzoic acid 0.92 gr. salicylic acid per gal.	25.45	24.98	.....	1.8	....
A + $2^{1}/_{3}$ grs. quinine sulfate 1 gr. saccharin per gal.	16.08	15.97	13.82	0.7	14.0
B + $2^{1}/_{3}$ grs. quinine sulfate 1 gr. saccharin per gal.	25.42	24.91	21.63	2.0	14.9
A− No addition	16.00	14.63	10.11	8.5	36.8
B− No addition	25.42	23.89	16.63	6.0	34.5

Ordinarily, 24 grains of acetanilide are added to each gallon of hydrogen peroxide as a preservative. It has been the author's experience that $2^{1}/_{3}$ grains of quinine sulfate to each gallon are as efficient a preservative and introduces only one-tenth the amount of foreign substance. Moreover, acetanilide causes the development of yellowish or brownish tint and unpleasant odor. The author's experiments have shown that an odor identical with iodoform is developed in solutions of hydrogen peroxide which contain a slight excess of acid. Quinine sulfate does not cause any foreign odor or color to develop. As mentioned before, quinine is used in one of the most widely sold medicinal hydrogen peroxide solutions, and it certainly has advantages over acetanilide, especially in view of the fact that the law does not require its presence to be declared upon the label of the product.

Du Pont Chemical Fellowships

It is interesting to note, in these days of retrenchment, that the du Pont fellowships in chemistry in twenty colleges and universities throughout the United States are to be continued for the academic year 1922–23. These fellowships were established four years ago, at the time when the war made necessary the development of a self-contained chemical industry in this country.

The fellowships are for graduate work. Recipients must be graduates devoting the major part of their time to the study of chemistry, and are selected by the university authorities, not by the Company.

The plan differs from the usual one for industrial fellowships in that the research is not necessarily to be directed along some line in which the Company is interested, but the student is left free, under the direction of his instructors, to follow whatever line of investigation seems to him most promising.

The institutions which receive these fellowships are:

Brown University, Providence, R. I.
California Institute of Technology, Pasadena, Cal.
University of California, Berkeley, Cal.
University of Chicago, Chicago, Ill.
Columbia University, New York, N. Y.
Cornell University, Ithaca, N. Y.
Delaware University, Newark, Del.
Harvard University, Cambridge, Mass.
University of Illinois, Urbana, Ill.
Johns Hopkins University, Baltimore, Md.
Lafayette College, Easton, Pa.
Massachusetts Institute of Technology, Cambridge, Mass.
University of Michigan, Ann Arbor, Mich.
University of Minnesota, Minneapolis, Minn.
Ohio State University, Columbus, Ohio
Princeton University, Princeton, N. J.
University of Virginia, University, Va.
University of Washington, Seattle, Wash.
University of Wisconsin, Madison, Wis.
Yale University, New Haven, Conn.

Rates of Absorption and Heat Transfer between Gases and Liquids[1]

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Within the last few years the introduction of solvent recovery and air-conditioning systems in the chemical industry has focused the attention of engineers upon the general problem of interaction between gases and liquids. The commercial scope of this subject includes many processes, such as the separation of ammonia and light oils from by-product coke-oven gas, the recovery of volatile solvents in the rubber industry, air conditioning for the drying of soap, lumber, leather, etc., and ventilation for hospitals and plants handling certain materials such as paper, cloth, and kodak films. The purpose of this article is to present a mathematical treatment for this type of problem and to give results obtained in certain specific cases.

UP to a short time ago, the only method available for the purpose of predicting or altering the capacity of any specified apparatus which transferred matter or energy between gases and liquids was a very indefinite one gained by the experience of the operator. The necessity of working under variable conditions of liquid or gas supply often increased or decreased capacity or efficiency, and accordingly the experienced operator understood in a qualitative manner how to alter the capacity or function of his own particular unit. In 1916, W. K. Lewis[3] developed an expression for the performance of gas scrubbers and other countercurrent absorption devices. The data on the subject available at that time were very meager, and accordingly the theory could not be given a thorough test. Recently, however, considerable data on the transfer of energy and matter have been obtained on various types of commercial and laboratory equipment, and with the aid of these data and a modified treatment of the theory developed by Lewis, transfer coefficients have been obtained for a number of important cases. For any given piece of apparatus the coefficient is a variable quantity directly influenced by the conditions of operation, and is a measure of capacity and efficiency. This article, therefore, is devoted to the following subjects:

1—A presentation of the theory involved in liquid-gas interactions.
2—A summary of Lewis's mathematical treatment with modifications.
3—A verification of the theory.
4—A presentation of equations showing the effect of operating variables on the coefficients for various types of apparatus.

THEORY OF RATE OF INTERACTION

The theory involved in this problem is based upon the rates of interaction of the two components for the various conditions encountered in practice.

The rate at which energy or matter is transferred from gas to liquid or vice versa is determined by the general law which governs the flow of heat and electricity. In all cases any definite system tends to adjust itself to a condition of equilibrium, and the rate of this adjustment or interaction within the system decreases as equilibrium is approached. In fact, the driving force or potential of the interaction for any given conditions is directly determined by the distance from equilibrium. For problems in heat flow this driving force is the temperature difference, for electricity the voltage drop, and for liquid-gas interactions it may be either a temperature or pressure potential operating on the transfer of heat or matter.

HEAT TRANSFER—The mechanism of heat transfer between gases and liquids can be illustrated (Fig. 1) by the case of a drop of water at a temperature, t, suspended in warmer air at a temperature, T. Heat flows from the air into the water because of the difference in temperature between the two. The actual mechanism is a combination of the two processes of convection and diffusion—convection in the main bodies of the gas and the liquid, and diffusion through the comparatively quiet layers in the surface phases. It is well known that the layer of gas against any solid or liquid surface is almost at rest compared to the mass of gas outside, and it is this so-called "film," through which heat must pass by the slow process of diffusion, which offers high resistance to the flow of energy. Similarly a liquid film exists on the surface of the water drop, and the combination of gas and liquid films in series gives a "two-film" resistance. The flow of heat can therefore be expressed by the formula

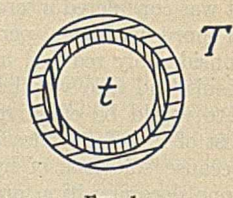

FIG. 1

$$\frac{dQ}{d\Theta} = \frac{(T-t)}{R_G + R_L} = \frac{\Delta T}{R_G + R_L}$$

where $dQ/d\Theta$ = B. t. u. from gas to liquid per min.
$(T-t)$ = Driving temperature potential in ° F. = ΔT.
R_G = Resistance of gas film.
R_L = Resistance of liquid film.

The values for R_G and R_L will of course vary widely with the specific conditions.

The above method is fundamentally sound in treating the phenomenon as a matter of series resistances. It is customary, however, to handle the calculations from the standpoint of film conductance, *i. e.*, the reciprocal of film resistance. The formula then becomes

$$\frac{dQ}{d\Theta} = hA\,\Delta T$$

where hA = Over-all conductance of the two films = $\frac{1}{R_G + R_L}$.
A = Surface area of contact.
h = Over-all conductance per unit area.

Since it is usually impossible to determine A, the area of contact, in any given equipment, the term ha V is substituted for hA, with V the total volume of the equipment where interaction takes place, a the contact surface per unit of volume, and h the conductance per unit of surface. It is obvious that h and a will vary widely with the type of apparatus and the operating conditions, and that they cannot be separated if the actual surface area is not known. In the following general equation,

$$\frac{dQ}{d\Theta} = ha\,V\,\Delta T,$$

ha is the coefficient of heat transfer in B. t. u. per cu. ft. per ° F. per min. and is consistently treated as a unit. This equation is the one employed throughout the remainder of the article.

ABSORPTION—The rate of absorption of matter from gas to liquid or vice versa is a process paralleling that of heat

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[1] Received November 17, 1921.

[2] Assistant Professor, School of Chemical Engineering Practice.

[3] "The Principles of Countercurrent Extraction," THIS JOURNAL, 8 (1916), 827.

transfer. The action can be visualized in the same manner with a two-film resistance to diffusion through the two surface layers, but the driving potential is caused by a difference in pressures or concentrations, rather than by a temperature difference. The previous illustration may be modified for this case by assuming that ammonia is diffusing from a concentrated mixture with air into a dilute solution inside the drop (Fig. 2). Denoting the pressure of ammonia in the gas by P and its concentration in the drop by x, the driving pressure of the diffusion is $(P-\alpha x)$, or $(P-p)$. p is the equilibrium or back pressure of ammonia above a solution of concentration, x, the concentration being determined from the solubility of ammonia in water at the temperature of the drop. In simple cases p and x are related by Henry's Law, *i. e.*, $p = \alpha x$. It is to be understood that this treatment probably cannot be used for problems in which Henry's Law does not hold approximately over the range in question, as, for example, for the absorption of hydrogen chloride gas in water.

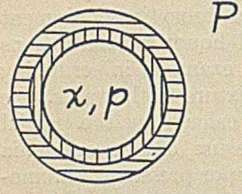

FIG. 2

The general equation for absorption is similar in form to that for heat transfer:

$$\frac{dW}{d\Theta} = k'a\,V\,(P-p) = k'a\,V\,\Delta p$$

where $dW/d\Theta$ = Lbs. of material absorbed per minute.
$k'a$ = Coefficient of absorption in lbs. of material absorbed per cu. ft. per min. per mm. mercury pressure difference.
V = Volume of apparatus in cubic feet.
Δp = Driving pressure in mm. of mercury.

This equation could also be expressed in the resistance form given under heat transfer.

RELATION BETWEEN HEAT TRANSFER AND GAS ABSORPTION—The similarity between the mechanisms of heat transfer and diffusion of matter between liquids and gases, which has already been pointed out, suggests that the two processes may be directly connected in some simple manner. W. K. Lewis[4] has developed this relationship in a recent article, proving that the ratio of the coefficients $(ha/k'a)$ is practically proportional to the humid heat of the gas. Humid heat is defined as the amount of heat in B. t. u. necessary to raise 1 lb. of inert carrier plus the solute associated with it 1° F. By expressing the Δp pressure difference in pounds of absorbable material per pound of inert carrier instead of in mm. of mercury, the proportionality factor becomes unity:

$$\frac{ha}{ka} = \text{B. t. u. per lb. carrier per } ^\circ\text{F.} = s \text{ (humid heat)}$$

The mathematical derivation of this expression may be found in Lewis's article.

VARIABLES INVOLVED—The main variables affecting heat transfer and diffusion are character of equipment, gas velocity, rate of liquor flow, temperature, and nature of gas, solute, and liquid. Since ha and $k'a$ are connected by direct ratio, it follows that the effect of any variable in design or operation for a definite gas and liquid will be the same for either process.

Character of Equipment—Some of the various types of apparatus used for transferring energy or matter between gases and liquids are packed towers, spray chambers, plate columns, bubbling caps, rotary gas washers, etc. Design is undoubtedly the most important variable to be considered and the coefficients obtained with various machines may be regarded as direct measures of their absorbing or heat transfer effectiveness per unit of volume. It is obvious that any equipment giving large surface area per unit volume will tend to have a high coefficient, other conditions being constant. The influence of character of equipment on other variables will be discussed under the individual variables themselves.

Gas Velocity—The velocity of gas past the liquid surface has an important bearing on the transfer coefficients. High gas velocity exerts a brushing or tearing action on the surface films, reducing their effective thickness and thus decreasing the resistance. The exact nature of this effect can be predicted qualitatively from the character of the apparatus, remembering that the important factor is gas velocity relative to the surface of the liquid rather than the apparent velocity measured past the walls of the equipment. For example, in a coke-filled tower where air is being heated or cooled by water trickling down over the coke, the water is held on the solid coke, and an increase in gas velocity through the tower will cause a corresponding increase in gas velocity past the water. The effect of changing gas velocity should therefore be great for this case. On the other hand, a spray chamber for conditioning air where the gas flows horizontally against a water spray from nozzles illustrates the other extreme. In such a chamber the drops of water are not held on any solid surface, and a definite increase in gas velocity tends to carry the drops along in the air without producing the same increase in the relative motion between gas and liquid. For this case gas velocity should have much less effect than in the coke tower mentioned above. Fig. 3 shows how this effect varies with certain specific designs of apparatus. For ease in comparing effects of gas velocity a power function has been fitted to each of these curves, of the form $ha = kv^n$. The value of this power will be greater in those cases where gas velocity has a greater influence on the coefficient and it will be noted that the results bear out the predictions made above.

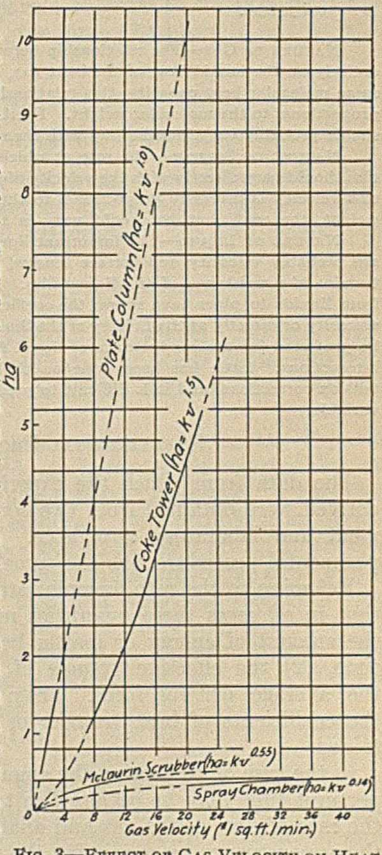

FIG. 3—EFFECT OF GAS VELOCITY ON HEAT TRANSFER COEFFICIENTS

Rate of Liquor Flow—The rate of liquor flow through the apparatus should influence the coefficient in two ways. First, an increase in amount of liquor in any given apparatus should increase the surface area of contact up to a certain limit varying with the nature of the apparatus—beyond this limit, a further increase in liquor rate is of little advantage. For example, in a spray device, increasing the liquor rate would produce a greater number of drops of practically the same size, but finally larger drops would result because of interference and coalescence of the smaller ones, and the relative increase in surface of contact would be small. In a packed tower, increase in liquor rate beyond the point necessary to keep the entire packing surface wet

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[4] "The Evaporation of a Liquid into a Gas," to appear in *Mech. Eng.*

would merely cause a thicker layer of liquor with relatively little increase in surface of contact. Second, in the case of packed towers, the increased flow of liquor would in some cases cause more turbulence and motion in the liquor phase, thus reducing the liquid film resistance and increasing heat transfer.

Temperature—Temperature has two effects on the total absorption of a definite system. The first of these is obvious, *i. e.*, a change in temperature changes the equilibrium pressure over the solution and hence changes the driving potential. This is completely allowed for in the potential term and does not affect *ka*, the specific coefficient per unit of potential, in the slightest degree. The other effect is a small increase in the coefficient due to increased molecular activity, and should theoretically be proportional to the square root of the absolute temperature of the gas. Liquor temperature is closely correlated with viscosity and is discussed under "Nature of Liquid."

Nature of Gas, Liquid, and Solute—The specific properties of the components in the system have an important bearing on the rate of interaction between the phases. From the physical concept previously presented, certain results can be predicted.

Nature of Gas—The relationship between *ha* and *ka* depends almost entirely on the humid heat of the inert gas, and since most gases have the same molecular heat capacity, this relationship should be almost inversely proportional to the molecular weight. Furthermore, the gas film resistance should probably vary in some way with the nature of the gas.

Nature of Solute—The rate at which the solute diffuses through a film should vary directly with the velocity of the diffusing molecules. Since this velocity is inversely proportional to the square root of the molecular weight, the coefficient *ka* should vary in the same way.

Nature of Liquid—The important liquor properties to be considered are probably viscosity and surface tension, since these would largely determine the resistance of the liquor film. Experiments on heat transfer from liquids to pipes have shown the coefficients to vary inversely as the viscosity or directly as the fluidity of the liquid, and the same results would be predicted for the conductance of liquid films encountered in liquid-gas interactions. Little has been done on the question of applying surface tension corrections, and it is difficult to predict the exact influence of this variable.

Experimental Procedure

The data from which the experimental coefficients were derived were obtained from two sources, commercial equipment and laboratory apparatus. For both cases the experimental procedure was the same.

Referring to the rate formulas stated above, it is obvious that in all cases three quantities must be determined: (1) the amount of energy or matter being transferred per unit time, (2) the effective volume of the equipment, and (3) the average driving force. From these three quantities the coefficients of heat transfer or diffusion are easily obtained.

In the case of absorption the amount of matter transferred per unit time may be obtained in two ways: by measuring the rate of flow of the gas and analyzing it at both ends of the apparatus, or by measuring the rate of flow of the liquid and analyzing it at both ends of the equipment. For problems in the transfer of heat the requirements are analogous to those stated for the previous case except for the fact that temperatures are used in the place of analyses. One exception is to be noted in this case, namely, the problem of dehumidification for which only the sensible heat change is used in determining the coefficient of heat transfer. The latent heat of condensation is transferred through a process of diffusion and is accounted for in *ka*. Accordingly the change in temperature of the liquid cannot be used as a measure of the heat transfer since this variation is caused by both the heat of condensation and the sensible heat removed from the gas. Therefore, for dehumidification the transfer is always calculated from the gas data.

The total active volume of the equipment is determined by direct measurement. For example, for a packed tower, it is the total volume of the tower minus any inactive portions, such as liquor storage or supports, and for a spray chamber, the total volume is the volume of the chamber minus storage space in the bottom of the chamber. In the case of a bubbling column the total volume is somewhat arbitrary, but for this work the entire available volume between the plates is used to represent this quantity.

The average driving force in any gas absorption equipment is calculated from observed gas and liquor concentrations at both ends of the apparatus. For example, in scrubbing ammonia out of an ammonia-air mixture with water, the average driving force is obtained by calculating the partial pressure difference between the pressure of the ammonia in the gas phase and the equilibrium vapor pressure of ammonia over the liquid at both ends of the apparatus and averaging the differences. In heat transfer the driving force is the average temperature difference between the gas and the liquid throughout the apparatus and is obtained by averaging the corresponding differences at both ends of the apparatus. The logarithmic mean average should be used in place of the arithmetic mean for all cases in which the difference at one end of the equipment is less than half that at the other end. Otherwise the arithmetic mean is used.

Experimental Results

In order to substantiate the theory and to present coefficients obtained in specific cases, the results of numerous tests on different types of apparatus, classified according to type of apparatus studied, are summarized in the following paragraphs. Many of these experiments were designed to show the effect of varying volume and driving potential, and in all cases the formula was found to apply.

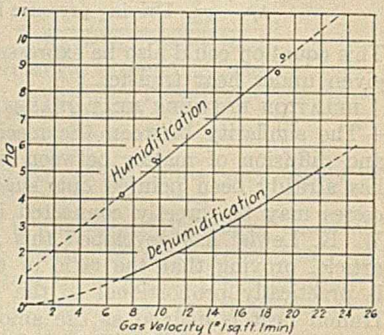

Fig. 4—Effect of Gas Velocity on Heat Transfer Coefficients in a Coke Tower
(Data at 20 lbs. water/sq. ft./min.)

PACKED TOWERS—One of the authors[5] ran tests on an experimental tower (1 ft. in diam. × 5 ft. high), packed with 3-in. gas coke, working with air and water and studying humidification and dehumidification. The results may be briefly summed up as follows. In *humidification* (Fig. 4) the heat transfer varies as a straight line function of the gas velocity and is expressed by the equation

$$ha_H = \frac{1}{R_G} = 1.20 + 0.42\ G,$$

in which G varied from 7.1 to 18.7 lbs. of dry air per sq. ft. per min., and *ha* increased from 4.2 to 9.1 B. t. u. per min. per cu. ft. per ° F. temperature difference. The dotted portion of the plot indicates the extrapolated zone. It is inadvisable to extrapolate this equation beyond the limits of the experimental work because the results might also have been expressed by power curves passing through the origin, but values showing this function at low gas velocities could not be obtained because the apparatus as constructed could not be operated over that range. Humidification runs made with variable liquid rate showed that the heat transfer was independent of the water rate. This is ex-

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[5] J. L. Keats, "A Study of Heat Transfer and Diffusion in a Coke Tower," M. I. T. Thesis, June 1921.

plained by the fact that in adiabatic humidification the water remains at a constant temperature, and accordingly there is no heat transfer through the liquid film, thus eliminating one of the resistances. The increase in active surface with increased liquid rate is negligible in a packed tower.

In *dehumidification* (Fig. 4) the equation

$$ha_D = \frac{1}{R_G + R_L} = \frac{1}{\frac{1}{1.20 + 0.42\,G} + \frac{1}{(0.000387)\,(G)^{1.8}\,(L)^{1.54}}}$$

was obtained within the experimental limits of 7.1 to 22.1 lbs. of dry air per sq. ft. per min. and 9 to 43 lbs. of water per sq. ft. per min. Values of ha_D increased from 1.2 to 5.3 and were calculated from the sensible heat lost by the air. The latent heat transfer accompanying the condensation and diffusion of water vapor into the liquid should not be considered here, as this part of the process is actually a diffusion of material rather than of heat. This equation checks up the predicted results fairly well and shows that both gas velocity and water rate have an effect upon the liquid film resistance. The limits of temperatures used did not allow for an appreciable variation in viscosity, and therefore this variable does not appear in the results.

These results show clearly that the coefficient for humidification is always greater than that for dehumidification at the same water and gas velocities. This is explained by the additional liquid film resistance encountered in the latter case.

The twenty-five runs made on this tower checked up the relationship $ha/ka = s$ within an average deviation of 15 per cent. The results were obtained with air velocities much higher than those used in commercial operation, and therefore the power required to force air through the tower was excessive.

MCLAURIN GAS SCRUBBER—Experiments[6] were carried out on an installation of this standard apparatus in order to study humidification, dehumidification, and acetone absorption. For *humidification* the effect of gas velocity is expressed by the equation

$$ha_H = 0.0722\,G,$$

in which G varies from 3.5 to 15.3 lbs. of dry air per min. per sq. ft. maximum cross section and ha_H varies from 0.25 to 1.10. The water rate was held constant at 100 lbs. per sq. ft. per min. This agrees in theory with the results obtained on the coke tower, but the heat transfer values are lower for the McLaurin apparatus because the active area of contact per unit volume is smaller in the latter. The effect of water rate in this case is found to be

$$ha_H = \frac{0.61\,L}{L + 14.0}$$

at 7.58 lbs. of dry air per sq. ft. per min. L varied from 3.4 to 117 lbs. of water per sq. ft. per min. and ha_H varied from 0.12 to 0.54. This equation shows that increased water rate increases the heat transfer coefficient as a hyperbolic function, *i. e.*, rapidly at low liquor rates and less rapidly at higher. This is to be expected in this type of equipment, owing to the change in active surface under varying water rate.

In *dehumidification* the effect of gas velocity on the heat transfer was found to be a hyperbolic function

$$ha_D = \frac{G}{G + 9.07}$$

at 98 lbs. of water per sq. ft. per min. The limits of G were 2.8 to 13.0 lbs. of dry air per sq. ft. per min. and ha_D from 0.18 to 0.60. This equation shows that the addition of the liquid film resistance has cut down the over-all heat transfer. The effect of water rate in this case is also a hyperbolic function

$$ha_D = \frac{0.53\,L}{L + 12.1}$$

with L varying between 13.8 and 110 lbs. of water per sq. ft. per min. and ha_D varying from 0.30 to 0.48. The form of this equation is similar to those obtained above and indicates that water rate probably affects the active surface exposed. The results obtained on this gas scrubber seem to indicate that the heat transfer varies inversely as the viscosity of the water, but positive proof of this fact was not obtained.

All of the runs on humidification and dehumidification checked up the relationship $ha/ka = s$ as well as the results obtained on the coke tower. In the nine runs on acetone absorption the concentration of acetone in the entering air was varied from 0.03 to 0.20 per cent by volume, and the apparatus was run with 8.43 lbs. of air per sq. ft. per min. and 98 lbs. of water per sq. ft. per min. The average value of $k'a$ was 0.0037 lb. of acetone per cu. ft. per min. per mm. mercury pressure difference. In order to compare this value with ha for water vapor, the former had first to be converted to the basis of ka:

$$ka = 0.0037 \times \frac{29}{58} \times 760 = 1.40 \text{ lbs. acetone absorbed per min. per cu. ft. per lbs. of acetone per lb. of carrier,}$$

and then multiplied by the square root of the ratio of the molecular weights of acetone and water to account for the difference in diffusional velocities of the two solutes. In this way $1.40\sqrt{\frac{58}{18}} = 2.52$ (the calculated value of ka for water) which checks up $ha/ka = s$ within 1 per cent, using the ha_H obtained in humidification under the same conditions, and within 20 per cent using the heat transfer coefficient for dehumidification.

PLATE COLUMN FOR ABSORPTION OF AMMONIA—Reynolds and Sanders[7] continued an investigation started by one of the authors on the absorption of ammonia by one plate of a copper rectifying column. This plate had an area of 2 sq. ft. and the chamber was 10 in. high, giving an effective volume of 1.67 cu. ft. Five bubbling caps, each 3.5 in. in diameter and 2 in. high and provided with 40 vertical slots $^5/_8$ in. long were placed on the plate, and runs were made to determine the effect of air velocity, flow of water, water level, concentration of inlet gas, and the addition of a second plate in series.

The results showed that $k'a$ was directly proportional to air velocity, and that it increased only slightly with increasing water rate. Water level (varying between 1.5 and 4 in.), concentration of inlet gas, and addition of a second plate had no effect at all on the specific absorption coefficient. The final equation

$$k'a = 0.00114\,G\,(1 + 0.017\,L)$$

covers a range of velocity from 1 to 3 lbs. of air and from 3 to 19 lbs. of water per min. per sq. ft. of plate, with $k'a$ values ranging from a minimum of 0.0011 to a maximum of 0.0045 lb. of ammonia absorbed per min. per cu. ft. per mm. mercury driving potential.

The important conclusions from this work are (1) that for this equipment operating with ammonia and water at nearly constant temperature, gas velocity is the only variable exerting a marked effect, as predicted by theory,

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[6] M. B. Littlefield, P. C. Merrill and C. C. Stewart, M. I. T. Thesis, May 1921.

[7] "The Absorption of Gases by Liquids," M. I. T. Thesis, May 1920.

(2) that liquor rate increases the coefficient only by creating greater turbulence and causing more uniform mixing, and (3) that since the coefficient is constant at varying liquor levels on the plate, a large part of the absorption must take place in the spray above the main body of the liquor. Indeed, it seems probable that increased gas velocity helps absorption chiefly by causing a greater spray formation.

ABSORPTION OF AMMONIA IN A LABORATORY BUBBLING DEVICE—Harrop and Carlson[8] constructed a glass apparatus for absorbing ammonia in which a dilute ammonia gas mixture bubbled up through a 4-in. Büchner funnel into water which was fed and discharged from the apparatus at a constant rate. They studied the effect of air velocity and of concentration of ammonia, obtaining the same sort of results as found in the work on the plate column, *i. e.*, the coefficient varied directly with gas velocity and was unaffected by changes in concentration. The effective volume of their bubbler was about 0.045 cu. ft., and with gas velocities from 0.4 to 0.9 lb. of air per sq. ft. per min. the values of $k'a$ increased from 0.0012 to 0.0028 following the equation

$$k'a = 0.0037\ G.$$

These results serve to check the effect of gas velocity in bubbling equipment. It will be noted that the above equation gives values of $k'a$ higher than those obtained in the equation for the rectifying column at the same gas velocity. This is due to the fact that the bubbler construction gave more surface area for interaction and hence had more absorption capacity per unit of volume.

CENTRIFUGAL SPRAY CHAMBER—The writers were permitted the use of some unpublished data on the operation of a centrifugal spray chamber, and have calculated the heat transfer and absorption coefficients obtained in the two series of tests. The runs were made with varying gas and liquid velocities. In the first set the chamber was used to cool hot condenser water with air and in the second set to absorb ammonia from air with water.

The exact equations cannot be stated because of the confidential nature of these data, but the effect of gas velocity was considerably less than in the case of packed towers or of bubblers and of the general nature exhibited in the air-conditioning chamber discussed later. The general design of the apparatus makes this result reasonable, since the liquid is in the form of an unsupported spray of droplets. Increased water rate raised the coefficient rapidly at the start, but no further increase could be observed after a certain limit. Above this limit a greater rate merely formed larger drops without appreciably increasing the surface of contact.

The most important conclusion from these data is obtained by comparing heat transfer in the first set with absorption of ammonia in the second with other conditions constant. The calculated value of ha/ka differs from the humid heat of the gas by about 30 per cent, which further checks the validity of the relationship between heat transfer and absorption.

AIR-CONDITIONING CHAMBERS—Tests were run on humidifying and dehumidifying air in three-stage and four-stage horizontal conditioning chambers with varying air velocities. Each stage was 9 sq. ft. in area and 7 ft. long, and was equipped with nozzles spraying a constant amount of water at constant pressure against the air stream (details of construction confidential). The first stage of the series acted as a humidifier and the others as dehumidifiers, with water recirculating through the sprays and feeding from one chamber to the next countercurrent to the flow of the air.

The results of this work show the effect of gas velocity on heat transfer and a comparison of humidification and dehumidification under similar conditions. As stated under the discussion of packed towers, the resistance to heat flow in adiabatic humidification is due solely to the gas film, since the water remains at a constant temperature. For this case

$$ha_H = \frac{1}{R_G} = 0.64 + 0.037\ G.$$

In dehumidification

$$ha_D = \frac{1}{R_R + R_L} = \frac{1}{\frac{1}{0.64 + 0.037\ G} + \frac{1}{0.35 + 0.0040\ G}}.$$

The values of ha_H are from 1.4 to 2.3 and of ha_D from 0.33 to 0.43 with air velocities increasing from 20 to 45 lbs. of air per sq. ft. per min. A plot of ha against gas velocity showing one line for humidification and another for dehumidification would be similar in general nature to the one already presented for the results on the coke tower. Reference to Fig. 3 shows that air velocity has only a slight effect on heat transfer in this equipment.

SIGNIFICANCE OF RESULTS

In summarizing the results of this investigation the following facts are to be noted. The treatment suggested for liquid-gas interactions has been checked up by experimental data obtained from various types of laboratory and commercial equipment and has been found to apply in all the cases studied. The general formulas

$$\frac{dQ}{d\Theta} = ha\ V\ \Delta T$$

$$\frac{dW}{d\Theta} = ka\ V\ \Delta p$$

show that the rate of transfer varies directly with the active volume and the driving potential. The effect of other variables is accounted for by changes in the transfer coefficients ha and ka. These coefficients are mainly influenced by the type of equipment. In addition, for any specified unit the coefficients will vary with operating conditions such as gas velocity, liquor rate, temperature, etc. Of these operating variables gas velocity has shown the most marked effect in all cases which have been studied.

The following table gives the value of transfer coefficients obtained on some of the important types of equipment under the stated conditions.

COEFFICIENTS FOR VARIOUS TYPES OF EQUIPMENT

APPARATUS	ha (Dehumid.)	$k'a$	Gas Vel. (Lbs. /Sq. Ft. /Min.)	Water Rate (Lbs. /Sq. Ft. /Min.)
Coke tower	2.20	0.0072	12	20
McLaurin gas scrubber	0.57	0.0019	12	100
Spray chamber	0.29	(0.00095)	12	20
Plate column	(5.50)	0.0183[1]	12	20
Laboratory bubbler	(13.7)	0.045[1]	12	0.5

[1] Extrapolated value. Coefficients given in parentheses were obtained by using $ha/ka = s$.

In applying this method for designing absorption or heat transfer equipment it is obvious that the specific transfer coefficients, ha and ka, are not the only criteria to be considered. From an economic standpoint factors such as investment, labor, repairs, and power have a vital bearing. For example, it is impracticable to operate coke towers at very high gas velocity merely to obtain good absorption, since the increased friction drop through the system makes power costs prohibitive. It is therefore hoped that a continuation of the present work will modify the method of treatment and eventually allow transfer coefficients to be expressed per unit of cost.

The value of the method in its present form is twofold. First, it shows how a change in the operating variables will

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[8] "A Study of the Rate of Gas Absorption," M. I. T. Thesis, May 1920.

affect the capacity and efficiency of a definite industrial unit. In the second place, it helps the engineer to design new equipment and to predict the performance of a given type of apparatus on any heat transfer or absorption problem from data obtained in operating tests on the same type of machine. The theory is based on the fundamental principles of heat transfer and absorption, and serves to correlate and classify the performance of apparatus designed for these purposes.

The Colloid Content of Vegetable Tanning Extracts[1,2]

With Attempts to Correlate Astringency with the Potential Difference of the Particles against the Aqueous Phase

By Arthur W. Thomas[3] and Stuart B. Foster

Columbia University, New York, N. Y.

As recorded in the following paper, measurement of the potential differences of certain vegetable tanning extracts shows that the order of these values is approximately the same as the order of their degrees of astringency. The potential difference increases with dilution of the extract, decreases with rising acidity, and is increased by dialysis of the extract. These simple manipulations suggest possibilities for a more intelligent use of these extracts in vegetable tanning.

Precipitation tests were made on the extracts with various electrolytes. The conduct of the extracts shows that there is a large amount of colloidal matter present, that it belongs to a type of dispersion with properties between the intermediate and hydrophilic dispersions, and, hence, that the measurements reported in the first part of the paper are justified.

From the colloidal point of view, vegetable tanning extracts constitute an unexplored field, and the authors believe that the precipitation graphs included in this article will prove of value when interpreted in the light of future research.

ASTRINGENT properties of vegetable tanning extracts vary enormously, generally depending upon the source of the extract. If the fundamental reason for this variation could be discovered, rapid progress would be effected in the use of various extracts in vegetable tanning. It would be possible by varying the astringency of a given extract by simple chemical treatment to render an extract suitable for any process, thus avoiding the employment of a given extract or mixture of extracts for making a given kind of leather.

The simple theory of vegetable tanning proposed by Procter and Wilson[4] is based on a mutual neutralization of the opposite electrical charges of the colloidal tannin particles and the hide colloids. If this theory is correct the electrical charge of the tannin particles should be greater for an astringent extract than for a mild one.

The authors have endeavored to determine the potential difference of the tannin particles in various vegetable extracts against the aqueous phase, *i. e.*, the difference in potential of the negative electrical charges on the particles against the positive charges of the ions in the water immediately in contact with the particles.

Apparatus

The method used for the determination was the U-tube electrophoresis technic as described by Burton.[5]

The U-tube had limbs about 20 cm. in length and 2 cm. in diameter. The lower half of each limb was graduated in fifths of centimeters, from 0 at the top to 10 cm. at the lower portion. In the bottom of the bend of the U-tube was sealed a delivery tube with stopcock, bent upward and ending above the upper levels of the limbs in a funnel, for the purpose of filling the tube with the solution. The platinum electrodes were sections of cylinders, not spirals as used by Burton.

Before operating, the effective distance through the bend of the tube was measured, so that the potential gradient per centimeter could be calculated. The conductivities of known columns of 0.02 *M* KCl solution through the graduated portions of the tube were determined, and the conductivity between the lowest graduated marks on each limb through the bend was compared with these values. The effective distance through the bend was found to be 9.9 cm.

The conductivities of the solutions of all extracts were determined in the usual type of Wheatstone bridge apparatus with a Freas conductivity cell.[6] Solutions of potassium chloride of the same conductivity were superimposed upon the columns of the extract in the U-tube. The concentrations of chloride required for given conductivities were based upon the figures of Noyes and Falk,[7] and were obtained by plotting their specific conductance values against concentration of potassium chloride. When the conductance of a tanning solution was obtained the corresponding concentration of potassium chloride was found by merely reading from the curve of Noyes and Falk's data.

All measurements of conductivity and electrophoresis were made at 25° ±0.005° C. by submerging the cells and tubes in a large Freas water thermostat which contained 80 gal. of water at the temperature stated.

Method

The potassium chloride solution of the same conductivity as the extract to be studied was poured through the funnel and allowed to flow into the bend of the U-tube. The stopcock was closed, the excess chloride remaining in the delivery tube was removed, and the delivery tube was filled with the tanning extract. By gradually opening the stopcock, the extract was allowed to flow very slowly into the bend so that it would not mix with the layer of potassium chloride solution. The final result was a U-tube filled through the bend and up the limbs with extract, with a 2-cm. layer of potassium chloride solution on top of each column. By careful manipulation, the interfaces between colloidal dispersion and electrolyte solution were fairly sharp.

The platinum electrodes were carefully inserted, both to the same level, and submerged in the potassium chloride

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[1] Presented before the Section of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 383 from the Chemical Laboratories of Columbia University.

[3] Assistant Professor.

[4] *J. Chem. Soc.*, **109** (1916), 1327.

[5] "Physical Properties of Colloidal Solutions," Chapter VII (1916).

[6] Eimer and Amend, 1920 Catalog, No. 5202.

[7] *J. Am. Chem. Soc.*, **34** (1912), 454.

solution, not coming in contact with the tanning solution. The tube was then immersed in the water bath, and the electrodes were connected with a 115-volt direct house current.

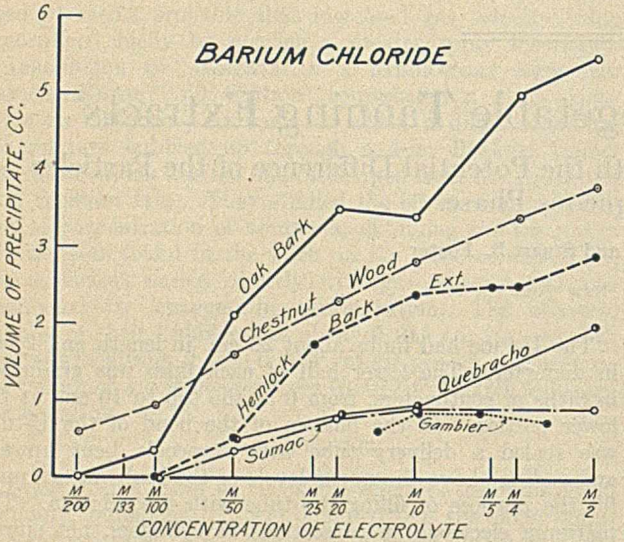

Fig. 1

The current was passed for 5 min., reversed, and passed an additional 5 min., in order to flatten the interfacial surfaces. The current was then passed through for 20 min., and the displacement noted during this period. From the values obtained the velocity of migration could be calculated.

The potential differences of the double layers of the particles were calculated by means of the well-known formula of Lamb,[8] as applied by Burton:[9]

$$\text{P. D.} = \frac{4\pi\eta v(300)^2}{\text{KX}}$$

where P. D. = Potential difference in volts.
η = Viscosity of dispersion medium (in this case water at 25° = 10.2×10^{-3}).
v = Velocity of migration in cm. per sec.
K = Dielectric constant of dispersion medium (K of water = 80).
X = Potential drop in volts per cm.

MATERIALS

The vegetable tanning agents listed in Table I were kindly analyzed and supplied by Mr. John Arthur Wilson.

For the electrophoresis measurements, the concentrations of tanning solutions were such that they contained 1 per cent tannin according to the above analyses, and the solutions were centrifuged for 5 min. to remove coarse suspended matter. The tannin percentages were determined by the A. L. C. A. official method. They are merely arbitrary values which are used for purposes of commercial evaluation of vegetable extracts and, as shown by Wilson and Kern,[10] do not represent the true values. When this work was commenced, however, they were the best figures available. Actually, with the exception of quebracho and osage orange, the solutions all contained about 4 g. total solids per 100 cc.

RESULTS

All the experimental data, accumulated over a 2-yr. period, cannot be recorded here. The following results are typical:

TABLE I—MATERIALS USED

	100 Per cent				
		Insol.	Soluble		
	Water	Matter	Nontannin	Tannin	Ash
Solid quebracho extract....	22.82	7.73	6.30	63.15	0.58
Hemlock bark extract.....	52.58	6.21	18.36	22.85	1.19
Hemlock bark (Wis.).....	...	...	...	...	...
Gambier extract..........	48.49	10.22	17.51	23.78	3.51
Cube gambier............	9.30	34.70	26.00	30.00	23.40
Palermo sumac...........	9.39	45.39	18.33	26.89	9.40
Sumac extract............	51.32	2.19	22.77	23.72	4.11
Chestnut oak bark extract	52.00	2.46	19.89	25.65	1.51
Larch bark extract.......	51.41	5.45	21.04	22.10	1.13
Oak bark extract 1.......	52.78	2.59	17.05	27.58	1.56
Oak bark extract 2.......	54.39	1.76	18.10	25.75	1.38
Aurantine (osage orange).	7.30	6.81	23.20	62.69	2.81
Black oak bark extract..	51.11	0.86	23.86	24.17	3.00
Quercitron bark extract...	46.08	3.44	22.22	28.26	2.46
Bengal cutch extract......	62.64	2.66	8.09	26.61	1.48
Camel cutch.............	23.77	3.06	18.63	54.54	5.49

TABLE II—ELECTROPHORESIS OF CUBE GAMBIER

4 g. dry gambier extract per 100 cc.; both electrodes set at 5-cm. mark

Levels of Gambier Solution			
Left Limb Anode Cm.	Right Limb Cathode Cm.	Time Min.	Displacement Cm.
7.8	8.0	0	Up 0.2
7.6	8.35	20	Down 0.35
			Av. 0.275 in 1200 sec.

Average voltage through 19.9 cm. = 114.3
∴ Potential gradient = 5.74 volts per cm.
P. D. = −0.005 volt[1]

[1] Negative because particles migrated to anode.

TABLE III—ELECTROPHORESIS OF QUEBRACHO

4 g. dry quebracho per 250 cc.; both electrodes at 5-cm. mark

Levels of Quebracho Solution			
Left Limb Anode Cm.	Right Limb Cathode Cm.	Time Min.	Displacement Cm.
7.8	7.75	0	Up 1.40
6.4	9.1	20	Down 1.35
			Av. 1.37 in 1200 sec.

Average voltage through 19.9 cm. = 116.2
∴ Potential gradient = 5.83 volts per cm.
P. D. = −0.028 volt

It will be noted in the electrophoresis of gambier that the displacement downward at the negative pole was greater than the upward movement toward the positive pole. This phenomenon is noted in the electrophoresis of all colloids. Burton referred to this effect in the electrophoresis of inorganic colloids as the "settling of the colloid." It is an error, however, that cannot be lightly turned aside. Unpublished results from this laboratory on the electrophoresis of iron oxide hydrosols show a downward displacement as much as

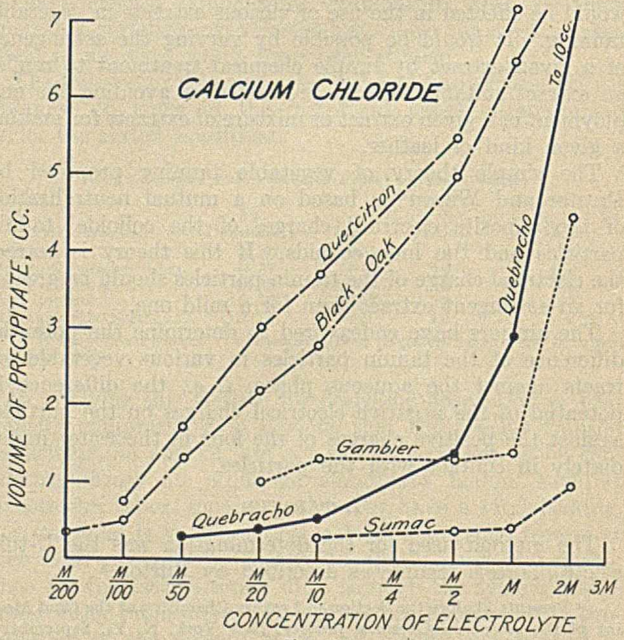

Fig. 2

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[8] *Phil. Mag.*, 1888, 60.

[9] *Ibid.*, 11 (1906), 425, 472.

[10] THIS JOURNAL, 12 (1920), 465.

five to ten times as great as the upward displacement, depending on the concentration of the hydrosol. It is evident that this effect throws great doubt upon all the absolute values of electrical charge of colloids that are found in the literature. In a recent article, Burton[11] promises an investigation of this "settling," which he attributes to the action of gravity accelerating the downward electrophoresis and retarding the upward movement.

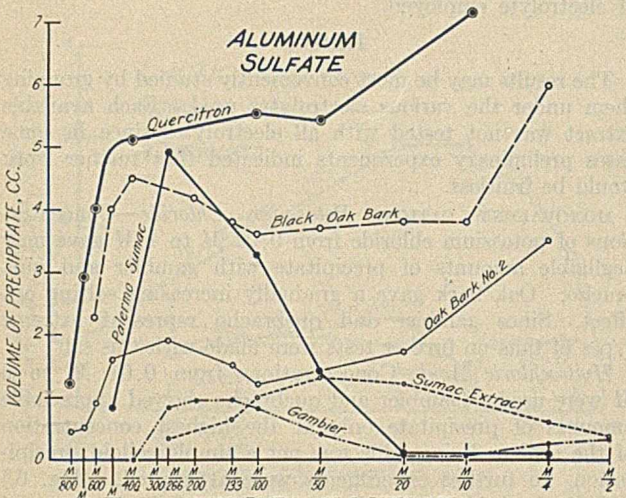

FIG. 3

The slightly greater upward movement noted in the particular quebracho experiment recorded was obtained with a number of extracts, and is probably due to a reprecipitation at the anode of some of the constituents of the liquor which were dissolved by the cathodic reaction in that limb of the U-tube during the preliminary 5-min. passage of the current in the reverse direction.

As a result of the effects of oxidation and reduction, as well as of formation of acid and alkali in the cathode and anode limbs, with the resulting dissolution and reprecipitation of some of the constituents of the tanning extract solutions, it was not always easy to tell just what was the electrophoresis displacement. The authors were obliged to make many preliminary experiments before they felt that they had one whose value they would care to publish. The behavior was not alike for any two extracts.

It is evident that the values which are given below for the electrical charges of the tannin particles are not absolutely correct. They are, however, not much more doubtful than the many published values obtained by electrophoresis. The authors do not attempt to calculate the values of the electrical charges per colloidal particle because such calculation involves the sizes of the particles. It is impossible to determine the sizes of colloidal particles by any method known at the present time and we are obliged to be content with values for the potential difference of the Helmholtz double layer only. The authors wish to emphasize the point that the published values for absolute electrical charges on colloidal particles are worthless, on account of the lack of a means for measurement of the sizes of colloidal particles.

RELATION BETWEEN P. D. AND ORDER OF CONDUCTIVITIES—The values obtained for the potential differences of the particles against the aqueous phase are listed in Table IV, together with the order of the conductivities. All the extracts showed anodic migration. The concentration in all the solutions was such as to give 1 per cent tannin, which meant about 4 g. total solids per 100 cc., except in cases of quebracho (2 g. per 125 cc.) and osage orange (1.6 g. per 100 cc.).

TABLE IV—POTENTIAL DIFFERENCES AND ORDER OF CONDUCTIVITIES

Increasing Potential Difference	Volt	Decreasing Conductivity
Gambier (cube)	−0.005	Sumac
Oak bark 2	−0.009	Gambier
Chestnut wood	−0.009	Oak bark
Hemlock bark (Wis.)	−0.010	Larch bark
Sumac	−0.014	Hemlock bark
Larch bark	−0.018	Chestnut wood
Osage orange	−0.018 (?)	Osage orange
Quebracho	−0.028	Quebracho

The value for osage orange is the only one concerning which there is any great uncertainty.

According to the theory that the combination of tannin with hide substance is a function of the electrical charge of the particles, the most drastically acting extract would be quebracho, and the mildest would be gambier, according to the above values of the P. D.

By comparison with the conductivity series, it is evident that while, in general, the more highly conducting extracts have the lower P. D. values, there are exceptions to this rule, so that it is apparent that the magnitude of the electrical charge is a function of the kind as well as the amount of nontannins present, as is to be expected.

TABLE V—P. D. OF QUEBRACHO EXTRACT

CONCENTRATION G. Dry Solids in 250 cc	P. D. Volt
8	−0.024
4	−0.028
2	−0.029
1	−0.030

RELATION BETWEEN P. D. AND CONCENTRATION—The results obtained upon measuring the P. D. of a quebracho extract at different concentrations are assembled in Table V.

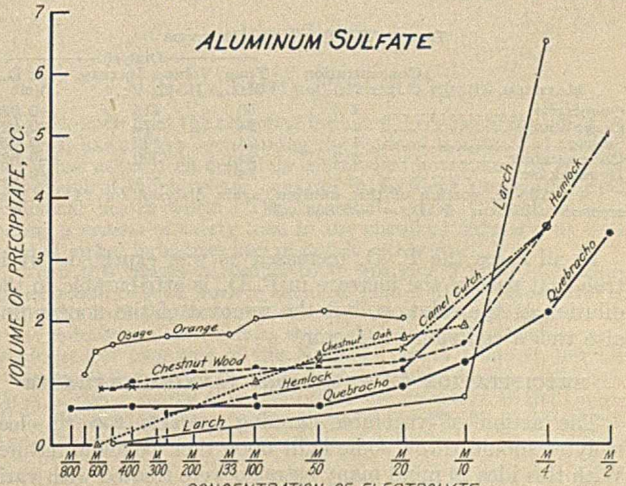

FIG. 4

The P. D. increases upon dilution of the extract, as is to be expected according to the "complex theory" of colloids, since dilution decreases the concentration of electrolyte in the outer layer surrounding the particle and permits greater ionization of the peptizing electrolyte adsorbed on the particle.

RELATION BETWEEN P. D. AND ACIDITY—Since the negative charge on a colloid is readily increased by the addition of hydrogen ion, such addition ought to lower the P. D. of a vegetable tanning extract. The data in Table VI show that this is true.

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[11] *Proc. Roy. Soc. London*, **95A** (1919), 480.

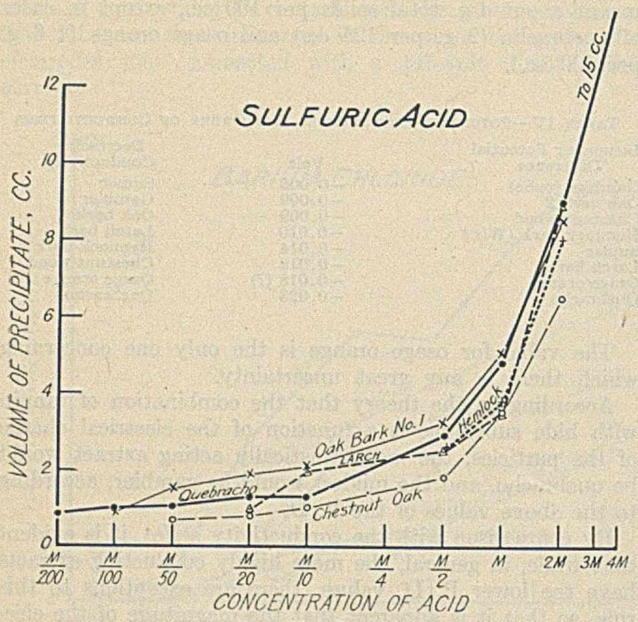

Fig. 5

TABLE VI—EFFECT OF ADDITION OF ACID
4 g. dry quebracho extract per 250 cc.

0.1 N HCl added per 100 Cc. Cc.	P. D. Volt
0	−0.024
1	−0.014
1.5	−0.010
2.0	Approx. 0

EFFECT OF DIALYSIS—On the other hand, dialysis of extracts ought to raise the P. D., as a result of the removal of nontannins from the solution. Table VII describes the results obtained by dialysis through collodion sacs against distilled water.

TABLE VII—EFFECT OF DIALYSIS

MATERIAL	Concentration G. per 250 Cc.	Dialysis Time Hrs.	Dialysis Volume Increase to Cc.	P. D. Volt
Quebracho	4	60	415	−0.033
Osage orange[1]	4	24	370	−0.024
Sumac	4	24	460	−0.026
Cube gambier	8.2	24	390	−0.029
Hemlock bark	...	24	...	−0.024

[1] A 200-cc. portion of this solution, again dialyzed for 24 hrs., increased to 240 cc. P. D. = −0.036 volt.

In all cases the P. D. increased as was expected. It is true that part of the increase in P. D., is attributable to the dilution of the solution, but the removal of the nontannins also was a contributing factor.

PRECIPITATION OF VEGETABLE TANNING EXTRACTS

The action of vegetable tanning extracts toward electrolytes should throw some light upon their colloidal nature. With this idea in mind many extracts were treated with various electrolytes in different concentrations and the volumes of precipitated material were measured.

TECHNIC

Aqueous dispersions or solutions of the extracts were made up so that 100 cc. of solution contained 4 g. of total solids. Before adjusting to the mark, the solutions were kept at 85° C., and cooled to 25° C. before adjusting to volume. The stock solution was then centrifuged for 5 min. at about 1000 "times gravity" in order to throw down coarse suspended matter.

Twenty-five-cc. portions were placed in 100-cc. graduated "oil tubes" (tubes tapering to a conical end). Equal volumes of electrolyte solutions of varying concentration were poured into each tube, allowed to stand for 15 to 30 min., since precipitation was not always instantaneous, and finally centrifuged for 5 min. at 1000 "times gravity." The volumes of the precipitates were plotted against the concentrations of electrolyte employed.

RESULTS

The results may be most conveniently studied by grouping them under the various electrolytes used. Each available extract was not tested with all electrolytes since in some cases preliminary experiments indicated that further work would be fruitless.

MONOVALENT CATION. *Potassium Chloride*—Concentrations of potassium chloride from 0.02 *M* to 4 *M* gave only negligible amounts of precipitate with gambier and quebracho. Oak bark gave a gradually increasing salting out effect. Since gambier and quebracho represent extreme types of tans no further tests were made with this salt.

Hydrochloric Acid—Concentrations from 0.01 *M* to 6 *M* were used. Gambier and quebracho showed appreciable amounts of precipitate only at the highest concentration of the acid and since this was not a simple colloid precipitation, no further experiments were attempted. (Fig. 6.)

Sulfuric Acid—Quebracho, hemlock, oak bark, chestnut oak, and gambier gave progressively increasing amounts of precipitate (salting out) with concentrations of acid from 0.005 *M* to 4 *M*. (Fig. 5.) No precipitate was obtained with sumac until molal acid was reached. Acid of this concentration threw down gummy masses, similar to those obtained with aluminium sulfate. At 4 *M* concentration a flocculent precipitate was formed.

Phosphoric Acid—Gambier began to give an appreciable precipitate only at 4 to 7 *M* concentration. With sumac a gummy mass was thrown out at 2 *M*, as was observed in the case of sulfuric acid and aluminium sulfate, and at 4 *M* to 7 *M* a flocculent precipitate formed which left the supernatant solution almost colorless. A salting out effect was obtained with quebracho. (Fig. 6.)

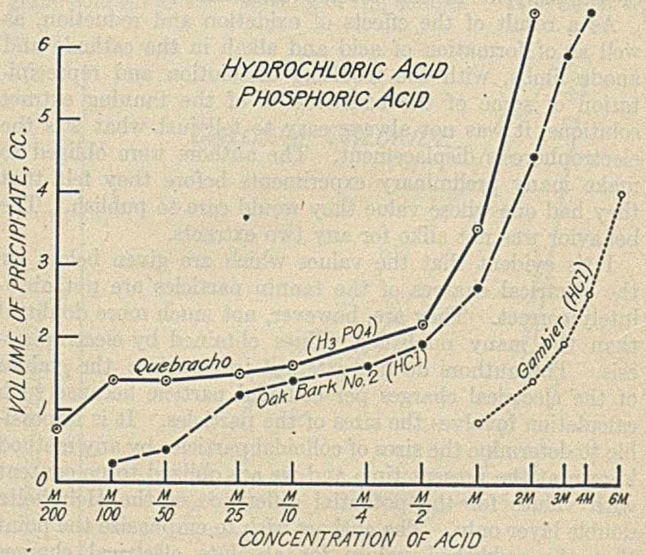

Fig. 6

Acetic Acid—Experiments with quebracho, sumac, gambier, and oak bark were run with concentrations of acid from 0.005 *M* to 4 *M*. There was no appreciable precipitation in any case. It is of interest to note that at the higher concentrations the suspended matter began to dissolve or peptize.

Formic Acid—Concentrations from 0.005 *M* to 12.5 *M* were used. Sumac, chestnut oak, hemlock, gambier, larch bark and oak bark gave no precipitation up to 4 *M*. The suspended matter began to dissolve or peptize at 4 *M*. Quebracho and quercitron were precipitated, but the precipitate dissolved at 2 *M* to 4 *M*. (Fig. 7.)

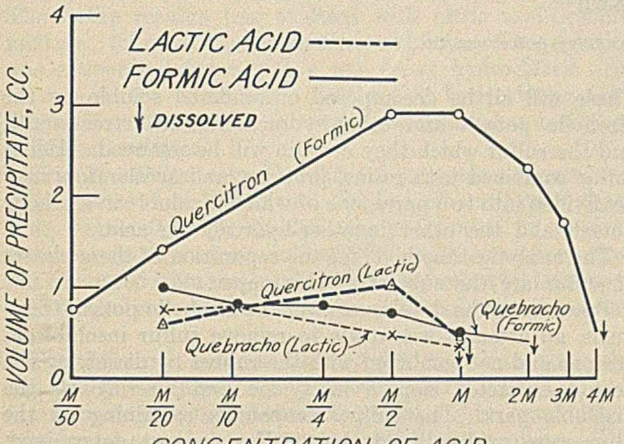

Fig. 7

Lactic Acid—Concentrations from 0.005 *M* to 2 *M* were employed. The effects of this acid were similar in kind, but not in degree, to those with formic acid. (Fig. 7.) The precipitates with quercitron and quebracho redissolved at lower concentrations of lactic acid than of formic acid. Since lactic is the weaker acid, and also since this redissolving was not found with hydrochloric or with sulfuric acids, the phenomenon must be due to chemical properties other than concentration of hydrogen ion.

DIVALENT CATIONS. *Barium Chloride*—On account of limitations of solubility, this salt was employed up to a final concentration of 0.5 *M*. Progressive salting out occurred with oak bark, chestnut wood, quebracho, gambier, and hemlock. (Fig. 1.)

Calcium Chloride—Final concentration of 2 *M* was possible with this salt. As with barium chloride, increasing amounts of precipitate were obtained with quercitron, black oak, quebracho, gambier, and sumac. At the same concentration of these salts the different extracts gave in some cases less, and in others more, precipitate, showing the presence of substances reacting with barium and calcium ions to form chemical compounds of different solubilities. (Fig. 2.)

TRIVALENT CATION. *Aluminium Sulfate*—In the precipitation of negatively charged colloidal dispersions, aluminium sulfate is not only a powerful precipitant, but it also gives the "irregular series" or "tolerance zone" which is typical of the action of weak base cation, strong acid anion salts, as shown by Buxton and Teague,[12] and by Freundlich and Schucht.[13]

The concentrations of aluminium sulfate used ranged from 0.00125 *M* to 0.5 *M*.

The "irregular series" effect was obtained with the following extracts: gambier, sumac, Palermo sumac, oak bark No. 2, black oak bark, and not so markedly with quercitron. Precipitation set in generally at 0.00125 *M* concentration of the salt, rose rapidly to a maximum, dropped off into a "tolerance zone," and then started upward again. (Fig. 3.)

Those which gave no "irregular series," at least up to 0.5 *M* concentration of the salt, were: Osage orange, chestnut wood, chestnut oak, hemlock bark, larch bark, quebracho and camel cutch. They began to precipitate at 0.00125 *M*, rising gradually to about 0.1 *M* where there was an abrupt upward trend similar to a salting-out effect. These extracts are not so sensitive to precipitation by aluminium sulfate as the first mentioned.

Bengal cutch is in a separate category, since it was unaffected by the addition of aluminium sulfate.

INTERPRETATION OF RESULTS

The interpretation of the effects of the several electrolytes is masked by the salting out and chemical precipitation of the molecularly dispersed substances present in addition to the colloidal tannins. The writers had hoped that the order of sensitiveness to precipitation by mono-, di-, and trivalent cations would help show the order of magnitude of the potential differences of the particles against the aqueous phase, but the interference by the large amounts of molecular dispersions of nontannins in salting out spoiled this anticipation. The presence of this salted-out, molecularly dispersed material was shown in several cases where the coagula caused by the calcium and aluminium salts were found to redissolve to a large extent upon addition of water. If it were all gel substance it should not be reversible.

The conduct of the extracts shows that there is a large amount of colloidal matter present, that it belongs to a type of dispersion with properties between the intermediate and hydrophilic dispersions, and, hence, that the measurements reported in the first part of the paper are justified.

From the colloidal point of view, vegetable tanning extracts constitute an unexplored field, and the authors believe that the precipitation graphs included in this article will prove of value when interpreted in the light of further research.

ACKNOWLEDGMENT

We take pleasure in expressing our indebtedness to Messrs. A. F. Gallun and Sons Co., of Milwaukee, for grants in aid of this investigation.

National Safety Council Census

It is known that the chemical industry, because of its inherent hazards, has always been among the leaders in industrial safety, but it has never been definitely established how many persons in the chemical industry are engaged in accident prevention and industrial health work. The National Safety Council is now taking a census of safety men in the chemical industry, as well as in all other industries and in public safety work.

When this census is completed it will give a good indication of the extent of such work in chemical plants all over the country, and will afford the first basis of comparison with similar work in other industries. The census will include not only members and employees of members of the National Safety Council, but all other persons engaged in safety and industrial health activities. Most of the principal chemical plants are members of the Council. The headquarters of the Council are at 168 N. Michigan Ave., Chicago, Ill.

Associated Technical Societies of Detroit

The Associated Technical Societies of Detroit, an affiliation of the architectural, engineering, and other technical societies of the city, has just been organized. The Detroit Section of the American Chemical Society is one of the members of the association.

The paramount use of the association to its members and to the public is its opportunity for public service for the city and for the state of Michigan. It will take an active interest in all matters where engineering, architecture, or technical subjects are of importance. The council will assist in furnishing definite and accurate information to the public. The association will offer its assistance and advice to city and state officials whenever required. The purpose of the association's activities is to provide the most reliable technical information for the proper consideration of public improvements and public undertakings.

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[12] *Z. physik. Chem.*, **57** (1907), 76.

[13] *Ibid.*, **85** (1913), 641.

Determination of True Free Sulfur and True Coefficient of Vulcanization in Vulcanized Rubber—II[1]

By W. J. Kelly[2]

Research Laboratories, The Goodyear Tire & Rubber Co., Akron, Ohio

The following paper describes methods of analysis by means of which a more complete study of the distribution of sulfur between the various ingredients of a rubber compound can be made. New light will also be thrown on the mechanism of vulcanization and acceleration. It is freely admitted that alcoholic potash and ether-hydrochloric acid have been long known as reagents in rubber analysis, but their application to the separation of the different forms of sulfur, except metallic sulfides, is entirely new.

If carried to their ultimate possibilities, including the use of other extraction media, these methods should be of considerable help in elucidating the theories of vulcanization.

In a previous paper,[3] it was shown that the sulfur present in vulcanized pure gum stocks could be divided into four parts as follows:

A—Sulfur soluble in acetone:
  (1) True free sulfur
  (2) Combined with resins and proteins
B—Sulfur insoluble in acetone:
  (1) Combined with rubber
  (2) Combined with resins and proteins

It is at once evident that this classification applies only to pure gum stocks and that if compounded stocks are analyzed there will be more classes in B, while A will remain the same. If basic inorganic substances such as ZnO and PbO are present there is always some metallic sulfide formed. All the organic accelerators react with sulfur during the cure, giving rise to new bodies which may or may not be soluble in acetone.

The acetone-soluble compounds will not interfere in any way with the procedure described in the previous paper, but in the case of the insoluble part an amplified classification is necessary. The following outline will account for all of the sulfur in compounded stocks with the exception of those containing insoluble sulfates, such as those of barium, calcium, or lead.

A—Soluble in acetone:
  (1) True free sulfur
  (2) Combined with resins, proteins, and accelerators
B—Insoluble in acetone:
  (1) Combined with rubber
  (2) Combined with resins, proteins, and accelerators
  (3) As metallic sulfides

It is evident that the acetone-insoluble sulfur combined with resins, proteins, and accelerators may be subdivided according to the means employed for its removal from the rubber. Treatment with alcoholic potassium hydroxide will remove at least part of the resin compounds and also render the proteins soluble by hydrolysis. The accelerators and compounds formed from them during the cure will also be more or less affected by the alcoholic potash, and especially by the ether-hydrochloric acid which is used to evolve hydrogen sulfide from the metallic sulfides. According to Bedford and Scott[4] and Bruni and Romani,[5] the accelerators form mercapto and polysulfide compounds during the cure. These will all be decomposed or rendered soluble by the alcoholic potash and ether-hydrochloric acid treatments, and the sulfur which they contain will be removed. Hence sulfur combined with resins, proteins, and accelerators may be divided into two parts, one of which is soluble in alcoholic potash and the other in ether-hydrochloric acid.

The analytical methods for the separation of these classes of sulfur are the subject of this paper.

Previous to the development of the alcoholic potash treatment, an attempt was made to remove sulfur insoluble in acetone and not combined with the rubber by dissolving the acetone-extracted sample in xylene and filtering off the insoluble part. The sulfur compounds remaining on the filter were oxidized and their sulfur content determined. Three analyses on a stock which yielded 0.34 per cent sulfur upon the alcoholic potash treatment gave 0.074, 0.085, and 0.053 per cent of sulfur insoluble in acetone and xylene. It is entirely possible that the compounds of resins and sulfur may dissolve in xylene and pass through the filter. The protein products may be insoluble, but the difficulty of obtaining a clean separation by this method is too great for ordinary use. It was therefore abandoned for the alcoholic potash method, which extracted a larger amount of sulfur and gave more concordant and dependable results.

Analytical Procedure

methods of oxidation—The method proposed by Kratz, Flower and Coolidge[6] gave the best results, especially with rubbers containing large amounts of organic matter. The sample was oxidized with a mixture of nitric acid and zinc nitrate, followed by bromine and potassium chlorate, and the solution was evaporated and baked. This method was used in the determination of total and combined sulfur. The free sulfur, total acetone-insoluble sulfur, and ether-hydrochloric acid-soluble sulfur were oxidized with fuming nitric acid-bromine mixture. The hydrogen sulfide evolved by ether-hydrochloric acid was collected and oxidized in potassium bromide-bromine solution, and the oxidation was completed with nitric acid. The alcoholic potash extract was oxidized, first with potassium bromide-bromine, then with nitric acid, in order to avoid adding the acid to solid potassium hydroxide.

oxidizing solutions—Nitric acid-zinc nitrate was made up by dissolving 16 g. of C. P. zinc in concentrated nitric acid and diluting to 100 cc. with the acid.

Fuming nitric acid was saturated with liquid bromine by shaking the two together.

The potassium bromide-bromine solution contained 12 g. of bromide and 16 g. of bromine per 100 cc.

total sulfur—A 0.5-g. sample was treated with 20 to 25 cc. of nitric acid-zinc nitrate solution, care being taken that the sample was kept cool until it was all dissolved; otherwise it was likely to catch fire. Ten cc. of the fuming nitric acid-bromine mixture were added to the solution, which was heated till all the bromine was evolved. About 0.5 g. of potassium chlorate was then added and the solution was evaporated to dryness. The flask was then heated to a dull red heat over a free flame, until the zinc nitrate had entirely decomposed and all the organic matter had oxidized.

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[1] Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Research Chemist.

[3] This Journal, 12 (1920), 875.

[4] *Ibid.*, 13 (1921), 125.

[5] *India Rubber J.*, 62 (1921), 63.

[6] *India Rubber World*, 61 (1920), 356.

After cooling the flask, its contents were dissolved in hydrochloric acid and diluted, and the sulfur was precipitated and weighed as barium sulfate.

ACETONE-SOLUBLE. *Total*—A 0.5–1.0-g. sample was extracted over night with acetone and the solvent evaporated. The entire residue was oxidized with nitric acid-bromine mixture, followed by potassium chlorate. The solution was evaporated twice with a few cc. of hydrochloric acid to remove the nitric acid, dissolved in hydrochloric acid, filtered if necessary, and the sulfur precipitated and weighed as barium sulfate.

True Free Sulfur—Another 0.5–1.0-g. sample was extracted with acetone and the solvent distilled off until only about 5 cc. were left. The residue was evaporated in an oven at a temperature not exceeding 60° C. The true free sulfur was separated from the organic material present by treatment with alcohol saturated with sulfur, as described in the earlier paper.

The difference between the two determinations gave the organically combined, acetone-soluble sulfur.

ACETONE-INSOLUBLE SULFUR. *Total*—This was determined on a sample previously extracted with acetone. The oxidation and precipitation were carried out in exactly the same way as for total sulfur.

Sulfur Combined with Resins, Etc., Soluble in Alcoholic Potash—The sample previously extracted with acetone was boiled for 8 hrs. in a 5 per cent alcoholic potash solution, after which the solution was poured off and the rubber washed three or four times with alcohol. It was next extracted over night in an underwriter's apparatus with 95 per cent alcohol, in order to remove all the alkaline solution. The two solutions were combined and evaporated, and the residue was oxidized with 10 cc. of potassium bromide-bromine solution, followed by nitric acid. After the removal of any silica produced by the action of the potash on the glass, the sulfur was precipitated as barium sulfate.

Metallic Sulfide—The method used to evolve hydrogen sulfide from the metallic sulfides present was a modification of that proposed by Stevens,[7] who treated the sample with a mixture of aqueous hydrochloric acid and ether. Owing to the fact that ether penetrated very rapidly into the rubber, a solution of dry hydrochloric acid in ether was used. After extraction with acetone and alcoholic potash, the sample was treated with 50 cc. of ether-hydrochloric acid in a flask fitted with a separatory funnel and a delivery tube, and the hydrogen sulfide evolved was collected in potassium bromide-bromine solution. The last traces of hydrogen sulfide were removed by distilling over about half the ether. The bromide-bromine solution was treated with nitric acid, and the sulfur precipitated and weighed as barium sulfate.

Combined with Accelerators, Etc., Soluble in Ether-HCl—The sample which had been treated with ether-hydrochloric acid was washed several times with ether, and the solvent was evaporated. The residue was oxidized with nitric acid-bromine and the sulfur determined as barium sulfate.

Combined with Rubber—The sample which had been extracted successively with acetone, alcoholic potash, and ether-hydrochloric acid was finally treated exactly as described for the total sulfur.

EXPERIMENTAL RESULTS

In order to test these methods, seven stocks were mixed, cured, and analyzed. The results are given in Table I. In some cases it will be noted that the total sulfur determined does not check with that calculated from the formula. As the results of the single determinations all checked very well, the discrepancy is probably due to an error in weighing out or in mixing the batch. All of the figures are the averages of at least two analyses and the checks obtained were all within 0.03 to 0.04 per cent calculated on the total stock.

TABLE I

	STOCK NUMBER						
	1	2	3	4	5	6	7
Composition							
Pale crepe	100	100	100	100	100	100	100
Zinc oxide	25	..	10	..	15	15	15
Sulfur	8	5	6	6	5	5	5
Hexamethylenetetramine	..	..	..	..	1	1	1
Thiocarbanilide	..	2	2	..	..	..	..
Litharge	..	..	..	10	..	..	..
Glue	..	..	..	..	..	5	..
Gas black	..	..	..	..	..	..	10
Cure							
Time, minutes	105	90	25	30	60	60	60
Temperature, ° C.	141	141	141	141	141	141	141
Percentage of Sulfur							
Total sulfur:							
Calculated	6.02	4.94	5.32	5.17	4.13	3.97	3.82
Determined	6.19	4.88	5.43	5.19	4.14	3.96	3.81
Total acetone-soluble sulfur	4.47	3.30	4.24	2.35	2.42	2.18	1.96
True free sulfur	4.03	3.18	3.95	2.28	2.12	2.06	1.80
Sulfur combined with resins (by diff.)	0.44	0.12	0.29	0.07	0.30	0.12	0.16
Acetone-insoluble sulfur:							
(1) Sol. in alc. KOH	0.17	0.13	0.06	0.26	0.06	0.17	0.11
(2) Sol. in ether-HCl	....	0.12	0.17	....	0.21	0.04	0.25
(3) Sulfide sulfur	0.17	0.00	0.20	0.72	0.19	0.47	0.25
(4) Combined with rubber	1.42	1.38	0.84	1.82	1.30	1.03	1.19
TOTAL 1, 2, 3, 4	1.76	1.63	1.27	2.80	1.76	1.71	1.80
TOTAL ACETONE-INSOLUBLE SULFUR (DETERMINED)	1.73	1.59	1.20	2.85	1.75	1.74	1.85

DISCUSSION OF RESULTS

The results obtained show beyond doubt that there is, in the acetone extract, a considerable amount of sulfur which is combined with organic matter. This sulfur is not available for further vulcanization as such, but in the light of Bedford and Scott's work the compounds thus formed may very well be a part of the natural accelerator of the rubber.

The classification of acetone-insoluble sulfur into four parts is susceptible of expansion, for in the case of some of the accelerators it is not at all certain that their sulfur reaction products can be entirely removed by the methods described. It is certain, however, that a large amount of sulfur, heretofore considered as combined with the rubber, has been removed by means which leave no doubt as to the fact that it was not combined with the rubber.

It is of course well known that both alcoholic potash and ether-hydrochloric acid have been used before in rubber analysis, but the analysis of the extracts for sulfur has not been made.

No series of cures have been analyzed according to these methods, but their value as a means of throwing light on the mechanism of vulcanization can be estimated by the following example:

Two stocks containing about the same amount of sulfur, one with zinc oxide and one without, were cured for 1 hr. 45 min. at 141° C. The analyses are listed in Table II, all figures being based on 100 parts of rubber.

TABLE II

I—PALE CREPE 100, SULFUR 7.5; II—PALE CREPE 100, ZnO 25, SULFUR, 8

SULFUR	I	II
True free	5.04	5.37
Acetone-soluble	0.20	0.59
Soluble in alcoholic KOH	0.08	0.23
As ZnS	0.00	0.23
Combined with rubber	2.14	1.89
TOTAL	7.46	8.31

The values for total sulfur check quite well with the amount added. In Sample 2 the discrepancy may be due either to an error in weighing or to sulfur in the zinc oxide used.

It will be seen that the amount of sulfur combined with the rubber in Sample 2 is less than that in Sample 1 in spite of the fact that there was more sulfur present in Sample 2. This shows that the zinc oxide holds back the reaction between rubber and sulfur to a marked degree.

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[7] *Analyst*, **40** (1915), 275.

Alleged Adsorption of Alumina from Aluminium Sulfate Solutions by Cellulose[1]

By Alfred Tingle[2]

The E. B. Eddy Co. Ltd., Hull, P. Q.

The work here described was undertaken with the object of obtaining some first-hand information as to the extent to which alumina is adsorbed from its sulfate solution by cellulose in general and paper-making pulps in particular. The occurrence of this phenomenon is asserted or assumed by many writers, but the evidence on which these assertions are made is seldom cited.

Adsorption of alumina by cellulose is appealed to by Cross and Bevan, for example, as a factor of importance in the theory of paper sizing.[3] The only reference in original literature which the present writer has been able to find is to the work of Schwalb and Robsahm[4] and of Sutermeister.[5] The phenomena observed by Schwalb and Robsahm were obviously not connected with adsorption at all, but were simple precipitations of alumina by the noncellulose constituents of the pulp. Sutermeister found much lower figures for the amount of $Al_2(SO_4)_3$ decomposed, but the origin of the phenomena observed remains a little obscure. More lately Kolthoff,[6] using purified filter paper, has concluded that positive ions are separated from salts not by cellulose, but by the ash constituents.

Expts. 2 and 3, described in detail below, show that neither acid-washed filter paper nor well-washed bleached sulfite pulp removes any analytically appreciable amount of alumina from a basic solution of aluminium sulfate, when brought in ordinary contact therewith. Expt. 3 shows that pure filter paper does not adsorb alumina from a nonbasic solution of sulfate even when the two are very thoroughly beaten together, while Expt. 4 shows conditions under which a retention of alumina may occur. In this case the pulp used had an alkaline reaction. Some precipitation took place (shown by the reduced amount of "total Al_2O_3"), while the still greater reduction in the combined alumina present indicated the formation of a "basic salt," but these changes were obviously due to chemical action, not to adsorption or any related phenomenon. Expt. 5 serves to show that even when a neutral solution of aluminium sulfate is converted into a basic one in the presence of a *well-washed* sulfite pulp, the cellulose adsorbs no alumina.

Some errors on the subject may well have arisen from manipulative mistakes. It is sometimes forgotten that dilution of a basic aluminium sulfate solution will cause the precipitation of alumina, so that apparent failures to wash aluminium salts completely out of cellulose must not be taken as conclusive evidence of adsorption till all surrounding factors have been very carefully scrutinized.

The present work is not regarded by the author as justification for drawing a final conclusion, but as establishing grounds for reasonable doubt as to whether the alleged adsorption actually takes place. It makes it reasonable for the matter, which has a very practical bearing if the theory of paper sizing is ever to be put on its feet, to be investigated further in an authoritative manner when the supply of pure cellulose which has been promised to the Cellulose Section of the Society is available for research purposes.

Analytical Methods

"combined Al_2O_3"—Either Method A or Method B,[7] described previously, was used. Whichever method was chosen as more convenient was adhered to throughout the same set of determinations.

"total Al_2O_3"—The method was that of W. Blum.[8]

"basic Al_2O_3"—When not found by difference between "total" and "combined" Al_2O_3, the Craig-Scott method[9] was used with a slight modification of no importance.

Preparation of Strongly Basic Aluminium Sulfate Solutions

To 300 cc. of a 10 per cent solution of pure $Al_2(SO_4)_3$, 100 cc. of 4 per cent NaOH solution were added. The resulting precipitate was well stirred and poured into another 300 cc. of the same $Al_2(SO_4)_3$ solution. After a few hours the mixture was filtered. The filtrate was diluted for use as required, but when so diluted could not be preserved for long without change.

Description of Experiments

Expt. 1—Approximately 6 g. (dry weight) of well washed and beaten, bleached sulfite spruce pulp, in a 500-cc. graduated flask, were treated with 100 cc. of a basic aluminium sulfate solution. The mixture was agitated, diluted to 500 cc., and filtered. A blank experiment was made at the same time by diluting 100 cc. of the same basic sulfate solution to 500 cc. with water, and filtering.

"Basic Al_2O_3" was determined in 100 cc. of each filtrate, with the following results:

	Pulp Present	Blank
NaOH equivalent to "Basic Al_2O_3," cc.	24.1	24.0
Titer of NaOH	0.27 *N*	0.27 *N*
"Basic Al_2O_3" in 100 cc. filtrate, grams	0.1140	0.1135

Expt. 2—A filter was prepared by folding together 15 No. 30 Whatman 15-cm. filter papers (total weight approx. 20 g.), and 100 cc. of a clear, rather strong solution of basic aluminium sulfate were poured thereon. Only 55 cc. of filtrate passed through, the remainder being absorbed by the papers. Determinations were made as follows on 50 cc. of the original solution and on the same volume of filtrate:

	Original Solution Grams	Solution Passed through Filter Grams
Total Al_2O_3	0.1287	0.1291
"Combined Al_2O_3"	0.1018	Not determined
"Basic Al_2O_3" (by difference)	0.0265	Not determined

Expt. 3—Twenty-two Whatman No. 44 9-cm. filter papers (approx. weight 10 g.) were beaten in a ball mill for 2 hrs. with 200 cc. of $Al_2(SO_4)_3$ solution (containing no "basic Al_2O_3") and 400 g. of pebbles. The resulting pulp was pressed and filtered. The total Al_2O_3 found in 100 cc. of the original solution was 0.1620 g.; in 100 cc. of the filtrate, 0.1619 g. A microscopic examination of the fibers before and after the beating indicated that a considerably increased degree of hydration had been induced during the process.

Expt. 4—About 20 g. of air-dry, bleached sulfite spruce pulp, washed only by an ordinary mill process, were beaten in a ball mill with 400 cc. of aluminium sulfate solution under the conditions of Expt. 3. The solution was then filtered from the pulp. Determinations were made on this filtrate and on the original solution, as follows:

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[1] Presented before the Section of Cellulose Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Chemist to the E. B. Eddy Co. Ltd.

[3] "Paper Making," 5th ed., 248.

[4] *Wochbl. Papierfabr.*, **43** (1912), 1454.

[5] *Pulp Paper Mag. Can.*, **11** (1913), 803.

[6] *Pharm. Weekblad.*, **57** (1920), 1510, 1529.

[7] This Journal, **13** (1921), 420.

[8] *J. Am. Chem. Soc.*, **38** (1916), 1282.

[9] This Journal, **7** (1915), 1059.

	Total Al_2O_3 in 100 Cc. Grams	"Combined Al_2O_3" in 100 Cc. (Determined on 20 cc.) Grams	"Basic Al_2O_3" in 100 Cc. by Difference Grams
Original solution	0.1809	0.1807	0.0002
Solution after beating and filtration	0.1793	0.1783	0.0010
Change	−0.0016	−0.0024	+0.0008

The solution which had been in contact with the pulp gave a slight precipitate with $(NH_4)_2C_2O_4$ after precipitation of the Al_2O_3.

An aqueous extract made from another sample of the same pulp was alkaline to methyl red, and gave a precipitate when boiled with a dilute solution of $Al_2(SO_4)_3$.

Expt. 5—Approximately 6 g. of well washed and beaten sulfite spruce pulp were introduced into a 500-cc. graduated flask. To this were added 200 cc. of "white rosin size" and the mixture was well agitated. While the agitation continued 100 cc. of $Al_2(SO_4)_3$ solution (approximately 10 per cent) were added. The contents of the flask were made up to 500 cc. and filtered.

A blank experiment was made in every respect similar but omitting the presence of pulp. Under these conditions it has been shown in the course of work not yet published that the aluminium resinates are hydrolyzed, the alumina remaining in solution as "soluble basic sulfate."

The "combined Al_2O_3" and "basic Al_2O_3" were determined in aliquot portions of the filtrate, 50 cc. being taken for the former and 100 cc. for the latter determination. Unfortunately a note of the titer of NaOH solution used in the determination of "basic Al_2O_3" has been lost, but as the same solution was used both for main experiment and blank, the results can still be compared, though not stated in weight of Al_2O_3.

"COMBINED Al_2O_3"

	NaOH Used 0.3246 N Cc.	"Combined Al_2O_3" in 50 Cc. Filtrate Grams
In presence of pulp	26.0	0.1438
In absence of pulp	25.9	0.1432

"BASIC Al_2O_3"

	NaOH Used for 100 Cc. Filtrate Cc.
In presence of pulp	26.0
In absence of pulp	26.1

The differences shown may therefore be considered as within reasonable experimental error.

CONCLUSIONS

1—The observed withdrawal of Al_2O_3 from solutions of $Al_2(SO_4)_3$ in the presence of cellulose is due to chemical precipitation by noncellulose material present as an impurity.

2—No adsorption of Al_2O_3 by cellulose of reasonable purity could be observed in such solutions, ordinary analytical methods being adopted. Basic and neutral solutions were both tried.

3—The question should be thoroughly investigated and an authoritative decision reached when pure standard cellulose becomes available for research.

4—Methods of investigation which depend on attempts to separate aluminium salts from cellulose by repeated washing can only be employed when great caution is used as to the nature of the materials. They can never be trusted when basic solutions are in question.

The Penetrability of Filter Paper[1]

By R. C. Griffin[2] and H. C. Parish

Arthur D. Little, Inc., Charles River Road, Cambridge, Massachusetts

In the following paper the common methods of testing the penetrability of filter paper are discussed, and a new penetrability tester is described. Attention is called to the effect of temperature and time upon the speed of filtration of distilled water. Comparative penetrability figures are given for five representative grades of quantitative papers.

Various methods of testing the speed of filtration or the penetrability of filter paper have been proposed. The method probably in most common use is to fit a circle of the paper into a funnel and fill it with water or some other liquid. The speed of filtration is then either (1) judged arbitrarily, (2) measured by timing the flow of a definite volume of liquid through the paper, or (3) compared with some other paper as a standard, which is tested in the same way on a similar funnel.

Such a test, if properly carried out, will undoubtedly provide a "rough and ready" comparison between different filter papers. It is obvious, however, that there are numerous factors which will affect the results, principally: (1) the length and internal diameter of the stem of the funnel; (2) the angle of the funnel; (3) the way in which the paper is folded and fitted into the funnel; and (4) the amount of liquid filtered and the manner in which it is poured upon the filter. Obviously, therefore, very misleading conclusions may be reached by such a test. Furthermore, it does not furnish a ready means of obtaining figures that may be recorded for future comparisons.

Herzberg has designed an apparatus[3] (Fig. 1) which consists essentially of a vertical, cylindrical, glass water-reservoir with an air-tight cover through which passes the stem of a funnel nearly to the bottom. A stopcock in the cover allows the water pressure to be adjusted according to the volume of air above the water in the reservoir. Connected to the reservoir at the bottom, by means of a U-tube with a valve cock, is a cylindrical box, 5 cm. in diameter, to hold the paper. In operation the upper half of this box is taken off and the cock opened slowly until the water reaches the upper edge. The paper is then laid in position, the upper half of the box replaced, and the cock again opened until water issues in a regular stream. The water is collected in a 100-cc. volumetric flask and the time required to fill the flask is determined, under a definite head of water, usually 5 cm.

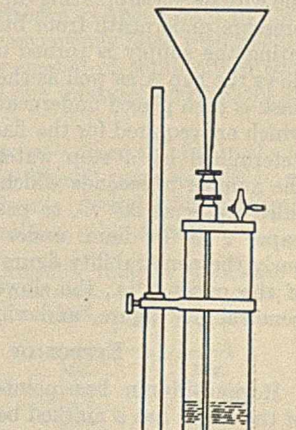

Fig. 1—Herzberg's Penetrability Tester

In attempting to use the Herzberg tester for routine control tests in filter paper manufacture the writers have found difficulty in getting consistent results. This was probably largely due to failure of the operator to maintain conditions

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[1] Received July 9, 1921.

[2] Director of Tests, Arthur D. Little, Inc.

[3] H. P. Stevens, "The Paper Mill Chemist," Scott, Greenwood & Son, London, 1919, 2nd ed., p. 267.

uniform, particularly as regards the water pressure. It is, of course, desirable to have any instrument which is to be used in routine control tests as nearly automatic as possible. With this in view, there has been developed a penetrability tester which after many months' trial has been found to give consistent results. It is also of rugged construction, compact, and simple to manipulate.

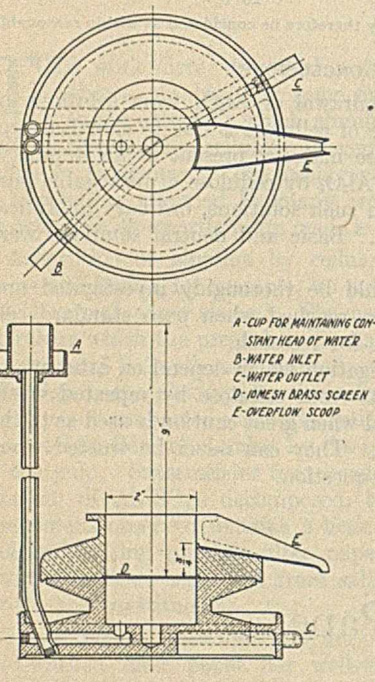

Fig. 2—Penetrability Tester for Filter Paper

Fig. 2 shows a horizontal and a vertical cross section of the tester. The entire apparatus, with the exception of the tube leading from the overflow cup to the base of the apparatus and the wire screen, is made of lead. The part carrying the overflow dam E and the wire screen D lifts off from the lower portion, both contact surfaces being planed. The distilled water supply enters the vertical tube at right angles at a point about 4 in. above D. This water supply is controlled by means of a stopcock. It is kept in any suitable form of reservoir and feeds by gravity.

In operation the upper portion of the apparatus is lifted off and a circle of the paper to be tested is laid across the 2-in. opening in the base. The upper half is then replaced, the wire screen supporting the filter paper and preventing the pressure underneath from bursting it. The stopcock regulating the supply is turned on slowly until the water overflows the cup A as well as the dam E. A 100-cc. volumetric flask is then placed underneath E and the number of seconds which are required for the flask to fill to the 100-cc. mark is determined by a stop watch. The penetrability figure is the number of seconds which are required for 100 cc. of distilled water at 20° C. to pass through a circle of the filter paper 2 in. in diam. under a constant 9-in. head. Obviously the penetrability figure varies inversely with the speed of the paper, *i. e.*, the slower the paper, the higher is the penetrability figure, and vice versa.

EFFECT OF TEMPERATURE

Regaud-Monin has pointed out[4] that the temperature of the water has a marked bearing on the speed of filtration. It was found that water at 30° C. passes through a paper more than twice as rapidly as water at 0° C. under otherwise similar conditions. Table I is given in order to correct values obtained at a temperature other than 20° C.:

TABLE I

TEMPERATURE ° C.	CORRECTION FACTOR
0	0.563
10	0.769
15	0.883
20	1.000
25	1.124
30	1.256

EFFECT OF LONG FILTRATION

It is well known that a filter paper will slow up considerably after having been used for a short time, even though the solution filtered does not contain sufficient precipitate to fill up the pores appreciably. This also holds true when distilled water alone is used, and is due to hydration and expansion of the fibers. During our investigation of the various factors affecting the penetrability of filter paper we have determined the effect of long filtration under a constant head. Some of the results are shown in Fig. 3.

In order to determine the relative effect of time upon speed of filtration an unusually slow paper and a fast paper were selected, and the penetrability of each sample was taken immediately and at the end of 10- or 20-min. periods for 1 hr. in the case of the slow paper, and for 2 hrs. in the case of the fast paper, allowing distilled water to run through the paper continuously during the intervals. In Fig. 3 A and A′ are the curves of two fast papers, taken from the same box, and B and B′ are the curves of two circles taken from a box of slow paper. The water was maintained at 20° C., and precautions were taken to keep it clean as well as all parts of the apparatus with which the water came in contact.

It will be seen that in the case of one of the fast papers, which originally had a penetrability of about 25 sec., the penetrability was slowed down to 1000 sec. by allowing distilled water to run through it for 2 hrs. Obviously, to obtain the greatest speed efficiency, the fastest paper that will hold the precipitate in question should be employed; the solution should be filtered as hot as possible, and the entire operation should be carried through without any unnecessary delay.

PENETRABILITY FIGURES

The penetrability figures obtained upon several brands of well-known quantitative filter papers are given in Table II. The tests were made on five circles taken at random from each lot and the figure given is the average of the five tests.

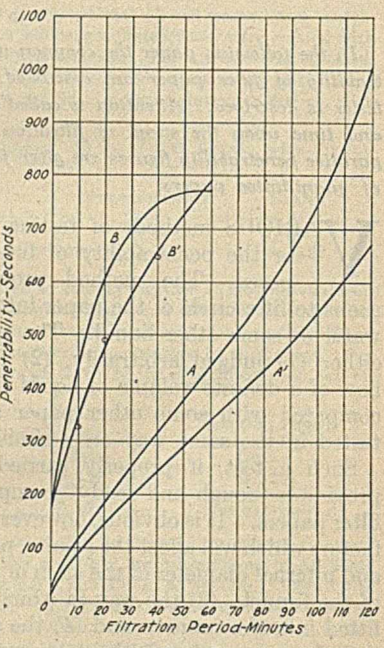

FIG. 3
A—FAST PAPER (A. D. L.); B—SLOW PAPER (WHATMAN) NO. 44

TABLE II

	PENETRABILITY SECONDS
Paper A (rapid, double washed, for general all-round use)	
Lot 1	16
Lot 2	20
Lot 3	20
Paper B (single washed, thin, rapid)	
Lot 1	16
Lot 2	16
Paper C (double washed, extra rapid, for gelatinous precipitates)	8
Paper D (double washed, very low ash)	
Lot 1	28
Lot 2	78
Lot 3	61
Paper E (dense formation, specially made for finest precipitates)	
Lot 1	85
Lot 2	54
Lot 3	120

It will be noted that paper C is about ten times as rapid as paper E.

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[4] *Papeterie*, **42** (1920), 818.

Quantitative Method for Determination of Peroxidase in Milk[1]

By Frank E. Rice[2] and Torataro Hanzawa[3]

Department of Chemistry, Cornell University, Ithaca, New York

A SATISFACTORY method for the quantitative determination of peroxidase in milk is described in this paper. It should find application in determining if milk has been heated to a temperature much above the usual pasteurizing temperature. If reconstituted powdered or evaporated milk or if boiled milk has been added to raw milk, application of this method will give proof of the fact, whereas qualitative tests for peroxidase will give no indication.

....

No method for making quantitative comparisons of peroxidase activity is found in the literature, although practically all other enzymes of milk are estimated quantitatively. Many qualitative tests for peroxidase have been suggested. In all of these, hydrogen peroxide is present, together with some reagent which undergoes a change in color when oxidized, such as guaiacol, paraphenylenediamine, benzidine, pyramidone, ortol, and other photographic developers. The peroxidase is believed to act as a carrier of oxygen from the hydrogen peroxide to the dye. Attempts to modify some of the qualitative tests so that quantitative interpretations could be made were not entirely successful. It was possible to compare the peroxidase activity of different samples only in a general way.

Bach and Chodat[4] have suggested a method for quantitatively determining peroxidase in extracts from plant tissue, involving the oxidation of soluble pyrogallol to insoluble purpurogallin. When an excess of hydrogen peroxide and pyrogallol is present, the extent to which the reaction takes place depends upon the amount of the peroxidase, all other conditions such as time and temperature being the same. The weight of the final product is taken as a measure of the peroxidase activity.

The reaction is probably as follows:

$$\underset{\text{pyrogallol}}{3C_6H_3(OH)_3} + 2O = \underset{\text{purpurogallin}^5}{C_6H_3(OH)(OOC_6H_3(OH)_2)_2} + 2H_2O$$

Application of Bach and Chodat Method to Milk Samples

Ten cc. of milk were diluted with 50 cc. of water, and treated with 20 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. The mixture was stirred well, allowed to stand several days at room temperature (19° to 21°), and filtered on a dried and weighed filter. The precipitate was first washed with a freshly prepared mixture similar in composition to the precipitating solution, made by adding to 50 cc. of distilled water 20 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. It was finally washed with 100 cc. of distilled water and dried to constant weight at the temperature of boiling water.

TIME NECESSARY FOR COMPLETING THE REACTION—Although Bach and Chodat found that 24 hrs. was sufficient time to complete the reaction with plant juice extracts, with milk much longer time is necessary before the reaction has reached an equilibrium. Seven days is a satisfactory reaction time.

Expt. 1—Several identical mixtures were started on the same sample of milk. Each day one was filtered and weighed. In all cases 10 cc. of milk were used, and the weights of purpurogallin in Table I are given in mg. per 10 cc. of milk.

Table I

Time of Reaction Days	Raw Skim Milk	Pasteurized Skim Milk	Boiled Skim Milk
1	14.6	10.4	.....
2	25.4	19.8	.....
3	28.0	21.4	0
4	30.5	26.8	.....
5	31.2	27.0	Trace
6	31.8	28.0	.....
7	31.5	28.2	8.2
8	32.0	29.0	.....

EFFECT OF PRESENCE OF AIR—In the sample containing boiled skim milk (Table I) it is seen that some purpurogallin precipitated out in 7 days. The precipitation took place at the surface of the liquid and since the determinations were run in beakers, it was believed that the air had influenced the reaction. Certainly there should be no peroxidase in boiled milk.

The following observations were made: A solution containing boiled milk together with pyrogallol alone, or with hydrogen peroxide, and in presence of air precipitated purpurogallin after about 5 days. A mixture of boiled milk, pyrogallol, and hydrogen peroxide, covered with paraffin or filled into a bottle so that air was excluded, never precipitated purpurogallin. From this it is evident that it is necessary to prevent the access of air to the reacting mixture; otherwise all the purpurogallin precipitated could not be attributed to the action of peroxidase.

To avoid this difficulty, glass-stoppered bottles of 100- to 130-cc. capacity were employed. After the measured amounts of milk, water, hydrogen peroxide, and pyrogallol had been mixed, the bottles were entirely filled with a solution of hydrogen peroxide and pyrogallol of composition similar to that which was already in the mixture, and tightly stoppered.

REMOVAL OF FAT FROM RESIDUE—Since any fat in the milk would probably remain on the filter, it was desirable to wash the precipitate with a fat solvent. Ethyl ether readily dissolves purpurogallin, but petroleum ether does not.

Expt. 2—Two of the purpurogallin residues from skim milk were washed five times with petroleum ether, and after each washing the filter was dried and weighed.

	Residue A Mg.	Residue B Mg.
Precipitate	36.0	31.8
After 1st washing	30.8	27.0
After 2nd washing	30.4	26.8
After 3rd washing	30.2	27.0
After 4th washing	30.4	27.0
After 5th washing	30.4	27.0

These results showed that in applying the method to milk it was necessary to wash the residue finally to remove the fat. In all subsequent determinations after the last washing with water the filters were dried and washed twice with petroleum ether before finally drying and weighing.

PROPORTIONS OF HYDROGEN PEROXIDE AND OF PYROGALLOL—In order that the enzyme may have opportunity to exert its full effect, it is important that hydrogen peroxide and pyrogallol be present in excess. In the two following experiments the effect of varying these constituents was determined:

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[1] Presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Assistant Professor of Agricultural Chemistry, Cornell University.

[3] Professor of Chemistry, Agricultural College of Japan.

[4] *Ber.*, **37** (1904), 1342.

[5] H. Wichelhaus, *Ibid.*, **5** (1872), 846.

Expt. 3—In each mixture the hydrogen peroxide was varied, while the other ingredients were kept constant.

1 Per cent Hydrogen Cc.	Hydrogen Peroxide Per cent	Water Added Cc.	5 Per cent Pyrogallol Cc.	Skim Milk Cc.	Purpurogallin in 7 Days Mg.
2	0.025	58	10	10	22.4
4	0.050	56	10	10	27.4
6	0.075	54	10	10	27.6
8	0.100	52	10	10	27.2
10	0.125	50	10	10	27.4
12	0.150	48	10	10	28.2
14	0.175	46	10	10	27.6
16	0.200	44	10	10	28.0
18	0.225	42	10	10	27.4
20	0.250	40	10	10	28.4

Expt. 4—The proportion of pyrogallol was next varied.

5 Per cent Pyrogallol Cc.	Pyrogallol in Mixture Per cent	Water Added Cc.	Hydrogen Peroxide Cc.	Skim Milk Cc.	Purpurogallin in 7 Days Mg.
2	0.125	58	10	10	18.8
4	0.250	56	10	10	22.6
6	0.375	54	10	10	28.4
8	0.500	52	10	10	31.2
10	0.625	50	10	10	31.0
12	0.750	48	10	10	31.6
14	0.875	46	10	10	31.4
16	1.000	44	10	10	31.6
18	1.125	42	10	10	30.8
20	1.250	40	10	10	31.4

These results show that all proportions of hydrogen peroxide above 0.05 per cent and of pyrogallol above 0.5 per cent are sufficient. In further experiments, therefore, 10 cc. of hydrogen peroxide were continued, but the quantity of pyrogallol was reduced to 10 cc.

COMPARISON OF WHOLE AND SKIM MILK—A sample of skim milk taken from a cream separator was compared with the whole milk from which it came. Ten cc. of the whole milk yielded 34.2 mg. of purpurogallin; with the skim milk there were obtained 32.0 mg. In another instance whole milk was placed in a tube, warmed slightly, and centrifuged. Ten cc. of the skim milk layer gave 31.8 mg., and an equal volume of the whole milk 33.2 mg. purpurogallin.

Exceedingly great difficulty was always found in filtering the mixture containing the whole milk, while the skim milk mixture filtered readily. For this reason it is recommended that before a sample of milk be run by the pyrogallol method it be first centrifuged to remove most of the fat.

DESCRIPTION OF METHOD

Place sample in a tube, warm slightly, and centrifuge. Transfer 10 cc. of the skim milk to a glass-stoppered bottle of about 100-cc. capacity, add 50 cc. of distilled water, followed by 10 cc. of 5 per cent pyrogallol and 10 cc. of 1 per cent hydrogen peroxide. Shake well, and fill up the bottle with a solution prepared by mixing 60 cc. of water with 10 cc. of 1 per cent hydrogen peroxide and 10 cc. of 5 per cent pyrogallol. Stopper tightly, and let stand for 7 days[6] at room temperature. Filter on a weighed Gooch, wash the precipitate, first with the pyrogallol-hydrogen peroxide mixture just described, and finally with distilled water. Use no more than the necessary quantity of water in the washing, since purpurogallin is slightly soluble. When the washings do not give a dark blue color with ferric chloride solution, all the pyrogallol has been removed and the filter has been sufficiently washed. Dry the filter thoroughly, wash two or three times with petroleum ether, dry, and weigh. The weight of purpurogallin (in mg.) yielded by 10 cc. of milk is to be called the *peroxidase number*.

RELATION BETWEEN AMOUNT OF PEROXIDASE IN MILK AND THE PEROXIDASE NUMBER

In order to show that the relative amounts of peroxidase in milk could be determined by the amount of purpurogallin precipitated, raw and boiled skim milk were mixed in various proportions and run by regular method (Expt. 5):

Raw:Boiled	100:0	75:25	50:50	25:75	0:100
Peroxidase numbers	28.2	21.4	15.4	8.2	0
Ratio	100	75.8	54.6	29.0	0

EFFECT OF PASTEURIZING AND OF PRESERVATIVES ON PEROXIDASE ACTIVITY

In Expt. 1 a comparison may be made of the peroxidase numbers of raw and pasteurized milk. The pasteurization was brought about by bringing the milk to 145° F. in 10 min., holding at that temperature for 30 min., and finally cooling to 60° F. in 10 min.

Expt. 6—In this experiment the peroxidase numbers of portions of skim milk were determined after different heat treatments. The samples were heated at the various temperatures for 30 min. except for the blank which was untreated; the peroxidase numbers were as follows: blank, 31.8; 145° F., 25.6; 155° F., 24.2; 165° F., 0; 180° F., 0.

Heating at 145° F. and at 155° F. is seen to reduce the peroxidase number to some extent, though the critical point is evidently between 155° and 165°.

A sample of skim milk, 10 cc. of which yielded a peroxidase number of 30.2 when fresh, gave 27.6 after being held at 40° F. for 2 days.

A portion of the same milk was preserved with 1 per cent mercuric chloride, and to another portion was added formaldehyde at the rate of 1 cc. to a pint. The sample containing mercuric chloride could not be determined on account of a precipitate, resulting probably from a precipitation of the casein by the mercury. The sample containing formaldehyde gave a peroxidase number of 0, which is probably due to the reducing effect of the formaldehyde.

Evidently neither mercuric chloride nor formalin can be used to preserve samples of milk in which the peroxidase number is later to be determined.

When milk is held on ice for 2 days the peroxidase activity is seen to fall off to some extent.

SUMMARY

1—The method proposed by Bach and Chodat for the estimation of peroxidase in plant juices is adapted with modifications for milk.

2—The method depends upon the oxidation of pyrogallol by hydrogen peroxide, the reaction being catalyzed by peroxidase. The weight of purpurogallin which precipitates out (mg. resulting from the action of 10 cc. of milk) is called the "peroxidase number."

3—Seven days are necessary for the reaction to reach an equilibrium. Since in this length of time air is a factor in the precipitation of purpurogallin, the reaction must take place in absence of air.

4—To remove fat the residue is washed with petroleum ether, in which purpurogallin is insoluble.

5—Whole milk and skim milk are about equal in peroxidase activity.

6—By mixing raw and boiled milk in varying proportions it was shown that the peroxidase number varies quite regularly with the concentration of peroxidase.

7—Heating milk below 155° F. for 30 min. reduces but does not destroy peroxidase activity. Holding on ice for 2 days reduces the action slightly.

8—Samples of milk for peroxidase estimation cannot be preserved with mercuric chloride or formaldehyde.

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[6] Other modifications of the method of Bach and Chodat have been offered, such as that of Willstätter and Stoll [*Ann.*, **416** (1918), 21]. In general these methods have been adapted to the determination of peroxidase in fractions from plant materials. In these fractions the peroxidase activity is much greater than in milk, and for this reason a considerable amount of purpurogallin is produced in a very short time. Under such conditions the reaction is not allowed to run to completion but is stopped after a short period and the amount of purpurogallin produced during this time is taken as a measure of the amount of peroxidase. In milk, however, the activity of the enzyme is so weak that even by allowing the reaction to go to completion (which requires about 7 days), a relatively small weight of purpurogallin is obtained. On this account the authors consider it wise to allow the full time for the determination; however, it would be possible to obtain comparative results in from 1 to 3 days.

The Preservation of Fish Frozen in Chilled Brine[1,2]

II—The Keeping Quality of the Fish

By L. H. Almy[3] and E. Field

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The following paper concludes the work published last year on "The Preservation of Fish Frozen in Chilled Brine." In this part of the work, fish were frozen in air at −10° and in 15 per cent brine at its freezing point. In general, fish frozen in air lost somewhat in weight, while there was a slight gain upon freezing in brine. On storage, brine-frozen fish usually lost less than air-frozen fish. Brine-frozen fish could be successfully glazed, after a preliminary rinsing in cold water. The method of freezing had no effect on the amounts of fat-free solids, ammonia, and amine nitrogen, on the rate of decomposition after removal from freezer storage, or on the number or general character of the bacterial flora in the skin, flesh, and intestines. Cooking tests showed that air-frozen and brine-frozen fish were perfectly edible at the end of the storage periods, but the texture and flavor of the latter were slightly superior to the other.

During the one or two hours that fish are in contact with cold brine during freezing by the newly advocated process of brine freezing, a small amount of salt is absorbed in spite of attempts to prevent it.[1,*] The extent of penetration varies in different species of fish, and appears to be influenced somewhat by the presence of fat in the tissues, the fatty tissues not absorbing as much as the lean.

The texture of brine-frozen fish differs from that of air-frozen fish in that during chilling and freezing the muscular tissue of the former is little affected, whereas that of the latter is somewhat altered as a result of the separation of water from the tissues.[2] Because of this difference in texture and also of the fact that the brine-frozen fish have a small amount of salt in the outer layers, the keeping qualities of the two kinds of fish during storage may show interesting differences.

Plank and Ehrenbaum[3] found that during 30 hrs.' freezing in air at −7° C. and 85 per cent relative humidity cod lost 3 to 4 per cent, haddock about 5 per cent, and flat fish like flounders about 6 per cent, and that during freezing in brine there was no loss and quite often a slight gain in weight. During storage the fish in the majority of instances lost in weight, and among fish of the same species but of different size the loss was approximately in inverse proportion to the cube roots of the weights. These authors show that the evaporation of water is lower in fatty fish and is less the more nearly the form of the fish resembles a sphere, in which shape the proportion of surface to mass is least. A few examples of weight changes observed by them are given in Table I. They show that the weight losses in fish hanging free in a room at −7° C. are very large. Protected by wrapping in parchment paper, the fish changed in weight but little. Droogleever Fortuyn[4] reports a loss in weight of 12 to 24 per cent in soles stored for 4 to 5 wks. at −2° to −6° C.

Method of Investigation

Uneviscerated weakfish (*Cynoscion regalis*), whiting (*Merluccius bilinearis*), mossbunkers (*Brevoortia tyrannus*), butterfish (*Poronotus triacanthus*), and spot (*Leiostomus xanthurus*) were frozen in air and in brine in the manner previously described.[1] The brine solution was approximately 15 per cent and was held at its freezing point during the freezing of the product. All brine-frozen fish were frozen singly. Most of the air-frozen fish were frozen in pans and stored in the form of solid cakes of fish; a few were frozen singly in order to facilitate the determination of individual weight changes.

Table I—Examples of Weight Changes in Stored Fish Observed by Plank and Ehrenbaum

Fish	Manner of Freezing	Manner of Storing at −7° C. and 85% Relative Humidity	Duration of Storage Period Days	Change in Weight before Thawing Per cent	Change in Weight after Thawing in Air Per cent
Mackerel	In air at −7° C.	Uneviscerated, hanging free, glazed	66	−12.5	.....
Mackerel	In concentrated NaCl at −14° C.	Uneviscerated, hanging free, glazed	84	−17.2	.....
Mackerel	In NaCl brine by Ottesen method at −15° C.	Uneviscerated, wrapped in parchment paper	50	.....	−0.3
Plaice	In air at −12° C.	Uneviscerated, hanging free, glazed	40	−23.5	.....
Plaice	In air at −12° C.	Uneviscerated, hanging free, glazed	56	−36.6	−33.3
Plaice	In NaCl brine by Ottesen method at −15° C.	Eviscerated, wrapped in parchment paper	50	.....	+ 0.5
Flounders	In air at −7° C.	Uneviscerated, in open basket	165	−60.3	.....

After glazing, the weakfish, mossbunkers, and spot were stored for 5 mo. and part of the whiting for 3 mo. in a room whose temperature during these periods remained fairly constant at −10° F.; during the next 3 mo. of storage, beginning March 1, the temperatures fluctuated between −5° and +15° F. The remainder of the whiting were stored for 6 mo. at a uniform temperature of 12° to 15° F. in a room in a separate storage house. The fish were packed in covered wooden boxes lined with vegetable parchment paper.

Physical Tests

Whiting frozen singly in air at −10° F. lost 2.32 per cent of their weight in the 18.5 hrs. following their entrance into the freezer. The same species of fish gained 0.15 per cent in weight during 1 hr.'s freezing in brine, and during the succeeding 17 hrs. in cold storage at −10° F. gained 0.38 per cent more in weight. Surface water was removed from these fish before freezing in air. The apparent loss in weight of fish during the freezing is higher if this water is not taken into account. For example, it was found that whiting, after washing in water, when frozen singly, lost in 3, 6, and 22 hrs. 2.54, 3.60, and 4.03 per cent in weight, respectively, when the wash water was allowed to remain on the surface, and 1.55, 2.44, and 2.74 per cent, respectively, when the exterior of the fish was freed from excess moisture prior to the initial weighing and entrance into the freezer. When whiting, the exterior of which had been dried, were frozen in a pan in a compact layer, the loss in 3, 6, and 22 hrs. was much smaller and more uniform, being 0.33, 0.59, and 0.80 per cent, respectively.

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[1] Received October 31, 1921.

[2] Published by permission of the Secretary of Agriculture.

[3] Food Research Chemist, Bureau of Chemistry.

* Numbers in text refer to Bibliography at end of paper.

TABLE II—PERCENTAGE OF FAT-FREE SOLIDS IN FLESH OF BRINE-FROZEN AND AIR-FROZEN FISH DURING STORAGE[1]

B. = Brine-frozen; A. = Air-frozen

Date of Analysis	Weakfish		Mossbunkers		Spot		Whiting No. 1		Whiting No. 2	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
October 11, 1919	19.43	20.05	22.47	19.11	21.54	19.05	...	...	...	...
December 3, 1919	...	...	...	...	...	...	17.66	17.17	17.66	17.17
March 8, 1920	20.20	20.18	20.20	18.23	21.82	19.78	18.86	18.16	16.67	18.67
June 9, 1920	19.13	...	21.64	20.32	20.27	19.81	18.57	18.51	18.66	18.45

[1] The weakfish, mossbunkers, and spot were stored at −10° F. from October 6, 1919, to March 1, 1920, and at −5° to +15° F. from March 1 to June 1920. Whiting No. 1 was stored at 12° to 15° F. beginning December 3, 1919. Whiting No. 2 was stored at −10° F. from December 3, 1919, to March 1920, and at −5° to +15° F. from March 1 to June 1920.

TABLE III—PERCENTAGE OF AMMONIA AND AMINE NITROGEN IN FLESH OF BRINE-FROZEN AND AIR-FROZEN FISH DURING STORAGE[1]

(Dry Basis)

B. = Brine-frozen; A. = Air-frozen

Date of Analysis	Weakfish		Mossbunkers		Spot		Whiting No. 1		Whiting No. 2	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
October 11, 1919	0.091	0.094	0.092	0.100	0.091	0.108	...	...	...	...
December 3, 1919	...	...	...	...	...	...	0.087	0.093	0.087	0.093
March 8, 1920	0.082	0.086	0.084	0.093	0.079	0.091	0.121	0.127	0.104	0.099
June 9, 1920	0.094	0.086	0.101	0.096	0.101	0.099	0.134	0.122	0.098	0.095

[1] See footnote to Table II.

TABLE IV—PERCENTAGE OF AMMONIA AND AMINE NITROGEN IN FLESH OF BRINE-FROZEN AND AIR-FROZEN FISH DURING 8 DAYS' HOLDING AT 50° TO 55° F. AFTER STORAGE FOR 3 TO 5 MO. AT FREEZER TEMPERATURES (DRY BASIS)

B. = Brine-frozen; A. = Air-frozen

Number of Days Held at 50°–55° F.	Weakfish after 151 Days' Storage at −10° F.		Mossbunkers after 144 Days' Storage at −10° F.		Spot after 144 Days' Storage at −10° F.		Whiting No. 1 after 96 Days' Storage at 12–15° F.		Whiting No. 2 after 96 Days' Storage at −10° F.	
	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.
0	0.082	0.086	0.084	0.093	0.079	0.091	0.121	0.127	0.104	0.099
1	0.082	0.098	0.091	0.097	0.100	0.103	0.144	0.131	0.114	0.115
2	0.095	0.095	0.099	0.098	0.097	0.096	0.152	0.165	0.122	0.134
5	0.129	0.115	0.135	0.118	0.118	0.114	0.165	0.172	0.178	0.138
8	0.170	...	0.154	0.144	0.149	0.169	0.205	0.210	0.216	0.189

WEIGHT CHANGES UPON STORAGE—That the change in weight of frozen fish during storage need not be so great as reported by European investigators is indicated by the results which were obtained in the following study of weight changes in weakfish and whiting stored at the comparatively low temperatures prevalent in cold storage houses in this country. For these experiments the fish, after freezing singly in air and in brine, were weighed individually, then glazed, and reweighed at the end of the periods of storage, the glaze being removed before each weighing. Air-frozen weakfish lost 0.25 per cent during the first 5 mo. when the temperature was −10° F., the total loss during the entire 8 mo. of storage being 2.18 per cent. Air-frozen whiting lost 0.24 per cent during 3 mo. at −10° F., the total for the 6 mo. being 5.03 per cent. Brine-frozen weakfish and whiting gained 0.5 and 1.45 per cent, respectively, up to March 1, but suffered a loss during the remainder of the storage period when the temperature was higher and fluctuating, the amount being 2.90 and 2.12 per cent, respectively. The whiting stored at the comparatively high but uniform temperature of 12° to 15° F. lost considerably more in weight, the air-frozen and brine-frozen fish losing 9.55 and 6.48 per cent, respectively, during the entire 6 mo. It should be remarked that the latter storage temperature is higher than that which is generally employed in the storage of fish in this country.

The increase in the weight of the brine-frozen fish in the early storage period was rather surprising. It may possibly be that a small amount of moisture is attracted to and held by the salt in the exterior tissues of these fish.

GLAZING—The most convenient and efficient method of preserving the exterior appearance of fish and of minimizing the evaporation of water during storage is by means of an ice glaze. Just after the fish have frozen through completely they are dipped momentarily in cold water, a thin film of ice forming on the surface. The treatment is repeated until a substantial glaze is provided. The original glaze may remain for 4 or 5 mo. or even longer on fish which are packed in boxes and stored at low uniform temperatures. Where the fish are stacked in bins in the storage room without boxing, reglazing at intervals of 3 mo. or less may be necessary.

When brine-frozen fish are immersed in cold water immediately after removal from the brine, they do not take a glaze. It was thought at first that this would be a serious objection to the use of this method of freezing fish for storage. However, further attempts in this direction were successful. Fish which had been rinsed in cold water and then held in the storage room for 12 hrs. took a glaze as readily as the air-frozen fish.

Brine-frozen and air-frozen weakfish, whiting, mossbunkers, and spot were glazed and examined at the end of 5, 6, and 8 mo. storage. The fish were not reglazed during these periods. It was found that the brine-frozen fish retained the glaze fully as well as the air-frozen. The weakfish, mossbunkers, and spot, both air-frozen and brine-frozen, possessed a good glaze at the end of 5 mo. storage, although none of the fish had a glaze 3 mo. later, largely on account of the temperature fluctuations during the latter period of storage. The whiting retained a thin glaze at the end of 6 mo. The surface of the brine-frozen fish had a fresher and more attractive appearance than that of the air-frozen at the end of the maximum holding period.

CHEMICAL TESTS

SALT CONTENT—Analyses of the salt content of the two succeeding layers of muscular tissue $^3/_{32}$ in. thick just beneath the skin of whiting immediately after freezing in brine and after storage for 6 mo. seem to indicate that some of the penetrated salt travels inward during storage. The proportion of salt in the outer layer to that in the inner layer was about 2 : 1 at the beginning of storage, but the amounts present in the two layers after storage were usually less and were more nearly equal. Possibly there exists a tendency for the salt to distribute itself more or less uniformly through the tissues, although a definite conclusion on this point must await a more extended investigation. Such a decrease in the salt content of the outer layers might explain the lack of interference of the salt with the permanence of the glaze during storage.

TABLE V—NUMBER OF BACTERIA IN FISH AS AFFECTED BY FREEZING AND STORAGE

B. = Brine-frozen fish; A. = Air-frozen fish

Expt. No.	Fish	Part of Fish	Number of Bacteria per Gram: Before Freezing	Immediately after Freezing		After Storage for X Days		After Storage for Y Days		X Days	Y Days	Temperature of Storage[1] ° F.
				B.	A.	B.	A.	B.	A.			
6037 (*b*)	Spot	Skin	....	6,900	9,000	....	....	....	....	...	...	...
		Flesh	....	4,100	260	....	....	....	....			
		Intestines	....	11,100	40,000	....	....	....	....			
6035 (*a*)	Spot	Skin	....	....	....	8,700	80,000	8,300	29,000	144	236	−10 to +15
		Flesh	....	....	....	700	640	390	430			
		Intestines	....	....	....	1,700	1,250	900	1,400			
6038	Butterfish	Skin	8,770	1,680	25,710	....	....	....	....	...	...	...
		Flesh	2,210	420	2,170	....	....	....	....			
		Intestines	530	500	0	....	....	....	....			
6034	Weakfish	Skin	....	....	....	30,900	8,800	23,000	12,900	151	243	−10 to +15
		Flesh	....	....	....	930	190	100	110			
		Intestines	....	....	....	4,000	10,200	1,200	9,400			
6035 (*b*)	Mossbunkers	Skin	....	....	....	8,200	27,000	7,000	17,400	144	236	−10 to +15
		Flesh	....	....	....	900	280	250	1,330			
		Intestines	....	....	....	8,000	6,900	1,600	6,000			
6042	Whiting	Skin	7,540	1,340	175	1,800	220	....	....	108	...	−10
		Flesh	1,600	0	0	100	40	....	....			
		Intestines	193,280	350	2,130	4,600	3,200	....	....			
6043	Whiting	Skin	200	3,500	240	26,000	6,000	3,200	350	96	188	−10 to +15
		Flesh	910	0	0	8,300	120	100	50			
		Intestines	3,000	420	0	16,000	2,600	900	460			
	Whiting	Skin	....	....	....	380	90	600	228	96	188	12 to 15
		Flesh	....	....	....	40	0	350	16			
		Intestines	....	....	....	51,100	4,800	9,200	2,600			

[1] The temperature for X days was fairly constant at −10° F. The remainder of the time the temperature fluctuated between −5° and +15° F.

FAT-FREE SOLIDS—The percentage of fat-free solids of fresh fish does not vary appreciably in individuals of the same species and size. Determinations of fat-free solids in stored fish afford a means of estimating the extent of the drying out, the proportion of this constituent increasing with the desiccation of the product. As shown in Table II, there is a tendency toward decreased moisture content in the older storage samples. However, there are no pronounced differences attributable to the method of freezing, as was apparent from the results of gross weight determinations on individual fish.

AMMONIA AND AMINE NITROGEN—As a chemical method for following the changes in the flesh of fish during storage, determinations of the ammonia and amine content by a modified Folin aeration method[5] were employed. It had previously been found that the amounts of these bases increased slowly in the flesh of frozen fish during storage.[6] Their accumulation in the flesh is the result of the action of tissue enzymes, of bacteria, or of both. The content of the bases, therefore, is an index of quality only in the sense that it indicates somewhat the extent of the aging which has taken place. Supported by careful physical and bacteriological examinations it is of assistance in the determination of wholesomeness. During storage the content of ammonia and amine nitrogen increased in all fish except the weakfish, mossbunkers, and spot which had been frozen in air. (Table III.) Except in the case of Whiting 1, however, the increases were exceedingly small. At the end of the storage period in June, the percentages of these bases were slightly higher in the brine-frozen fish than in the air-frozen, though the difference is not sufficiently great to justify the conclusion that a difference in keeping quality is indicated.

RATE OF DECOMPOSITION—Additional chemical evidence of the relative keeping qualities of air- and brine-frozen fish was obtained by comparing the rate of decomposition of the fish after removal from storage. The fish, before thawing, were placed in a compartment of a large household refrigerator where the temperature was 50° to 55° F., and were examined immediately and at the end of 1, 2, 5, and 8 days for the content of ammonia and amine nitrogen in the flesh. The experiments (Table IV) did not indicate any consistent difference in the keeping qualities resulting from the method of freezing.

Several whiting which had been stored for 6 mo. were cooked (fried) and tasted by several persons. The consensus of opinion was that the brine-frozen fish had a slightly better flavor than the air-frozen, though both kinds were perfectly edible. A difference in texture of the cooked product was also noted. The flesh of the brine-frozen product seemed a trifle firmer. On comparing sections of the muscular tissue prior to cooking it was observed that it was possible to squeeze more of the juices from the samples of air-frozen fish than from those of the brine-frozen. Apparently the difference in texture produced during the chilling and freezing persists during the storage period.

BACTERIOLOGICAL TESTS*

The surface of fresh caught fish† contains many bacteria obtained from the water, air, hold of the boat, and other sources. Quite frequently also the flesh harbors bacteria which may have entered the tissue through the skin, the wall of the belly cavity, or through the blood system by way of the gills. Many investigators have found *B. coli* in the intestines of fish taken from polluted water.[7] In general, the digestive tract contains bacteria when food is present, but is usually sterile when food is absent. Important contributions on this subject have been made by Hunter,[8] Obst,[9] Browne,[10,11] and others.

When fish are immersed in chilled brine the bacteria on the surface may be affected in two ways. The number may be increased or decreased, depending on the purity of the brine from a bacterial standpoint. Furthermore, the entrance of small amounts of brine into the superficial tissues may carry some of the surface bacteria through the skin into the flesh. Obviously the prevention of the former condition is accomplished by keeping the brine as free from bacteria as possible. The latter may be minimized by preliminary cleansing of the surface of the fish and by the adoption of procedures, such as precooling of the fish in air, which will tend to reduce the extent of salt penetration during the freezing.

Whiting, weakfish, butterfish, spot, and mossbunkers were examined for bacteria at various stages in the processes of freezing in brine and in air and at the end of periods of storage. The slime and scales were aseptically removed from an area near the dorsal fin and the exposed skin was removed with sterile instruments, after which a portion of the underlying flesh was cut out. Likewise the contents of a section of the intestines were aseptically removed. The three samples were macerated by shaking in flasks with bits of sterile broken glass in sterile water, and aliquot

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* The bacteriological examinations were made by Mr. C. H. Werkman, Assistant in Poultry and Egg Handling, Food Research Laboratory, Bureau of Chemistry, and Drs. Albert C. Hunter and Stuart A. Koser, Bacteriologists, Microbiological Laboratory, Bureau of Chemistry.

† The term "fresh caught" is here applied to the fish as landed from the fishermen's boats.

portions plated on plain agar. The plates were incubated at 20° C.

The figures in Table V give the average of three tests of composite samples of two fish each. The variation in the extent of bacterial contamination among the individuals of the different species before freezing is quite great and renders difficult an interpretation of the results of this nature. The data show, however, that there are no consistent differences in the numbers of bacteria in the skin, flesh, and intestines of the various fish before and after freezing and after storage, which might be attributed to the method of freezing.

Examination of the character of the bacterial flora in the fish failed to reveal outstanding differences in the two sets of fish. The predominating microörganisms before and after storage appeared to be mainly those which are usually present in air and water. Among the bacteria identified were *M. citreus* Sternberg, *M. luteus* Cohn, *M. aureus, M. flavus, M. roseus, M. aquatilis, staphylococcus aureus, albus* and *citreus, Bact. refractans* Wright, and *Bact. desidiosum* Wright. Pigment-producing yeasts and various molds, particularly *Aspergillus niger,* were fairly common.

It thus appears that there is very little choice between the two methods from the standpoint of bacterial decomposition during storage.

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Report on Chemo-Medical Research

Under the title of "The Future Independence and Progress of American Medicine in the Age of Chemistry," the Chemical Foundation is circulating the report of the Committee on Chemo-Medical Research, appointed by the American Chemical Society in January 1919.

The report draws a lesson from the results accomplished during the war, when chemists, pharmacologists, and experimental pathologists joined in defensive and offensive work on poison gas at the American University Experiment Station. Great results may be expected in the battle against disease, says the report, through *coöperation under ideal conditions of time and equipment for research.*

How can chemistry, coöperating now with medicine as it coöperated with the war and naval departments, help best in the battle against disease? The constructive chemist can serve in three ways. First, he can aid by the preparation of specific medicaments for the cure or alleviation of specific diseases, either by the synthesis of new products or by the improvement of natural remedies already known. So, too, the study of the pure principles of our organs of secretion opens up a field rich in promise; and another great line of effort in this direction should be the attempt to isolate the pure principles of antitoxins and serums. The third opening for the constructive chemist is the complete ultimate analysis of the constituents of our body cells and the components of our blood and tissues, together with the complete ultimate analysis of the components of our foods. For example, Fischer's work on the structure and chemistry of the sugars opened the way for all the more recent work on carbohydrate metabolism and its pathologic variations. His work on the amino acids forms the foundation of all modern work on protein metabolism. The physical chemist has an important part to play in this coöperation, for the matter of health is closely bound up in the delicate adjustment of speed of the various chemical reactions taking place in the body. Many of our bodily functions are dependent on the action of enzymes (or catalysts). So, too, in nerve and cell, the questions to be dealt with are largely those of colloidal chemistry.

While there are in the United States a number of institutes and foundations for medical research, there is none in which problems are approached primarily from the chemical standpoint. To a large extent, chemo-medical research in this country has followed a few lines opened up in Europe. The professor in the medical school has little time for concentrated work on fundamental problems. Almost the only research work of the government laboratories bearing upon health is that of the Public Health Service, and especially of the Hygienic Laboratory. Data in regard to the amount of medical research in industrial establishments have been hard to obtain. It may be said, however, although many pharmaceutical and chemical manufacturers maintain research organizations which have been an important factor in reaching our present stage of progress, no commercial establishment can maintain a staff of specialists in the various branches of science such as would be required to accomplish effective work of the character now required.

It must be said, without fear of contradiction, (the report concludes) that there is not a single organization whose purpose is a determined coöperative attack on the problems of disease and health, where intense chemical and physical research goes hand in hand with the medical and biological study of disease. The importance of chemistry and physics has been recognized, but the direction of research is still essentially in the hands of medical men. No one of the scientific groups alone should be entrusted with leadership. All are needed for coping successfully with the complex and formidable problems. Complete coöperation of a staff of experts, peers in every sense, each in his own field, with emphasis on the fundamental chemical and physical character of the problems, has nowhere been accomplished. Consequently it is proposed that the attack be actually coöperative, from the selection of the problem and the formulation of the plan of work through the whole concentrated effort to grapple with Nature and ultimately to conquer outpost after outpost of the complex world of life.

Petroleum Statistics

Production of petroleum in the United States in 1921 amounted to 469,639,000 bbls., representing an estimated value at the wells of $753,300,000. This is the greatest quantity ever produced in the United States in any one year and represents an increase of 26,237,000 bbls. over the production of 1920 and is more than double the quantity produced in the United States in 1912. World's production figures for 1921 are not yet known, but preliminary estimates indicate a total not far from 750,000,000 bbls., as compared with 695,000,000 bbls. produced in 1920.

Imports of crude oil into the United States during 1921 amounted to 125,307,000 bbls., as compared with 106,175,000 bbls. in 1920 and with 52,822,000 bbls. in 1919, these figures corresponding, respectively, to 27, 24, and 14 per cent of the domestic production of the past three years. Exports of crude oil during 1921 amounted to 8,940,000 bbls. and during 1920 to 8,757,000 bbls.

Estimated consumption (deliveries to consumers) of domestic and imported crude oil during 1921 amounted to 525,407,000 bbls., as contrasted with 530,474,000 bbls. in 1920. Consumption for the year just ended therefore amounted to 55,768,000 bbls. more than the country produced.

Errors Caused by Nitrates and Nitrites in the Determination of Arsenic by the Distillation Method, and a Means for Their Prevention[1]

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It has been found that nitrates and nitrites interfere in the official method of the Association of Official Agricultural Chemists for total arsenic in insecticides, causing low results. This is probably brought about by the formation of nitrosyl chloride, which passes into the distillate, and there slowly oxidizes the trivalent arsenic to the pentavalent form.

This interference can be prevented by the application of the method of Jannasch and Seidel in which hydrazine sulfate and sodium bromide are used as reducing agents. In addition to giving greater accuracy, this method hastens the volatilization of the arsenic, thereby decreasing the time and the amount of hydrochloric acid required.

THE determination of arsenic by the method of reduction and distillation as arsenic trichloride has been the subject of numerous investigations. An exhaustive review of the literature concerning this problem is given by Roark and McDonnell in a paper[2] describing the application of this method to the determination of arsenic in insecticides. After testing many substances, these authors selected cuprous chloride as the most suitable reducing agent. Following their work, the Association of Official Agricultural Chemists adopted this as an "official" method,[3] and it has since been used in the Bureau of Chemistry with generally satisfactory results. However, in the analysis of commercial calcium and lead arsenates it was found that sometimes duplicate determinations did not agree, and that the results were low in comparison with those obtained by the modified Gooch and Browning method.[4]

It was also observed that delay between distillation and titration accentuated the difference. Impurities in the reagents were at first suspected as the cause of the trouble, but after investigation it was proved that the disturbing factor lay in the sample itself.

The decrease in the titrations with the lapse of time indicated oxidation in the distillate and led the writers to suspect the presence of an oxidizing substance in the sample. In order to cause the effect noticed, the interfering substance or substances must either be volatile or produce volatile products which are oxidizers. These conditions, considered in connection with the process of manufacture of calcium and lead arsenates, practically limit the possible oxidizing substances to nitrates and nitrites. Qualitative tests on a sample of calcium arsenate giving discrepant results showed the presence of a considerable amount of nitrate and a trace of nitrite. Subsequent determination of the nitrogen in this sample gave results equivalent to 3.50 per cent of nitrogen pentoxide. In all cases in which trouble was experienced nitrates were found. Working upon this suggestion, experiments were planned to determine more definitely the action of nitrates and nitrites and to devise a modification of the method to overcome this source of error.

STANDARD SOLUTIONS

The following standard solutions were prepared:

ARSENIC ACID—A solution was prepared from solid arsenic acid which had been purified by several crystallizations from water. It contained 26.05 g. of arsenic pentoxide per liter, as determined by analysis both by the official distillation method[3] and by the Gooch and Browning method of reduction with potassium iodide and subsequent titration with standard iodine solution.

NITRATE SOLUTIONS—(1) a solution containing 10.0 g. of lead nitrate per liter; (2) a solution containing 4.954 g. of calcium nitrate per liter.

NITRITE SOLUTION—A solution containing 4.167 g. of sodium nitrite per liter (the same concentration of nitrogen as in the standard nitrate solutions).

EXPERIMENTAL PROCEDURE

The analyses were made on 25-cc. samples of the arsenic pentoxide solution to which were added varying amounts of the nitrate or nitrite solutions. (The weight of calcium arsenate usually taken for analysis is 1.5 g., so that on this basis the amount of nitrate introduced with 25 cc. of the standard nitrate solutions is equivalent to about 5.4 per cent of nitrogen pentoxide in a commercial sample.) In the experimental procedure the official method was followed except as noted, and all determinations were made in duplicate. The reducing agents were first introduced into the distillation flasks, then aliquot portions of the arsenic pentoxide and of the nitrate or nitrite solutions were added by means of pipets, followed by 100 cc. of concentrated hydrochloric acid. A total of 250 cc. of hydrochloric acid was used in each determination. The distillates were made to 1 liter, and aliquot parts were titrated according to the bromate method of Gyory,[5,6] as presented to the Association of Official Agricultural Chemists by the referee on insecticides and fungicides at the 1920 meeting. As the proceedings of this meeting have not yet been published, the details of the method will be quoted here:

> Transfer 200-cc. aliquots of the distillate to 500-cc. Erlenmeyer flasks, heat to 90° C., and titrate with the standard potassium bromate solution (1.688 g. potassium bromate to 1 liter of water standardized against arsenious oxide in approximately 2 *N* HCl), using methyl orange as indicator. The indicator should not be added until near the end of the titration, and the solution should be rotated continuously to avoid any local excess of the titrating solution. The end of the reaction is indicated by a change from red to colorless and is very sharp.

The first experiments showed conclusively that both nitrates and nitrites had a marked effect on the results. When 0.25 g. of lead nitrate was used the distillate in the receiving flask was decidedly yellow and even 0.05 g. caused a slight yellow coloration. Nitrites produced the same effect. This color disappeared when the distillates were made to volume in a liter flask. On heating, the distillate slowly destroyed the color of methyl orange, but the fading was not sufficiently rapid to interfere with the titration. Aliquot portions titrated at successive intervals showed a steady decline in the arsenic value.

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[1] Received October 22, 1921.

[2] THIS JOURNAL, 8 (1916), 327.

[3] Assoc. Official Agr. Chemists' Methods, 2nd edition (1920), 54.

[4] Dept. of Agriculture, *Chem. Bull.* 105 (1907), 166.

[5] *Z. anal. Chem.*, 32 (1893), 415.

[6] Enough experiments were made to show that the bromate method gave the same results as the iodine titration method, and it was used because of its directness and greater speed.

TABLE I—EFFECT OF NITRATES AND NITRITES ON DETERMINATION OF ARSENIC BY DISTILLATION
(Arsenic pentoxide taken in each experiment 0.1303 g.)

REDUCING AGENTS					ARSENIC PENTOXIDE FOUND, GRAMS						PROPERTIES OF DISTILLATE	
Cuprous Chloride Grams	Additional Grams	Lead Nitrate Taken Grams	Calcium Nitrate Taken Grams	Sodium Nitrite Taken Grams	Titrated Immediately	Titrated after 4 Hrs.	Titrated after 1 Day	Titrated after 2 Days	Titrated after 3 Days	Titrated after (*) Days	Color	Bleaching Action on Methyl Orange at 90° C.
5	......	..	...	...	0.1303	....	....	0.1303	....	0.1303 (18)	None	None
5	......	0.05	...	...	0.1303	....	0.1279	0.1268	....	0.1258 (10)	Light yellow	Marked
5	......	0.25	...	...	0.1289	....	0.1146	0.1082	....	0.1051 (10)	Decided yellow	Marked
5	......	..	0.124	...	0.1301	0.1270	0.1200	0.1169	....	.....	Decided yellow	Marked
5	......	..	...	0.104	0.1257	....	0.1075	....	0.0950	0.0920 (5)	Decided yellow	Marked
15	......	0.25	...	...	0.1296	....	0.1220	0.1206	....	0.1186 (18)	Decided yellow	Marked
5	$FeSO_4$ 10	0.25	...	...	0.1276	....	0.1234	0.1215	....	0.1193 (18)	Decided yellow	Marked
5	$FeSO_4$ 10	..	0.124	...	0.1303	0.1291	0.1256	0.1235	....	.....	Decided yellow	Marked
5	NaBr 1	0.25	...	...	0.1277	....	0.1170	0.1120	....	0.1054 (18)	Decided yellow	Marked
5	NaBr 1	..	0.124	...	0.1303	0.1277	0.1195	0.1169	....	.....	Decided yellow	Marked
5	Aniline oil 1 (cc.)	0.25	...	...	0.1300	....	0.1262	....	....	.....	Decided yellow	Marked†
5	Aniline oil 5 (cc.)	0.25	...	...	0.1323	....	0.1297	....	....	.....	Decided yellow	Marked†
5	Aniline oil 5 (cc.)	..	...	0.104	0.1341	....	0.1329	....	....	.....	Decided yellow	Slight†
5	NH_4Cl 2	0.25	...	...	0.1292	....	....	0.1113	....	0.1043 (5)	Decided yellow	Marked
5	NH_4Cl 2+NaBr 1	0.25	...	...	0.1291	....	....	0.1103	....	0.1015 (5)	Decided yellow	Marked
5	Hydrazine sulfate 2	0.25	...	...	0.1303	....	0.1303	0.1303	....	0.1303 (18)	Light brown	None
5	Hydrazine sulfate 2	..	...	0.104	0.1303	....	0.1303	....	0.1303	0.1303 (5)	None	None
5	Hydrazine sulfate 2	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None
5	Hydrazine sulfate 1	0.25	...	...	0.1303	....	0.1300	....	0.1295	0.1291 (5)	None	Slight
5	Hydrazine sulfate 1	..	0.124	...	0.1303	0.1301	0.1298	0.1298	....	.....	None	Slight
5	Hydrazine sulfate 0.5+NaBr 1	0.25	...	...	0.1299	....	....	0.1277	0.1277	0.1266 (10)	None	Slight
5	Hydrazine sulfate 1 +NaBr 1	0.25	...	...	0.1303	....	....	0.1303	0.1303	0.1303 (10)	None	None
5	Hydrazine sulfate 1 +NaBr 1	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None
Hydrazine Sulfate												
4	......	0.25	...	...	0.1212	....	0.1212	0.1212	....	0.1212 (18)	Light brown	None
2	......	0.25	...	...	0.1009	....	0.1009	0.1009	....	0.1009 (18)	Dark brown	None
2	......	..	0.124	...	0.0908	0.0908	0.0908	0.0908	....	.....	None	None
3	NaBr 1	0.25	...	...	0.1303	....	0.1303	0.1303	....	0.1303 (18)	Light brown	None
2	NaBr 1	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None
1	NaBr 1	0.25	...	...	0.1303	....	....	0.1303	0.1303	0.1303 (18)	None	None
1	NaBr 1	..	0.124	...	0.1303	0.1303	0.1303	0.1303	....	.....	None	None

* The numbers in parentheses indicate the number of days having elapsed at the time of the last titration.
† Strong odor of aniline.

REDUCING AGENTS

Having demonstrated that nitrates and nitrites cause low results, the next step was to find a method of reduction whereby the arsenic could be accurately determined in the presence of these substances. Experiments were made with various reducing agents and combinations thereof, using in every case 25 cc. each of the standard arsenic solution and nitrate or nitrite solution. The use of a larger quantity of cuprous chloride was first tried, but even 15 g. of this material made practically no change in the results. Ferrous sulfate in combination with cuprous chloride gave distillates which were decidedly yellow, oxidized methyl orange very rapidly, and showed a more rapid decline in the arsenic value than when cuprous chloride was used alone. Rohmer[7] noticed that hydrobromic acid accelerated the reducing action of sulfur dioxide, and attributed to it a catalytic effect. This suggested the use of sodium bromide in combination with cuprous chloride. Distillations made in this way, however, showed only a slight improvement over those made with cuprous chloride alone.

Jannasch and Seidel[8] found that hydrobromic acid together with a salt of hydrazine gave excellent results in the reduction of arsenic. Since hydrazine is such a strong reducing agent it seemed likely that it might destroy the nitrates as well as reduce the arsenic. It was used at first alone and then in combination with cuprous chloride and with sodium bromide. The use of hydrazine sulfate alone eliminated the yellow color and prevented the gradual oxidation of the distillate, but the arsenic was not completely reduced in the time required to obtain 250 cc. of distillate (30 to 40 min.), even when as much as 4 g. of hydrazine sulfate were employed. (This is in accord with the results of Jannasch and Seidel, who found that several hours were required to secure complete reduction by hydrazine sulfate alone.) When the distillations were made with 5 g. of cuprous chloride and 1 g. of hydrazine sulfate the arsenic was completely reduced, but the oxidation of the distillate was not eliminated. When, however, the hydrazine sulfate was increased to 2 g. the oxidation of the distillate was completely prevented. Jannasch and Seidel found that the addition of a bromide to the hydrazine sulfate greatly hastened the reduction of the arsenic, and the writers have found that sodium bromide and hydrazine sulfate when added to the cuprous chloride also completely destroy nitrates. Later experiments showed that equally as good results were obtained without the use of cuprous chloride. One gram of hydrazine sulfate and 1 g. of sodium bromide proved sufficient where the quantity of arsenic pentoxide present did not exceed 0.75 g.

The investigation included some attempts to find a satisfactory substance to destroy the nitrates, which would be cheaper than the hydrazine sulfate. Ammonium chloride and aniline, owing to their known action on nitric acid and nitrites, respectively, were tried but proved to be of no value. The conditions to be fulfilled in this distillation are so circumscribed that the list of possible substances as reducing agents is limited.

RESULTS OF EXPERIMENTS

The results given in Table I show conclusively that, in the presence of nitrates (or nitrites), the distillation method for arsenic as ordinarily carried out, using cuprous chloride or cuprous chloride and ferrous sulfate as the reducing agents, gives low results. This is due to some volatile substance, possibly nitrosyl chloride, carried over in the distillate that oxidizes the arsenic trioxide. The extent of this oxidation depends largely upon the length of time the distillate stands before titration. Where a number of distillations are being carried on at the same time, it is impossible to titrate all of them immediately and the error caused by this oxidation may be a very material one. This error may be avoided by the use of hydrazine sulfate as the reducing agent, or preferably hydrazine sulfate and sodium bromide, in which case the reduction takes place much more rapidly. The nitrates and nitrites are probably reduced to nitrogen by the hydrazine sulfate.

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[7] *Ber.*, **34** (1901), 33.

[8] *Ibid.*, **43** (1910), 1218; *J. prakt. Chem.*, **91** (1915), 133.

TABLE II—COMPARISON OF OFFICIAL AND HYDRAZINE DISTILLATION METHODS

			ARSENIC OXIDE FOUND, GRAMS					PROPERTIES OF DISTILLATES	
No.	Material Analyzed	Method of Distillation	Titrated Immediately	Titrated after 4 Hrs.	Titrated after 1 Day	Titrated after 2 Days	Titrated after 9 Days	Color	Bleaching Action on Methyl Orange at 90° C.
15794	Calcium arsenate	Official	0.1248	....	0.1241	0.1239	0.1231	None	Marked
		Hydrazine	0.1251	....	0.1251	0.1251	0.1251	None	None
15515	Calcium arsenate	Official	0.1242	....	0.1237	0.1234	0.1231	None	Marked
		Hydrazine	0.1246	....	0.1246	0.1246	0.1246	None	None
15468[1]	Calcium arsenate	Official	0.1287	....	0.1287	0.1287	0.1287	None	None
		Hydrazine	0.1293	....	0.1293	0.1293	0.1293	None	None
15792[1]	Calcium arsenate	Official	0.1219	....	0.1219	0.1219	0.1219	None	None
		Hydrazine	0.1222	....	0.1222	0.1222	0.1222	None	None
T 1127	Calcium arsenate	Official	0.1281	0.1270	0.1256	0.1250	0.1237	Yellow	Marked
		Hydrazine	0.1281	....	0.1281	0.1281	0.1281	None	None
T 1128	Calcium arsenate	Official	0.1241	0.1231	0.1210	0.1193	0.1172	Yellow	Marked
		Hydrazine	0.1241	....	0.1241	0.1241	0.1241	None	None
T 1776	Calcium arsenate	Official	0.1099	0.1089	0.1067	0.1053	0.1048	Yellow	Marked
		Hydrazine	0.1101	....	0.1101	0.1101	0.1101	None	None
16333	Lead arsenate	Official	0.1188	0.1185	0.1179	0.1175	....	Very light yellow	Slight
		Hydrazine	0.1188	0.1188	0.1188	0.1188	....	None	None

[1] Contained only a trace of nitrates by phenolsulfonic acid test.

MODIFIED METHOD[9]

REAGENTS. *Starch Indicator*—Mix about 0.5 g. of finely powdered potato starch with cold water to a thin paste; pour into about 100 cc. of boiling water, stirring constantly, and discontinue heating immediately after the paste is added.

Standard Arsenic Trioxide Solution—Dissolve 2 g. of pure arsenic trioxide in a beaker by boiling with about 150 to 200 cc. of water containing 10 cc. of concentrated sulfuric acid, cool, transfer to a 500-cc. graduated flask, and dilute to the mark.

Standard Iodine Solution—Prepare an approximately 0.05 *N* solution as follows: Mix intimately 6.35 g. of pure iodine with twice its weight of pure potassium iodide. Dissolve in a small amount of water, filter, and dilute the filtrate to 1 liter in a graduated flask. Standardize as follows: Pipet 50 cc. of the arsenic trioxide solution into an Erlenmeyer flask, dilute to about 200 cc., neutralize with sodium bicarbonate, add 4 to 5 g. in excess and add the standard iodine solution from a buret, shaking the flask continuously, until the yellow color disappears slowly from the solution, then add 5 cc. of the starch indicator and continue adding the iodine solution drop by drop until the permanent blue color is obtained. Calculate the value of the standard iodine solution in terms of arsenic trioxide and arsenic pentoxide.

Standard Bromate Solution—Dissolve 1.688 g. of pure potassium bromate in water and dilute to 1 liter. Standardize as follows: Pipet 25 cc. of the arsenic trioxide solution into an Erlenmeyer flask, add 15 cc. of concentrated hydrochloric acid, dilute to 100 cc., heat to 90° C., and titrate with the bromate solution, using methyl orange as indicator. The indicator should not be added until near the end of the titration, and the flask should be rotated continuously in order to avoid any local excess of the bromate solution. The end-point is shown by a change from red to colorless, and the bromate should be added very cautiously when approaching the end of the titration.

Hydrazine Sulfate and Sodium Bromide Solution—Dissolve 20 g. of hydrazine sulfate and 20 g. of sodium bromide in 1 liter of dilute (1:4) hydrochloric acid.

DETERMINATION—Weigh accurately an amount of the sample containing the equivalent of not more than 0.6 g. of arsenic pentoxide and transfer to a distilling flask. Add 50 cc. of the solution of hydrazine sulfate and sodium bromide and close the flask with a stopper through which passes the stem of a dropping funnel. Connect to a well-cooled condenser, the delivery end of which is attached to the system of flasks described by Roark and McDonnell,[3] omitting the third flask. Boil for 2 or 3 min., then add 100 cc. of concentrated hydrochloric acid by means of the dropping funnel and distil until the volume in the distilling flask is reduced to about 40 cc.; add an additional 50 cc. of concentrated hydrochloric acid and continue the distillation until the contents of the flask are again reduced to about 40 cc. Wash down the condenser, transfer the contents of the receiving flasks to a 1-liter graduated flask, make to volume, and mix thoroughly. Pipet a 200-cc. aliquot to a 500-cc. Erlenmeyer flask, nearly neutralize with sodium hydroxide, finish the neutralization with sodium bicarbonate, add 4 to 5 g. in excess and titrate with standard iodine solution, using starch solution as indicator; or to the 200-cc. aliquot add 10 cc. of concentrated hydrochloric acid and titrate with standard bromate solution, as previously described in this paper.

With a sample equivalent to 0.6 g. of arsenic pentoxide, practically all of the arsenic is distilled over in the first 50 cc. of the distillate, which is a much more rapid volatilization than that which occurs in the official distillation method. A total distillate of 150 cc. is sufficient to insure complete distillation of the arsenic. The method has been applied to the analysis of commercial samples of calcium arsenate, lead arsenate, and other arsenical insecticides containing nitrates, with most satisfactory results in all cases. Table II shows the results obtained by the "official" and by the modified method on commercial samples of lead and calcium arsenates containing nitrates. In the case of the calcium arsenates 1.5 g. of sample were taken for the determination and 2 g. in the case of lead arsenates. The titrations were made on aliquot portions representing 0.3 and 0.4 g. of sample, respectively.

The figures in Table II show that while there is fairly close agreement between the results by the two methods when the titrations are made immediately after distillation, in some instances the official method gives lower results, and when the titration is delayed for several hours the results by the official method are lower in every case. The maximum difference after 9 days amounts to more than 5 per cent of the arsenic present.

Turpentine and Rosin Statistics

The production of naval stores this season (1921–22) up to August 1, according to reports received from producers by the Bureau of Chemistry, United States Department of Agriculture, was approximately 227,000 casks of gum turpentine and 691,000 round barrels of gum rosin. Estimates on production for the balance of the season indicate a probable total production for the entire season of about 427,000 casks of gum turpentine and 1,320,000 round barrels of gum rosin.

Stocks held by producers at the stills on August 1, 1921, show an increase over similar stocks on April 1, 1921, of about 50 per cent. Stocks held by consumers on August 1, 1921, were practically the same as they were on April 1.

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[9] In working out the details of this method it was assumed that commercial calcium or lead arsenates would never contain nitrates in excess of 5 per cent N_2O_5. In the case of mixtures containing more than this amount, the method may require some modification.

Leavens: Their Action and Measurement[1,2]

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LEAVENING is the process of forming in a dough bubbles of gas which escape in baking and leave a light and porous texture in the baked product. A leavening action takes place when a carbonate or bicarbonate is acted upon by an acid or acid salt. The simplest form of leavening is by the aid of steam. A fairly good result is obtained by baking a mixture of flour and water, where the texture is produced by the escaping steam. The most familiar type of product leavened in this way is army bread or pilot bread.

Soda (sodium bicarbonate) through the agency of heat is a simple form of leavening agent and may be used alone in quantities which will not leave the bad aftertaste due to excess soda. This amount is about 1.5 lbs. sodium bicarbonate per barrel of flour. Ammonium bicarbonate (NH_4HCO_3) and the so-called ammonium carbonate, a mixture of the bicarbonate and the carbamate (NH_4HCO_3 and $NH_4CO_2NH_2$), decompose with heat, liberating ammonia gas and carbon dioxide and thus giving a double leavening value. More complex mixtures are represented by sodium bicarbonate with primary phosphates of sodium or calcium, phosphoric acid, tartaric acid, cream of tartar, sodium aluminium sulfate, etc.

Great confusion prevails as to the chemical reactions which occur when such chemicals are mixed. Hart[4] gives the following reactions:

$$\underset{702}{3\ CaH_4(PO_4)_2} + \underset{672}{8\ NaHCO_3} = \underset{352}{8\ CO_2} + \underset{144}{8\ H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\ Na_2HPO_4}$$

$$\underset{188}{KHC_4H_4O_6} + \underset{84}{NaHCO_3} = \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{210}{KNaC_4H_4O_6}$$

Leach[5] gives the following reactions:

$$\underset{234}{CaH_4(PO_4)_2} + \underset{168}{2\ NaHCO_3} = \underset{88}{2\ CO_2} + \underset{36}{2\ H_2O} + \underset{136}{CaHPO_4} + \underset{142}{Na_2HPO_4}$$

$$\underset{188}{KHC_4H_4O_6} + \underset{84}{NaHCO_3} = \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{210}{KNaC_4H_4O_6}$$

$$\underset{150}{H_2C_4H_4O_6} + \underset{168}{2\ NaHCO_3} = \underset{88}{2\ CO_2} + \underset{230}{Na_2C_4H_4O_6.2\ H_2O}$$

Patten[6] gives the following reactions:

$$\underset{702}{3\ CaH_4(PO_4)_2} + \underset{336}{4\ NaHCO_3} = \underset{176}{4\ CO_2} + \underset{72}{4\ H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{480}{4\ NaH_2PO_4}$$

$$\underset{702}{3\ CaH_4(PO_4)_2} + \underset{672}{8\ NaHCO_3} = \underset{352}{8\ CO_2} + \underset{144}{8\ H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\ Na_2HPO_4}$$

In order to determine the weight ratios of sodium bicarbonate and the different acids and acid salts, the chemical reactions must be definitely known. In the case of tartaric acid and cream of tartar the reactions needed to be checked for the purposes of the present investigation. In the case of phosphoric acid and primary calcium phosphate some question existed as to the ultimate end of the reactions. The purpose of the writers was to determine the weight of sodium bicarbonate or carbonate which would react with a given weight of phosphoric acid or primary calcium phosphate.

EXPERIMENTAL

TITRATION—Direct determinations of acidity by titration with standard sodium hydroxide gave the following results, in percentages of the acids involved:

	Per cent
Tartaric acid (Phenolphthalein)	99.6
Cream of tartar (Phenolphthalein)	100.4
Phosphoric acid (Methyl orange)	50.0

It was found impossible to analyze primary calcium phosphate by titration.

ELECTROMETRIC TITRATION—The acid reacting substances were titrated electrometrically with standard sodium hydroxide in order to discover any possible irregularities with the different acids. The method and apparatus used were those described by Beans and Oakes.[7] The apparatus was standardized by titration of 0.1 *M* hydrochloric acid with 0.1 *M* sodium hydroxide. (See Fig. 1.) Measurements were made with the same alkali against tartaric acid, cream of tartar, phosphoric acid (commercial), and primary calcium phosphate with the results indicated in Figs. 2, 3, 4, and 5. The curves represent simple electrometric measurements of hydrogen ion designed for comparison with the acidity shown by indicator titration. The abrupt changes in the curves correspond to the sudden changes shown by indicators and represent the end-points of the displacement of a first or second hydrogen. The middle points of the upward breaks represent these values:

	Per cent
Tartaric acid	99.8
Cream of tartar	99.4
Phosphoric acid	52.7
Primary calcium phosphate	86.8

CO_2 EVOLVED—In order to determine directly the weight ratios existing between the carbonate and the acid or acid salt, the weight of carbon dioxide given off by the reactions was measured by means of an absorption train. The reacting materials were weighed into an Erlenmeyer flask, CO_2-free water was added, and the reaction carried to the end by the aid of heat. Sodium carbonate was used because sodium bicarbonate breaks down with heat.

Table I shows the results obtained by actual carbon dioxide measurements.

TABLE I

Acid	Grams	Na_2CO_3 Grams	Measured CO_2 Grams	Theoretical CO_2 Grams
Tartaric	0.5000	0.3516	0.1441	0.1460
Cream of tartar	1.2370	0.3500	0.1440	0.1454
Phosphoric	1.3878	1.000	0.3225	0.3284

Tartaric acid and cream of tartar were mixed with sodium carbonate in stoichiometric proportions. In the case of phosphoric acid, the carbonate was added in excess. These results show the reactions in the cases of tartaric acid and cream of tartar to have been direct neutralization of all the hydrogen ion of the acids. (See equations in introduction.) In the case of phosphoric acid, two-thirds of the hydrogen ion were neutralized and there action came to an end with the formation of Na_2HPO_4, disodium phosphate:

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 3 from the Research Laboratory of the National Biscuit Co.

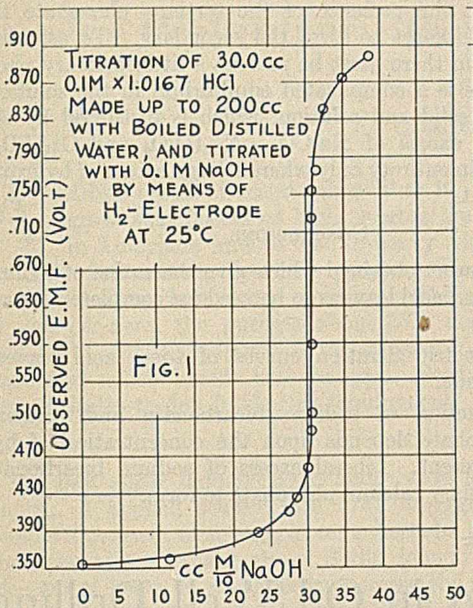
[3] Consulting Chemical Engineer, National Biscuit Co.

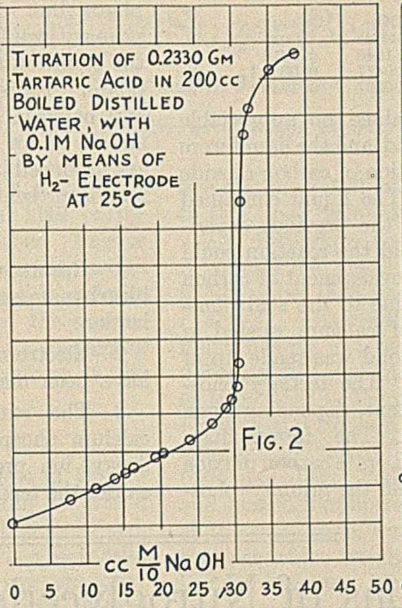
[4] "Leavening Agents," 52.

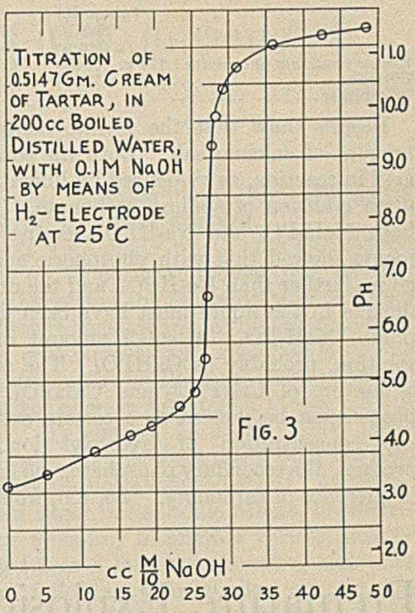
[5] "Food Inspection and Analysis," 4th edition, 349.

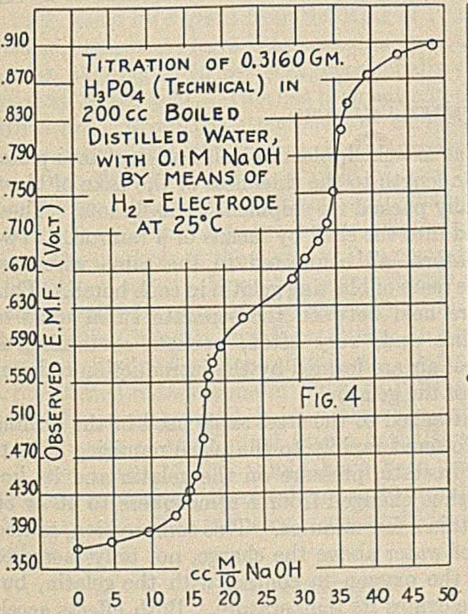
[6] *J. Assoc. Official Agr. Chem.*, **2** (1917), 227.

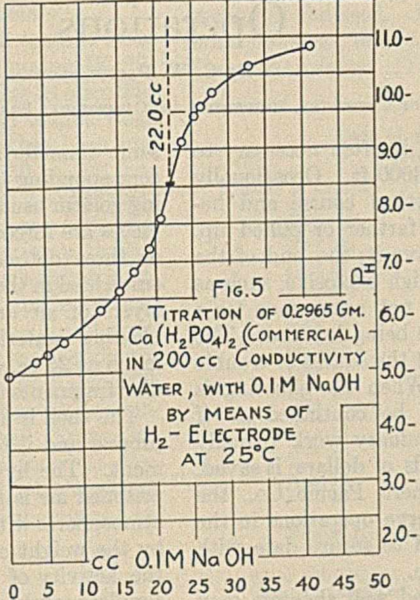
[7] *J. Am. Chem. Soc.*, **42** (1920), 2116.











$$\underset{98}{H_3PO_4} + \underset{106}{Na_2CO_3} \rightleftarrows \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{142}{Na_2HPO_4}$$

Converted to bicarbonate, this equation becomes

$$\underset{98}{H_3PO_4} + \underset{168}{2\ NaHCO_3} \rightleftarrows \underset{88}{2\ CO_2} + \underset{36}{2\ H_2O} + \underset{142}{Na_2HPO_4}$$

When primary calcium phosphate reacts with sodium carbonate, different results are obtained, depending on the ratio of acid to base and on the time of the reaction as indicated in Table II.

Table II

Primary Calcium Phosphate Grams	Na_2CO_3 Grams	CO_2 Produced Grams	Time Hrs.	Theoretical CO_2 Grams
1.000	0.4716	0.1755	1.0	0.1957
1.000	0.4716	0.1920	1.5	0.1957
1.000	1.000	0.2076	1.0	0.2170
1.000	1.000	0.2170	2.5	0.2170

In the first two experiments of Table II the theoretical carbon dioxide was calculated from the amount of sodium carbonate used, and an excess of acid phosphate was present. In the last two the theoretical carbon dioxide was calculated from the acid phosphate used, and sodium carbonate was in excess. This last experiment gave carbon dioxide corresponding to the reaction which has $Ca_3(PO_4)_2$, neutral calcium phosphate, and Na_2HPO_4, disodium phosphate, as its end-products, and did not stop with the formation of $CaHPO_4$, secondary calcium phosphate.

$$\underset{702}{3\ Ca(H_2PO_4)_2} + \underset{424}{4\ Na_2CO_3} \rightleftarrows \underset{176}{4\ CO_2}$$
$$+ \underset{72}{4\ H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{4\ Na_2HPO_4}$$

Converted to bicarbonate, the equation reads

$$\underset{702}{3\ Ca(H_2PO_4)_2} + \underset{672}{8\ NaHCO_3} \rightleftarrows \underset{352}{8CO_2}$$
$$+ \underset{144}{8H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{568}{Na_2HPO_4}.$$

In order to determine whether $Ca_3(PO_4)_2$ or $CaHPO_4$ is formed in a solution which is not strongly alkaline, sodium carbonate and primary calcium phosphate were used in proportions to give the reaction

$$\underset{234}{Ca(H_2PO_4)_2} + \underset{106}{Na_2CO_3} \rightleftarrows \underset{44}{CO_2} + \underset{18}{H_2O} + \underset{136}{CaHPO_4} + \underset{142}{Na_2HPO_4}$$

or, converted to bicarbonate,

$$\underset{234}{Ca(H_2PO_4)_2} + \underset{168}{2\ NaHCO_3} \rightleftarrows \underset{88}{2\ CO_2} + \underset{36}{2\ H_2O} + \underset{136}{CaHPO_4} + \underset{142}{Na_2HPO_4}$$

and the carbon dioxide was collected and weighed. The material remaining in the reaction flask was filtered and separate determinations with additional sodium carbonate were conducted on filtrate and precipitate. If carbon dioxide were developed by the action of the solid residue, it would prove that material to be not $Ca_3(PO_4)_2$ but $CaHPO_4$. The results are given in Table III.

TABLE III

	Na_2CO_3 Grams	CO_2 Grams	Calcium Grams	
Primary calcium phosphate 1.171 g.	0.460	0.1845	0.1810	
Filtrate	1.000	0.0477	0.0059	0.1799
Precipitate	1.000	0.0367	0.1740	

Results show that the filtrate contained no appreciable amount of calcium salt. Both the solid and the liquid were acid in reaction, as evidenced by liberation of carbon dioxide upon addition of sodium carbonate. The liquid contained both NaH_2PO_4 and Na_2HPO_4 because the previous experiments showed that with phosphoric acid the reaction could go no farther than Na_2HPO_4, and the development of carbon dioxide in the liquid must have been due to the acid phosphate, NaH_2PO_4. A small amount of calcium existed in solution, probably as $CaHPO_4$. The solid was made up of a mixture of $Ca_3(PO_4)_2$ and $CaHPO_4$. The tertiary phosphate must be present to a certain extent, depending upon the concentration of hydroxyl ion. The intermediate product, the secondary phosphate, will liberate carbon dioxide in presence of carbonate. So, too, would the primary phosphate, but in the presence of the tertiary phosphate the primary would react to form the secondary. To establish the equilibrium there must be present a little primary phosphate. There is a complicated equilibrium in the solution, and between solid and solution, which is disturbed by the action of an excess of Na_2CO_3. Na_2HPO_4 and $Ca_3(PO_4)_2$ are produced in entirety only where a large excess of hydroxyl ions is present.

CONCLUSIONS

1—Results were obtained which give the ratios of sodium bicarbonate and acid leavens to be used for complete neutralization.

2—Electrometric titration curves of some acid leavens have been made.

3—The reaction of sodium bicarbonate and primary calcium phosphate depends upon the concentration of hydroxyl ion present. Liberal excess of sodium bicarbonate causes the tertiary calcium phosphate to form.

Premature Explosions of Nitroglycerin in Oil Well Drilling Operations[1]

By C. W. Porter

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

IN the development of oil wells it is often necessary to drive pipes to depths exceeding 3000 ft. Occasionally a pipe is deflected from its vertical course and becomes "stuck." It cannot be driven farther or pulled up. Only one remedy can be applied to save it; the end of the pipe may be shot off by means of a high explosive, such as dynamite or blasting gelatin. It is not uncommon for a charge to explode spontaneously while being lowered. The pipe is then shattered at a point above the source of trouble and the well has to be abandoned. When the shooting is successful, drilling and driving may be continued as if nothing had happened, and the preliminary work (usually representing a value of many thousands of dollars) is saved.

Through the courtesy of the Southern Pacific Co., the writer has had an opportunity to observe operations in the Bakersfield and Coalinga oil fields and to secure data with reference to corrective work elsewhere.

Observations of the most experienced well shooters may be summarized as follows:

1—Premature explosions have not been known to occur in dry wells.

2—In wells filled with water, premature explosions seldom occur at depths of less than 1200 ft.

3—Most premature explosions occur at depths varying between 1600 and 2000 ft.

4—In a few instances detonators have been found intact after the explosions.

5—Explosions have occurred while the charges were in motion, *i. e.*, while being lowered. Others have happened while the charges were at rest, *i. e.*, during the intervals when the machinery was stopped to allow time for lashing to the sand line the insulated wire connected with the detonator.

6—Premature explosions seldom occur when the blasting charges are composed of wrapped sticks of dynamite.

From 4 and 5 it seems evident that the cause of trouble cannot be referred to electrical currents or to friction. It has occurred to the writer that the trouble may be due to the oxidizing effect of air mechanically held within the mass of blasting gelatin.

The shell ordinarily used is a tinned or galvanized sheet iron tube 4 to 6 in. in diameter and 6 to 18 ft. long, closed at the lower end only. By means of a short steel cylinder of the same diameter as the shell, blasting gelatin is cut into pieces corresponding in length to the thickness of the cake of blasting gelatin usually packed for shipment in 50-lb. lots. These pieces are forced into the shell by means of a ramrod. Two or three detonators—all connected to the same wire—are embedded in the mass of blasting gelatin in each bomb. Thin layers of air are held between the separate small units of blasting materials and, very often, pockets containing as much as 25 cc. of air are formed by the introduction of irregular fragments of the gelatin.

The shell is attached to the steel cable used in the drilling process and is lowered rapidly to the place requiring adjustment. The hydrostatic pressure on the gelatin and its imprisoned air is thus changed from 1 atmosphere to 40 or 50 atmospheres within a few minutes. This compression, caused by the weight of water above the charge, not only increases the activity of the oxygen in contact with the gelatin, but simultaneously elevates its temperature. Both effects accelerate the oxidation of nitroglycerin and the oxidation of other components of the mixture. Locally, *i. e.*, in the vicinity of an air bubble, the oxidation may go on rapidly enough to produce the temperature required for detonation.

EXPERIMENTAL EVIDENCE

Some experimental evidence in support of this view has been secured. If the accidents are due to this cause, pure oxygen should be much more active than air and pure nitrogen should be entirely harmless. Ten small glass tubes (1 in. in diameter and 10 in. long) were filled with blasting gelatin in which bubbles of oxygen gas were trapped. Ten other tubes were filled in an atmosphere of nitrogen. The tubes were lowered in an abandoned well 2200 ft. deep, which was filled with water having a temperature of 70° at the 1500-ft. level. Two of the tubes containing oxygen exploded spontaneously—one under 1400 and the other under 1800 ft. of water. The other eight reached the bottom and were brought back to the surface intact. None of the tubes containing nitrogen exploded spontaneously.

The writer believes that many accidents could be averted by replacing the air in shells by an inert gas before introducing nitroglycerin products.

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[1] Received September 19, 1921.

Preliminary Report on Sugar Beets in Louisiana[1]

By C. E. Coates[2] and A. F. Kidder[3]

Louisiana State University, Baton Rouge, Louisiana

A LONG series of results show that it is possible to grow sugar beets of high sucrose and high purity in Louisiana and to obtain heavy yields. This is probably true for the South in general. The best results are obtained by late spring planting. The yields average 18 tons per acre, the purities about 85.0, and the sucrose 14.0. The essential feature is the necessity for obtaining good seed which breeds true to type. Seed grown in the United States to-day fulfils this requirement.

. . . .

The beet sugar industry is in many ways one of the romances of applied science. In 1747 Marggraff of Berlin found 6.2 per cent of sucrose in some beets he had examined. Forty years later Achard, also of Berlin, found that by careful selection of beets he was able to increase the average sugar content considerably, and he established a small factory in 1801, aided by a grant from the King of Prussia.

Since then, beets have been raised in sucrose content from 6 to an average of 15 per cent, occasionally running 18, 20, and even 30 per cent. This has been entirely due to scientific agriculture. From the standpoint of chemical engineering, on the other hand, the manufacturing process has been improved so that now there is a yield of from 250 to 300 lbs. of sugar per ton, together with several valuable by-products. This sugar is chemically pure, without flavor of any sort, and enters the markets of the world in free competition with any other type of sugar. Here then is an industry which has been made possible by scientific agriculture and by applied chemistry working hand in hand, producing an agricultural crop worth hundreds of millions of dollars. There were produced in the United States alone in the year 1919 to 1920, 726,000 tons of beet sugar, which is more than the entire production of cane sugar of the United States with Hawaii thrown in. Not one pound of this would have been produced to-day under the conditions, chemical and agricultural, which existed a century ago. The industry is a magnificient monument to applied science.

SEED SELECTION

All this is well known, but it is necessary to repeat well-known facts in order that one may not lose sight of their significance. In this case, first of all, the sugar content of beets was steadily increased by careful seed selection. The growing of sugar beets for seed is, in reality, a fine art and must be done under the most careful scientific control, but the details of the technic have been mastered and for the last three or four years good beet seed grown in America has been obtainable.

One of the writers (Coates) gave this matter considerable study about twenty-five years ago and in 1899 carried out a series of experiments at the Louisiana State University. It was evident that if beets could be matured in the spring they could be worked into sugar in Louisiana sugarhouses and thus extend the sugar season three months or more. One of the weak points in the Louisiana sugar industry is the fact that the expensive sugarhouses can run only about two months out of twelve. If three months could be added to this, their value would be almost doubled.

The first experiments were made by Coates and Glenk. A commercial variety of Vilmorin Improved was planted in November 1898, and harvested the following May and June (Table I). The results were encouraging, as many beets were found having 14.5 per cent sucrose and a purity of 90. The difficulty was that other beets from the same row had grown so large that in them the sucrose had fallen to less than 9 per cent and the purity to about 70. A careful study of the situation convinced Coates that the beet seeds were not uniform in quality. Some of the beets weighed about 1.5 to 2 lbs. and looked like normal sugar beets, while others, harvested at the same time, were obviously of another variety, mostly mangels which weighed 6 or 8 lbs., or even more, and were low in sucrose. The following year similar experiments were run, from which similar inferences were drawn as to the quality of the seed. In November 1904, Coates made two more plantings, one of Vilmorin Improved, and the other of Klein Wanzleben (Table II). The seed labeled Klein Wanzleben gave beets which were abnormally large and which were low in sucrose. The seed labeled Vilmorin did much better, but this too gave results which were disappointing. It was just possible that these seeds were intentionally mislabeled, as the beet sugar industry in the United States was threatening to be an important factor in the sugar world.

TABLE I

Date of planting, November 10, 1898

Date of Analysis	Average Weight of Beet Grams	Sucrose Per cent	Purity
May 2	600	9.89	73.00
May 3	870	8.13	74.30
May 15	1200	10.76	80.70
May 16	1980	8.59	74.10
May 31	1140	11.54	83.60
May 31	1500	9.49	76.50
June 6	960	12.61	91.30
June 6	930	14.96	90.60
June 10	600	12.64	89.70
May 10	1500	13.64	85.70
June 10	1080	11.99	91.50
June 10	1440	9.24	75.70
June 12	900	12.94	92.40
June 12	630	13.74	84.20
June 12	720	14.04	87.70
June 12	660	11.04	72.10
June 12	4560	8.14	70.70
June 12	2100	8.39	66.30
June 13	480	14.50	90.60

TABLE II—AVERAGE POLARIZATION OF JUICE

	April	May	June	August
Klein Wanzleben.......	5.7	4.8	5.5	3.3
Vilmorin Improved......	9.2	6.8	7.6	7.3

Two years later more plantings were made of Vilmorin and Klein Wanzleben, some November 26, 1907, some January 30, 1908, and a separate lot in August 1908 (Table III). The August seed gave fairly uniform results, high sucrose and

TABLE III—AVERAGE POLARIZATION OF JUICE

Date of planting, November 26, 1910

	April	May
Vilmorin Improved.........	8.50	11.0
Klein Wanzleben...........	7.63	9.6

Date of planting, January 30, 1908

	April	May
Vilmorin Improved.........	6.6	8.9
Klein Wanzleben...........	6.13	7.9

Date of planting, August 31, 1907

	February	April
Vilmorin Improved.........	14.76	10.9
Klein Wanzleben...........	12.88	9.7

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Dean, Audubon Sugar School.

[3] Agronomist and Assistant Director, Louisiana State Experiment Station, Baton Rouge, La.

TABLE IV

Row	Variety	Source of Seed	Seed Grown at	Calc. Tons per Acre	Averages of Weekly Analyses, May 8–July 29					
					May		June		July	
					Sucrose	Purity	Sucrose	Purity	Sucrose	Purity
1	Klein Wanzleben	B. P. I.[1]	Blissfield, Mich.	20.66	13.4	85.0	13.7	86.5	12.50	83.03
2	Alvarado	B. P. I.	Blissfield, Mich.	25.54	14.15	85.98	13.63	83.44	12.06	80.52
3	Klein Wanzleben Elite	B. P. I.	Klein Wanzleben, Germany	20.90	13.4	83.88	14.13	83.21	12.18	81.88
4	Dippe	B. P. I.	Blissfield, Mich.	18.28	14.05	86.15	13.63	83.66	12.40	81.51
5	Jaensch Victrix, 12844	U. E. S.[2]	Logan, Utah	18.52	13.34	84.68	12.80	81.90	10.78	79.29
6	Unnamed	G. W. S.[3]	.....	21.16	14.5	85.65	13.92	80.88	11.92	80.41
7	Unnamed	G. W. S.	.....	17.42	15.16	86.5	14.18	84.74	12.74	81.99
8	Klein Wanzleben	B. P. I.	Blissfield, Mich.	18.72	14.73	85.78	13.62	84.68	13.08	83.66
9	Alvarado	B. P. I.	Blissfield, Mich.	17.22	14.42	86.54	13.41	84.21	11.86	76.29
10	Alvarado	B. P. I.	Blissfield, Mich.	16.70	14.08	85.72	15.16	84.79	12.08	78.75
11	Dippe	B. P. I.	Blissfield, Mich.	16.12	14.52	85.15	14.75	84.67	13.62	84.35
12	Jaensch Victrix, 12844	U. E. S.	Logan, Utah	16.50	13.7	86.59	13.56	83.69	11.96	81.63
13	Unnamed	G. W. S.	.....	19.65	14.49	82.83	14.97	81.66	13.82	83.76
14	Unnamed	G. W. S.	.....	18.65	14.54	84.38	13.50	82.90	12.56	82.33

[1] Dr. Townsend, Bureau of Plant Industry.
[2] Dr. Harris, Utah Expt. Station.
[3] Great Western Sugar Co., Denver, Col.

purity, and normal sized beets in February, but were obviously harvested too late, as is seen in the April figures.

Here again, the beets were so irregular in quality that Coates became convinced it was very difficult to get pure beet seed, and the experiments were discontinued until this important point could be settled.

Most of the previous plantings had been fall planting, which is the custom in Louisiana, and for this reason there was not as much sunshine on the plant when it was approaching maturity as might have been desirable. In fact, beets planted in January contained practically as much sugar in May as did those planted in November. Several sporadic attempts were made in the next ten years, but these developed nothing new, though individual beets were found which gave 20 per cent of sucrose and over.

In 1920, C. E. Coates and A. F. Kidder repeated these experiments, using in this instance late spring planting rather than fall planting. The seed obtained by Kidder was certified to as being pure and true to type. The chemical work was done by Coates and his assistants, the agricultural work by Kidder and his assistants. The results were so exceedingly good that it is thought well to present them in a preliminary form. It must be distinctly understood that this is merely a report of progress. It is the intention of the authors to carry out these experiments over a term of years with annual progress reports.

AGRICULTURAL DATA

The certified seed were furnished by the laboratories listed in Table IV. A fairly uniform plot 42 ft. × 105 ft. was selected for this purpose. The plot was flat broken early in the winter and replowed, disked, and harrowed the 24th of January. Rows were laid off 3 ft. apart with a small middle burster and the seed planted the day the soil was replowed.

The seed came up to an excellent stand and the plants were given the first hoeing on the 25th of February. Other agricultural operations are recorded in Table V.

TABLE V

DATE	Kind of Operation or Work	Cost per Acre
....	Plowing, broadcast	$3.00
January 24	Plowing, disking, harrowing, bedding, planting	4.50
February 25	First hoeing	.40
March 7	Second hoeing and first thinning	2.40
March 17	Cultivated, one horse	.20
March 24	Hoeing and second thinning	2.40
April 4	Cultivated, one horse	.20
May 17	Cultivated, one horse	.20
June 28	Hoeing	1.25
	TOTAL	14.55

This cost does not include harvesting and is not exactly what one would find on a commercial scale, but making all allowances it should not be less than $15 or more than $20 per acre. While it was difficult to calculate yields on the small plots employed, they ran from 16 to 25 tons per acre. There should be no difficulty in reaching the former figures on a commercial scale. The low cost of cultivation is due to the fact that during this particular growing season there is very little trouble from weeds in Louisiana.

Table IV shows the variety, the source of seed, estimated yield, and analytical composition for the three months indicated. Weight of beets, 1.5 to 2.5 lbs.

SUMMARY

1—Sugar beets can be grown successfully in Louisiana, and presumably in the South in general. They can be matured during May, June, and July, and probably during March and April as well.

2—The quality of the beet seed is the vital point. Standard beet seed of high quality is now grown in the United States and would seem to be somewhat better than the best European seed.

3—The tonnage per acre in Louisiana is probably heavier than the average elsewhere, and the sucrose and purity are high enough for commercial purposes. The cost of cultivation is much less than in most beet growing sections.

4—A series of analyses not indicated in these tables shows that the beets after harvesting will keep a week or more without appreciable loss in sucrose or purity. These results are probably too favorable, but it is reasonably sure that after harvesting, beets in Louisiana will not deteriorate more during May, June, and July than will cane in Cuba during the same months.

5—Beets planted on January 24 are ready for harvest by May 8 and probably earlier, and may be harvested in good condition until July 27 and probably later.

American Welding Society Proceedings

The American Welding Society recently issued its first number of proceedings. Beginning with January 1, 1922, the Society plans to issue *Proceedings* monthly in convenient form. In addition to technical papers, the *Proceedings* will include news items and reports of the Society, local sections, the American Bureau of Welding, and the industry. Certain sections will be devoted to editorials, employment service, bibliography of current welding literature, names of new members, etc.

Chandler Medal Award

The lecturer on the Charles Frederick Chandler Foundation this year will be Dr. Edgar Fahs Smith, president of the American Chemical Society. Dr. Smith's subject will be "Samuel Latham Mitchill—A Father in American Chemistry." Samuel Latham Mitchill was the first professor of chemistry at Columbia College and first senator from the state of New York.

The lecture, which is open to the public, will be given on March 2, 1922, at Havemeyer Hall, Columbia University, New York, N. Y.

Effect of Paraffin Wax on the Properties of Mineral Oils[1]

By A. P. Bjerregaard[2]

RESEARCH LABORATORY, EMPIRE REFINERIES, INC., OKMULGEE, OKLAHOMA

PARAFFIN wax decreases the viscosity of the more viscous mineral lubricating oils, raises the freezing point, and lowers the specific gravity. The amount of wax present may be quickly determined, with all necessary accuracy, by observing the freezing point and referring to Graph II*a* of the present paper, where the percentage of paraffin wax is plotted against temperature.

Since paraffin wax occurs naturally as a component of many native crude petroleum oils, and therefore also in many intermediate and finished petroleum products, it is of importance to know what influence it exerts on the properties of the various other components of the petroleum, especially those with which it is naturally associated. These are the various viscous and so-called "nonviscous" lubricating oils.

The present study was made from the synthetic viewpoint. Known quantities of components of known properties were mixed, and the viscosity, freezing point, and specific gravity of the mixtures were determined.

MATERIALS USED

PARAFFIN WAX—Three samples of paraffin wax were used: (1) prepared from Pennsylvania crude oil (nonasphaltic); (2) prepared from mid-continent crude oils, namely, a mixture of Illinois and Healdton crudes (semi-asphaltic); and (3) prepared from a central Oklahoma crude oil (semi-asphaltic).

The first two samples were prepared in the laboratory from "slack wax," which is the raw wax left in the filter presses of the refinery when the wax-containing fractions of the petroleum are filtered at a low temperature, usually about 15° to 20° F. This wax was pressed between blotting papers under a great weight, at a temperature of 80° to 85° F. until no more oil could be extracted. The blotting paper was changed from time to time as necessary. The resulting wax was melted at the lowest possible temperature, and an equal volume of petroleum spirit (usually called turpentine substitute) was added. After slow cooling, the excess of petroleum spirits was poured off, and the paraffin wax pressed as before. Next, the wax was exposed to the air for a short time, until all the remaining spirits had evaporated. The resulting wax was in each case free from oil, and it was not otherwise refined. By the "American method" the melting point of the Pennsylvania wax was 131° F.; that of the mid-continent wax was 130.5° F.

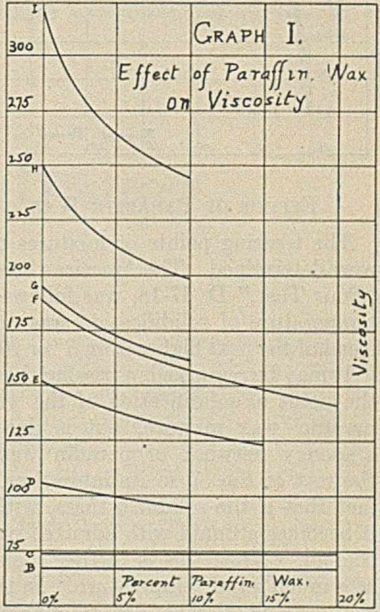
The third sample was a refined commercial wax of 122° F. melting point ("American method"). It was prepared in the refinery in the usual manner, by "sweating" the slack wax and "filtering" or percolating through fuller's earth to remove any color that might be present. The sample contained 1.45 per cent oil.

OILS—The characteristics of the oil samples are tabulated in Table 1.

EFFECT OF PARAFFIN WAX ON VISCOSITY

The viscosities of varying mixtures of waxes and oils were determined with the Saybolt Universal viscosimeter in seconds at 100° F. All mixtures are stated by weight. The data in Table 2 are plotted in Graph I. Paraffin wax has no effect on viscosity when this value is low. On the other hand, with oils of higher viscosity, such as the commercial "neutral" lubricating oils, the addition of dissolved paraffin wax decidedly lowers the viscosity. The higher the viscosity the greater the effect of the paraffin wax.

The effect of the paraffin wax is approximately the same as it would have been if an oil of about 70-sec. viscosity had been added instead of the paraffin wax. In other words, the wax acts as a thin oil.



Molten paraffin wax is in fact a thin oil. A sample, like No. 3 of melting point 123° F., "American method," showed a viscosity of 52 sec. at 125° F., and of 46 sec. at 150° F. Calculation from the observed figures to 100° F. leads to approximately 70 sec. for the viscosity of the paraffin wax at 100° F., on the assumption that it were liquid at that temperature.

TABLE 1—CHARACTERISTICS OF OILS

OIL	DESCRIPTION	Specific Gravity	Viscosity Sec.	Freezing Point ° F.	Color	Fluorescence
A	So-called "nonviscous neutral" oil, from Illinois and Healdton crude oils	0.8665	55	20	Very pale yellow	Blue
B	Pennsylvania "pressed distillate"[1]	0.8534	67	26	Pale brown	Blue
C	Western "pressed distillate"[2]	0.8805	72	25	Brown	Blue
D	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8827	106	22	Pale yellow	Bluish
E	Finished lubricating oil (source unknown, but mid-continent) (straight "neutral" oil)	0.8933	152	34	Pale yellow	Greenish blue
F	Finished lubricating oil, from central Oklahoma crude oil (blended "neutral" oil and "cylinder stock")	....	188	..	Red	Green
G	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8939	195	24	Red	Bluish
H	Finished lubricating oil, from central Oklahoma crude oil (straight "neutral" oil)	0.8961	249	27	Yellow	Greenish blue
I	Finished lubricating oil, from central Oklahoma crude oil (mixture "neutral" oil and "cylinder stock")	....	320	..	Dark red	Green

[1] This was some of the oil, derived from Pennsylvania crude, which flowed from the filter presses in the refinery during the process of separating the slack wax; in other words, dewaxed wax oil.

[2] Like B, from Illinois and Healdton crude oils.

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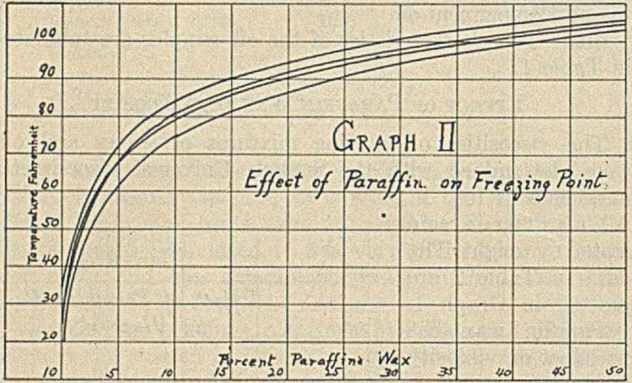
[1] Received September 20, 1921.

[2] Chief Chemist.

Table 2—Effect of Paraffin Wax on Viscosity

Oil used	B	C	D	E	F	G	H	I
Wax used	1	2	3	2	3	3	3	3
Amount of wax, Per cent								
0	67	72	106	152	188	195	249	320
2	67	73	103	146	...	183	230	...
5	..	73	99	138	...	170	211	...
10	..	73	94	130	158	162	198	244
15	..	73	...	122	...	...	...	...
20	68	73	...	...	141	...	...	...



Effect of Paraffin Wax on Freezing Point

The freezing points of mixtures of oils and paraffin waxes were determined. The American Society for Testing Materials "Pour Test," D 47-18, was followed except that the actual temperature of solidification was observed and recorded instead of the next higher even 5° or 10° mark.

It may be remarked in passing that this freezing point is not the point of solidification of the whole mass of the oil and paraffin wax mixture, but is due only to the growth of a spongy network of paraffin wax crystals which retains the rest of the oil in its interstices. This is proved by the fact that if the solidified mass, without warming, is stirred, it becomes a liquid with admixed paraffin crystals suspended therein. When this is further cooled it again solidifies, but at a much lower temperature. In this manner, by successive coolings and stirrings, several different freezing points may be obtained with the same solution of paraffin wax in oil. Only the highest solidifying temperature found, without any disturbance of the oil, is considered in this series of experiments.

Table 3 shows the data obtained, some of which are plotted in Graph II.

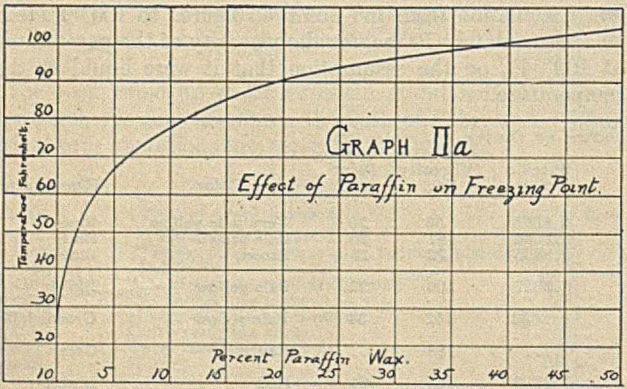


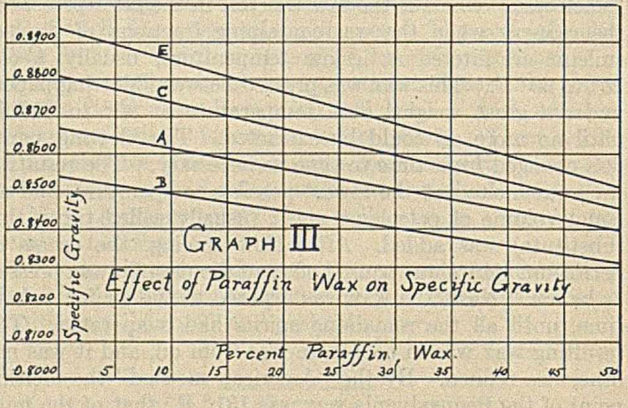
Table 3—Effect of Paraffin Wax on Freezing Point

Kind of oil used	A	B	C	D	E	G	H	
Kind of wax used	2	1	2	3	2	3	3	
Amount of wax Per cent								Av.
0	20	26	25	22	34	24	27	26
2	47	50	55	50	55	52	50	51
5	63	69	68	64	73	66	65	67
10	75	81	79	74	84	75	73	77
15	81	86	85	..	89	..	..	85
20	87	91	91	..	94	..	..	91
25	91	95	93	..	98	..	..	94
50	103	106	105	..	108	..	..	105

It will be noted that the freezing points of these mixtures do not depend at all upon the kind of oil used. While the freezing point does to some extent depend upon the freezing point of the oil used, the principal factor is the amount of paraffin wax present. Even a very small per cent of the wax causes a large rise in the freezing point. As more wax is added the increment of rise in the freezing point becomes less and less, as indicated in the graph.

The freezing points (before adding the paraffin wax) of the oils used are dependent on the amount of paraffin wax left in them by the manufacturing operations. It is possible to reduce them all to the same basis by simply shifting the location of the starting points on the graph all to the same place. The other end of the curve must not be shifted, because the wax is assumed to be the same in each case. Hence the curve will be shifted in a rotational way with the 100 per cent wax point as the center.

If by this means all the data be reduced to a common starting point, say at 26° F., the freezing points of all the oil and paraffin mixtures will fall on the same curve, within the limits of experimental error. This is virtually the same as making the assumption that all the oils used had originally a freezing point of 26° F., before adding the paraffin wax. The curve thus obtained is practically identical with that derived from the arithmetic averages of the freezing points for the mixtures with the same wax content. Such a curve is plotted in Graph II*a* and the figures are shown in the last column in Table 3.



Graph II*a* has been found very useful in the examination of wax distillates for paraffin wax content. Instead of the time-consuming and inaccurate Holde method of estimating the wax content, all that is necessary is to determine the freezing point and refer to the curve of Graph II*a*. Thus, if the freezing point is 70° F., there is a wax content of 6.5 per cent together with 93.5 per cent of oil of 26° F. freezing point. The writer has used this method for the past five years and has found it sufficiently accurate and reliable for all practical purposes.

Effect of Paraffin Wax on Specific Gravity

The specific gravities of mixtures of paraffin wax and oils were determined by means of a hydrometer, while the mixture was warm enough for all the wax to be in clear solution. In Table 4 these determinations have all been reduced to their equivalents at 60° F., by means of the tables commonly employed for that purpose in the petroleum industry.

Graph III (plotting the data of Table 4) shows clearly that the specific gravity becomes smaller with the addition of paraffin wax to the mineral oil, the more rapidly the heavier

TABLE 4—EFFECT OF PARAFFIN WAX ON SPECIFIC GRAVITY

Kind of oil used	A	B	C	E
Kind of wax used	2	1	2	2
Amount of wax Per cent				
0	0.8665	0.8534	0.8805	0.8933
2	0.8654	0.8529	0.8800	0.8922
5	0.8639	0.8514	0.8772	0.8888
10	0.8618	0.8498	0.8745	0.8838
15	0.8591	0.8478	0.8702	0.8805
20	0.8550	0.8448	0.8654	0.8755
25	0.8519	0.8423	0.8628	0.8718
50	0.8398	0.8304	0.8453	0.8519

the original oil. The fact that the graphs are all straight lines shows that there is no change of total volume when the paraffin wax is dissolved in the oil. In this respect paraffin wax behaves like any liquid mineral oil.

SUMMARY

1—When paraffin wax is added to mineral lubricating oils it decreases the viscosity of the more viscous oils, but not of the less viscous ones.

2—Paraffin wax in solution in mineral lubricating oils acts like a thinly fluid oil, so far as its effect on the viscosity is concerned.

3—The addition of paraffin wax to mineral lubricating oils raises the freezing point according to a definite relationship, dependent solely on the amount of paraffin wax present.

4—A quick and easy way of determining the amount of paraffin wax in waxy oils, to a sufficiently accurate degree for all practical purposes, is pointed out.

5—Paraffin wax lowers the specific gravity of mineral lubricating oils. The graph showing this relationship is a straight line. Hence there is no change of total volume on dissolving paraffin wax in mineral lubricating oils.

ACKNOWLEDGMENT

Part of the work herein recorded was done in the laboratory of the Canfield Oil Co., at Cleveland, Ohio, and part was done in the laboratory of the Empire Refineries, Inc., at Okmulgee, Okla. The writer's thanks are here expressed to the respective managers of these companies for permission to publish these data.

Manufacture of Chemically Pure Dextrose[1]

By Chr. E. G. Porst and Nicholas V. S. Mumford

CORN PRODUCTS REFINING CO., EDGEWATER, NEW JERSEY

The following paper describes the development of the process by which chemically pure dextrose is now manufactured on a commercial scale for medical use.

UP to a short time ago, chemically pure dextrose was used only for laboratory purposes and in small amounts. Several years ago, however, several physicians, individually, began to see possibilities in the use of chemically pure dextrose for medical purposes, and this laboratory was requested to furnish what, at that time, was a fairly large amount.

THE EARLIER METHODS

The method used at first was essentially that described by R. F. Jackson,[2] in which alcohol was used as a washing medium and as a precipitant for dextrins. By this means a 99.9 per cent dextrose was obtained from "Cerelose,"[3] but the use of large quantities of alcohol made the method too expensive for practical use.

A method suggested by Mr. C. S. Hudson of the Bureau of Chemistry, involving the use of glacial acetic acid in the ratio of one part of acid to one part of a 70 to 75 per cent solution of dextrose, was tested out. There was, however, danger of some acid being left in the final product, and since the cost of production was also high the method was abandoned in the experimental stage.

The method which was successfully used for two years or more involved solution of Cerelose in water to a density of about 63° Brix, treatment of this solution at 70° to 80° C. with from 0.5 to 1.0 per cent of "Eponite," filtration through a glazed stoneware Büchner funnel, crystallization in 10-gal., glazed stoneware crocks, and centrifuging. On re-solution and retreatment with Eponite a sugar was obtained which gave no test for dextrins and contained less than 0.1 per cent ash. A third recrystallization was usually made to insure the complete removal of dextrins, but it was not possible to reduce the ash content much below 0.05 per cent.

When, however, it became necessary to turn out C. P. dextrose at the rate of 200 lbs. per week, this process was not practicable. Sufficient Eponite could not be obtained and the capacity of the Büchner funnel was not great enough to handle the solutions. Furthermore, the number of crystallizations, which were the time-consuming factor, must be reduced.

IMPROVED AND SIMPLIFIED METHOD

For the decolorizing, two small boneblack filters, connected in tandem, were connected with a barrel which would give a 5-ft. head. These filters were filled with activated boneblack and the solutions were run by gravity through both of them. Except when the liquors had been excessively overheated in making them up, this treatment gave a clear, water-white solution for crystallization. When the solutions were not clear or white, the liquor was passed through the filters over fresh boneblack a second time before it was allowed to crystallize.

In order to reduce the number of crystallizations, the Cerelose was mixed for half an hour in a kneading machine with enough water to give a mixture which could be handled in the centrifugal. No definite ratio of water to Cerelose was adopted, because the amount of water necessary varied considerably, depending on how long the Cerelose had aged before being pressed and on how much pressure had been used. This treatment served to remove some of the color and also a considerable proportion of the impurities, the purity being raised to 99.0 per cent.

This magma was spun as dry as possible and the sugar obtained was melted with enough water to give a solution

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[1] Presented before the Division of Sugar Chemistry and Technology at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Bur. Standards, *Sci. Paper* 293.

[3] "Cerelose" is a corn sugar, made by allowing a highly converted corn sirup to crystallize, cutting the resulting mass into slabs, pressing out the mother liquor ("Hydrol"), and drying the pulverized cake. The sugar thus obtained is a light yellowish brown, granular substance of about 96 per cent purity.

of from 63° to 68° Brix, depending on the temperature out of doors. The melting was done in the barrel which supplied the boneblack filters, the barrel being fitted with a steam coil and an air agitator. Thirty to forty gallons of solution were made up at a time.

Before starting the liquor through the boneblack filters the water in the jacket surrounding them was heated to 70° to 80° C. and the temperature of the liquor was held at the same figure. On starting the liquor through the filters, it was invariably found that there was a certain amount of moisture in the bone which was displaced by the liquor. The liquor leaving the filter for the first 10 to 15 min. was, therefore, caught in a pail and returned to the barrel to be refiltered. When the gravity rose to the desired degree, the liquor was turned into 10-gal., glazed stoneware crocks. The density of the liquor in each crock was tested when full and adjusted to the value needed for that day's work by the addition of water. This adjustment was allowed for by making the density of the solution in the barrel slightly higher than that desired for crystallization. If the density was too low, it was necessary to return the liquor to the barrel, add more sugar, and run it through the filters again.

The liquor was allowed to stand without disturbance in the crocks. No seed was added, as it was found that seeding caused too rapid crystallization, giving fine crystals which went through the screen of the centrifugal. As the liquor cooled down, crystallization set in and the crystals sank to the bottom, increasing in size as they dropped. Ordinarily crystallization was complete, as determined by the temperature of the massecuite approaching that of the room, in from 48 to 72 hrs. Occasionally, however, owing to sudden changes in the weather from cool to very hot, the crystallization did not proceed after a layer of crystals an inch or so thick had settled to the bottom of the crock. It was then necessary to stir these crystals up; otherwise they would grow together, forming large lumps which could be broken up for treatment in the centrifugal only with great difficulty. After stirring, the crystallization proceeded very rapidly, being complete in another 12 to 24 hrs. The crystals very often grew to a length of 0.25 in. or more, but they were so soft that it was never found possible to separate any of this size, for they were broken up in transferring them from the crock to the centrifugal. However, they did not break up sufficiently to cause trouble by passing through the screen of the centrifugal.

When the massecuite was ready for swinging, it was stirred up in the crock as completely as possible, to break up lumps. The centrifugal used both for the massecuite and the magma of Cerelose and water was a 15-in. basket, underdriven machine, designed to turn at 3000 r. p. m. Owing to the difficulty experienced in starting up the machine when loaded, it was never driven over 1500 r. p. m. It was driven at about 900 to 1000 r. p. m. until practically all the mother liquor was out; then it was stepped up to full speed, and the wash water was added from an ordinary laboratory wash bottle fitted with a rubber tube so that the stream could be moved up and down over the whole depth of the basket.

The machine was kept running until practically no more wash water was running off, usually about half an hour. If the time went over three-quarters of an hour, it was judged that the crystals were too small and closely packed for good washing and the crock was remelted, run through the filters, and recrystallized.

The dry sugar, containing 20 to 30 per cent of moisture, was broken up by hand on trays, which were put in an air dryer from which dust was excluded as effectively as possible. The dryer was maintained at a temperature of 40° to 50° C. Although R. F. Jackson states that the crystal water of dextrose hydrate is given off at 60° C., no difficulty was experienced in reducing the moisture content of the dried sugar to less than 1 per cent at this low temperature.

The dried sugar, which had sintered slightly, was passed through a Mead mill to reduce it to a powder. Unless the dextrose was almost bone-dry the mill clogged up badly. Previous attempts to grind dextrose in a ball mill had given the same result. Owing to the amount of dextrose that did stick to the beaters and bars of the Mead mill, it was certain that sugar passing through did not pick up any impurities from the mill.

The dextrose obtained by this single crystallization had a purity of 99.90 to 99.95 per cent and was sufficiently pure for the purpose of milk modification for baby-feeding experiments, for which it was chiefly used. If a still higher purity was desired, as when the sugar was to be used for intravenous injection, another crystallization was made.

Preparation from "Refined Cerelose"

This process was continued until the new process of making high purity dextrose, developed by Dr. Chr. E. G. Porst and Mr. W. B. Newkirk, was put into operation. The use of the kneading machine was then abandoned and the high purity dextrose or "Refined Cerelose" is now melted and run through the boneblack filters. As the purity of the original dextrose is 99.0 per cent or better, a single crystallization is sufficient to give a product of 99.9 per cent purity, and a second crystallization gives a product whose purity can be improved only by the use of the most refined methods of purification.

International Conference of Chemistry

The International Union of Pure and Applied Chemistry announces that the next international conference will be held at Lyons June 28 to July 1, 1922. The International Commission on the Elements, discussed at the Brussels meeting, has been organized and will present its first report at the Lyons meeting. By unanimous vote the commission has agreed to the creation of three subcommittees (isotopes, radioactive elements, atomic mass). It has been decided to appoint three international commissions of nomenclature: (1) organic chemistry; (2) inorganic chemistry; and (3) biological chemistry. The Commission on Unification of Bibliographic Abbreviations, named at Brussels, recommended the system of abbreviations employed in *Chemical Abstracts* and the Bureau of the Union has decided to conduct an investigation to see whether the principal chemical periodicals will be willing to adopt this system of abbreviations.

Other questions taken up at Brussels and to be again considered at Lyons are: unification of chemical abstracts; international institute of chemical standards, of which there are three sections (bureau of physicochemical standards at Brussels; pure products for research in England; and service of documentation on industrial and technological products in Paris); international laboratory of analysis of food products, for the installation of which the French government has already provided; and the creation of laboratories fo the study of ceramic products and combustibles.

The Bureau of the Union would welcome suggestions as to what questions this country desires to have discussed, and in order that suitable arrangements may be made for the proper presentation of the subjects requests that replies be submitted before April 1, 1922. The Bureau urgently requests that each adhering country pay its subscription promptly.

In the arbitration of the Tacna-Arica controversy between Chile and Peru, the possibility is presented of Chile's losing the potentially valuable Chilean nitrate beds located in the territory under discussion. Bolivia has indicated that she should be included in the parley because Chile's title to the western seacoast was obtained in 1904 through a treaty executed under duress. Chile declares that Bolivia was paid £6,000,000 for her coastal territories, and that she will not enter the conference if Bolivia is admitted. The territory in question involves provinces at the northern end of Chile, one or two of which are said by government experts here to contain valuable nitrate beds.

An Unusual Type of Casinghead Gasoline[1]

By C. E. Coates[2] and B. Y. Tims

LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA

Gas from the Terrebonne Gas Field, about twenty miles below Houma, La., is piped to the town for use as a fuel. The condensate which forms in the pipes is the subject of the investigation recorded in this paper. It differs from ordinary casinghead gasoline in boiling point and other properties. Fractional distillation gives products of fairly constant boiling points, the lowest fraction having the formula $C_{12}H_{22}$. The condensate contains no paraffin hydrocarbons and is probably made up of dicyclopentyl, $C_{10}H_{18}$, and its homologs.

THE gas wells of Louisiana, and for that matter, gas wells in general have, during the last few years, been yielding, not only gas, but a fairly large quantity of a very light gasoline. The amount of this gasoline depends upon the nature of the gas, that yielding very little being called dry gas; that yielding considerable being called wet gas. It is commercially profitable to extract this gasoline down to a certain minimum content. Extraction was formerly accomplished at the well by compressing the gas, cooling the compressed gas, drawing off the condensed gasoline and allowing the remaining gas to expand around tubes containing the incoming gas, thus cooling the latter. This process took place at the head of the well, and the product was hence called casinghead gasoline.. At present it is considered cheaper to pass the wet gas through a heavy nonvolatile mineral oil, which absorbs the gasoline and from which the gasoline may be subsequently recovered by steam distillation, the oil being returned to process. This casinghead gasoline is exceedingly volatile, and is ordinarily mixed with somewhat high gravity gasolines, in order to make them more readily ignited in an internal combustion engine.

The only considerable deposits of gas in South Louisiana occur in the Terrebonne field, located about twenty miles south of Houma. In this field three producing wells have been, for a number of years, delivering gas at a pressure of about 1200 lbs. per sq. in. at the well. This gas is carried by pipes to Houma and its vicinity, and to the various sugarhouses in that section. The gas appeared to be wet, because quantities of a liquid condensed in the pipes in Houma and had to be collected in drips and removed at intervals. This liquid was considered casinghead gasoline, and was mixed with ordinary gasoline for use in automobiles in Houma. It, however, showed certain properties not possessed by ordinary gasoline, and for this reason Dr. C. M. Menville, at the request of Dr. Coates, collected and sent to his laboratory about 2 gal. of the crude condensate.

PHYSICAL PROPERTIES

The oil was light in color and slightly fluorescent, and had an odor like pine oil, or oil of cedar. On analysis it gave values listed in Table I.

TABLE I

Refractive index at 17° C. = 1.4590
Specific gravity = 0.84819 at 24.5° C./24.5° C.
Flash point = 61° C.
Burn point = 63° C.
Cold point = below −7° C.
Viscosity at 25.5° C. = 1.22
B. t. u. = 19.363
Per cent sulfur = 1.09

The flash point determination was carried out in an open cup, heat was applied very gradually, and the process repeated a number of times.

In burning, the gasoline gave off heavy, black smoke with an unpleasant odor.

The heating value of the gasoline was determined in an Emerson bomb calorimeter. Sulfur was determined from the washings of the bomb.

DISTILLATION

For the distillation, 500 cc. of gasoline were taken. Vaporization began at about 50°, and actual distillation at about 94° C. Only a few cubic centimeters came over between 94° and 100° C. The temperature then rose suddenly to 195° C., after which the distillation proceeded steadily. The distillate was collected in 2° fractions. All the fractions were colorless except the last two, which were slightly fluorescent. A small amount of tarry matter remained in the flask after distillation was complete. At 226° C., heavy yellow fumes were given off and no more distillate came over. Table II gives the results of distillation.

TABLE II—FRACTIONS OF DISTILLATE (Atmospheric pressure)

° C.	Cc.
Below 195	2
195–200	50
200–202	65
202–204	62
204–206	64
206–208	54
208–210	50
210–213	50
213–217	50
217–220	24
220–226	27
TOTAL	498

The fractions were purified by shaking with concentrated sulfuric acid, separating the oil, washing with water, shaking with sodium carbonate, decanting, and removing the excess water with powdered calcium chloride. The acid treatment removed a considerable amount of tarry matter. After purification, the turpentine-like odor of the original gasoline was greatly lessened, although it persisted in spite of acid treatment and subsequent redistillations.

REFRACTIONATION—The fractions, after purification, were distilled separately. The temperature of distillation varied in each case from 10° to 30° C. from that of the distillation temperature of the fraction. For lack of time, only the first three fractions, 200° to 202°, 202° to 204°, and 204° to 206° (in all 100 cc.), were redistilled in this way in a 200-cc. flask. As distillation in all cases seemed to cause a slight decomposition, it was carried on in this case under a vacuum of 61 mm., but even here there was decomposition. About 20 cc. of a brown liquid remained, but the fraction coming over from 207.5° to 209.5° C. was water-white and was taken for the subsequent work. It still had the odor of cedar or pine oil and contained no sulfur. Treated with bromine at the laboratory temperature of 25°, it seemed to behave as a saturated compound. Upon redistillation at 61 mm., it gave a water-white fraction for which the analytical results in Table III were obtained. For sake of comparison, they are tabulated against some figures obtained by Coates, who was working on a fraction obtained from the Jenning oil. In calculating molecular refraction, the formula of Lorentz and Lorenz was used.

From these data it will be evident that this condensate

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[1] Presented before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

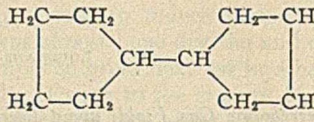
[2] Dean of Audubon Sugar School, and Head Professor of the Department of Chemistry.

TABLE III

	Coates	Coates and Tims
Formula	$C_{12}H_{22}$	$C_{12}H_{22}$
Molecular weight, calculated	166	166
Molecular weight, found	167	167
Carbon, calculated	86.74	86.74
Carbon, found	86.68	86.30
Hydrogen, calculated	13.26	13.26
Hydrogen, found	13.43	13.50
Specific gravity	0.8511 28°/4°	0.84819 24°/24°
Boiling point, 760 mm.	215°–217°	215°–217°
Refractive index	1.4640, 25° C.	1.4546, 29° C.
Molecular refraction, calculated	53.13	53.13
Molecular refraction, found	53.48	53.24

does not resemble in the least the ordinary casinghead gasoline. Its boiling point is far too high, as is also its specific gravity. A study of the particular fraction boiling from 215° to 217° shows it to be identical with a fraction obtained by Coates and his assistants in 1906 from the crude oil in Jennings, La.[3]

Schmidt and Sigwart[4] have identified the series $C_{10}H_{18}$ and its homologs found in Louisiana petroluem by Coates as being dicyclopentyl



and its methyl derivatives, which they made synthetically. The compound $C_{12}H_{22}$ would, therefore, be the dimethyl derivative. The higher and lower derivatives were also isolated by Coates from the South Louisiana petroleums and occur in this condensate as well.

This would indicate that inasmuch as the gas deposit at Terrebonne carries a condensate which is identical with that obtained at Jennings, the two deposits are probably similar in formation. It might also be a slight indication of the presence of an oil pool in Terrebonne, similar to that which has been found in Jennings.

[3] *J. Am. Chem. Soc.*, **1906**, 384.

[4] *Ber.*, **1912**, 1779.

Determination of Volatile Combustible Matter in Pitch Coke[1]

By H. E. Lloyd and F. W. Yeager

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Within a comparatively recent period pitch coke has found use in the manufacture of electrodes, and in certain metallurgical processes where a low volatile coke of high purity is required. Since only a coke of very low volatile content possesses sufficient conductivity to be suitable for electrode use, the accuracy of the determination of volatile combustible matter (V. C. M.) in this class of material takes on new significance.

The work described in the following paper indicates that variations in these analytical results are due to variations in the type of crucible cover used, the weight of sample, the size of crucible, and the method of calculating results. The method which gives the more accurate results, particularly with low volatile cokes, follows the procedure given in test A. S. T. M. D-37-18 under the determination of volatile matter in coke, with the exception of the use of a 2-g. sample and a second 7-min. heat correction.

CERTAIN factors operative in the determination of V. C. M. in pitch coke are particularly likely to affect the accuracy of the results on account of the low volatile content of the material. Considerable work has been done on this test, but the inaccuracies possible seem not to be generally recognized.

The authors had occasion to determine the V. C. M. of pitch coke by two different methods, the differences in which are listed in Table I. The coke was ground in porcelain to pass a 60-mesh sieve.

TABLE I—DIFFERENCES IN METHODS

	METHOD I	METHOD II
Type of crucible	Usual shape; capacity 20 cc.; lid of usual flat type	Capsule shape; capacity 10 cc.; lid tight-fitting inside crucible
Weight of sample	1.000 g.	2.000 g.
Manner of heating	Bunsen flame 20 cm. long (temperature 900°–950° C.)	Electric furnace 950° C. (A. S. T. M. D-37-18)
Time of heating	One 7-min. period	Two intermittent 7-min. periods
Calculation of results, giving V. C. M. as:	Loss in weight reported in per cent of sample weight	Loss on second heat subtracted from loss on first heat and remainder reported as per cent of sample weight

Method II, which is being used by the Aluminum Company of America for certain types of low volatile coke, has for its purpose a correction for the oxidation of the nonvolatile portion of the coke encountered during the first period of heating. This correction is based on the loss found on a second 7-min. heating. The use of a second heating correction factor was suggested by Meade and Attex,[2] who have shown that results so corrected approximate very closely the loss on heating in an inert gas.

Two samples of coke gave results listed in Table II.

TABLE II—PERCENTAGE OF VOLATILE COMBUSTIBLE MATTER[1]

SAMPLE	Method I	Method II	Ratio I:II
1	2.3	0.3	1:0.13
3	6.1	3.5	1:0.57

[1] All figures reported are the averages of two or more check results.

Considering the wide differences in methods used, the basic reasons for such results are apparent. However, the reason for the marked disproportion between the results on cokes of different volatile content as indicated by the ratios in Table II is not so evident.

A brief review of the literature shows that the loss due to oxidation by the air remaining in the large type of crucible was early investigated. To minimize this loss Shimer[3] proposed the use of two 15-cc. platinum crucibles, one fitting tightly within the other with the sample between. Meade and Attex[4] recommended making the test in an atmosphere of nitrogen. Shimer suggested the addition to the sample of alcohol, and Parr[5] of kerosene, for the same purpose. The variations in V. C. M. tests due to mechanical losses, variations in heat, type of crucible, character of flame, type of burner, etc., have been discussed by Parr.[6] Fieldner and Davis[7] have studied the influence of gas pressure, swelling of coal, type of burner, and condition of crucible, *i. e.*, dull

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[1] Received June 20, 1921.

[2] *J. Am. Chem. Soc.*, **21** (1899), 1137.

[3] THIS JOURNAL, **1** (1909), 518.

[4] *J. Am. Chem. Soc.*, **21** (1899), 1116.

[5] THIS JOURNAL, **3** (1911), 900.

[6] *Ibid.*, **4** (1912), 352.

Ibid., **2** (1910), 304.

or bright. Fieldner[3] determined the effect of change of temperature and of type of crucible.

In the present investigation attention was first given to the influence of a change in sample weight.

Change in Sample Weight

Sample 3, Table II, was used for the tests. Table III shows the results obtained in the electric furnace with both types of crucible, each with 1- and 2-g. samples.

Table III—Percentage Lost with Samples of Different Weight

	Weight of Sample	
	1.000 Gram	2.000 Grams
10-cc. Crucible (Capsule Type)		
1st heat, 7 min.	4.2[1]	3.99
2nd heat, 7 min.	0.79	0.53
20-cc. Crucible		
1st heat, 7 min.	5.25	4.55
2nd heat, 7 min.	2.17	1.19

[1] This result is by A.S.T.M. Method D-27-18 in all respects.

In every case the per cent loss in weight, irrespective of the size of crucible, is greatest where the sample is smallest. The cause for this is thought to be the variation in the depth of coke layer; in other words, the relative coke contact surface per gram of sample which is dependent upon the sample weight. This difference has an appreciable effect where the same crucible is used, but where the 2-g. sample is charged to the 10-cc. capsule and a 1-g. sample to the 20-cc. crucible, the difference in coke contact surface between the two combinations is considerable. Parr[6] regards variation in this contact surface as affecting the results of tests to a considerable degree, the cause being, in his opinion, the effect of differences in coke contact surface per gram on the speed with which the heavier volatile constituents are discharged.

The losses for the second period heats are due mainly to oxidation of the coke residue remaining after the first heat, either by the air in the crucible or that entering during the second heat. Under these conditions the coke contact surface is of less importance as a factor affecting the per cent loss and while the per cent loss is different the actual weight loss tends to be approximately the same for each crucible, respectively.

Type of Crucible

The data obtained in the above tests also serve to show the difference due to the type of crucible.

With the same weight of sample the loss is greater when the 20-cc. crucible is used. This may be attributed to two factors, (1) size of crucible, and (2) type of cover.

In their entirety these results show that the difference between the two methods as to type of crucible and amount of sample tend to produce a lower percentage loss in weight in Method II. When this difference in actual per cent loss is augmented by the correction in Method II which further reduces the figure for V. C. M., it is readily apparent that in any case lower results are inherent in Method II than in Method I.

However, these data do not account for the disproportionate results obtained in different cokes. The cause for this difference, as shown by Table IV, does not lie in the calculation of results, but is operative during the first 7-min. heating of the crucibles.

Table IV—Loss on First 7-Min. Heating

(Sample 1, low volatile coke; Sample 3, high volatile coke)

	Method I		Method II	
	Sample 1 *a*	Sample 3 *b*	Sample 1 *a*	Sample 3 *b*
Weight loss, gram	0.0225	0.0608	0.0109	0.0789
Per cent loss	2.25	6.08	0.55	3.99

Here the relation represented by b in terms of a is, for Method I, $b = 2.7\ a$; and for Method II, $b = 7.2\ a$.

It appears that the cause for this variation can be traced to some difference of conditions which permits unequal degrees of oxidation or combustion with respect to high and low volatile cokes in the two methods, such as (1) fit of crucible lids, (2) difference in relation of air volume to coke sample weight, or both.

Type of Crucible Lid

The effect of a loose-fitting lid was tried out on the 10-cc. crucible with a 2-g. sample. A comparison of these results with previous ones using the usual tight lid is made in Table V.

Table V—Effect of Type of Crucible Lid

(Per cent loss, 1st heat, 7 min., furnace 950° C.)

	Sample 1 *a*	Sample 3 *b*	b/a
10-cc. crucible, usual tight lid..............	0.55	3.99	7.2
10-cc. crucible, loose lid.....................	1.23	4.48	3.6
20-cc. crucible, flat lid......................	2.25	6.18	2.7

These results indicate that the relative tightness of the lids, of necessity causing a difference in amount of oxidation, is closely connected with the variation of the relation between the high and low volatile coke tests; particularly when it is seen that, not only is there an increase in loss in each case when the loose lid is used, but this increase is different for cokes of different volatile content, and brings the ratio of their apparent V. C. M. to a figure approximating the ratio obtained by the 20-cc. crucible method (see b/a).

EXPLANATION OF RESULTS—The explanation of the discrepancy in results of the two methods with samples of high and low volatile coke may be as follows: In Method II, with either high or low volatile cokes, the volatile matter evolved passes out of the small vent between the lid and rim of the crucible and is burned externally; during the test very little of the nonvolatile portion of the coke is consumed, on account of the protection afforded by the tight-fitting lid and the generally nonoxidizing atmosphere maintained in the crucible.

With Method I the amount of volatile matter evolved relative to the air accessible to it is considerably less than in Method II, because of the smaller sample, larger crucible, and loosely fitting lid, all of which make for its quicker dissipation and more readily expose the nonvolatile portion to oxidation, which results in a V. C. M. content considerably above the actual. This is particularly the case with low volatile cokes. As the actual V. C. M. content of the coke tested increases, the combustion of the nonvolatile portion is correspondingly delayed and the results more nearly approach the true value.

Continuous and Intermittent Heating

The high volatile coke was used in comparative tests in which the heats were made both continuous and intermittent for the same total period.

Table VI—Comparison of Loss Per cent with Continuous and Intermittent Heats

	7 Min.	14 Min. Continuous	14 Min. Intermittent
10-cc. capsule, 2-g. sample, furnace	3.99	4.22	4.52
20-cc. crucible, 1-g. sample, flame	6.12	8.42	8.51

The test with the 10-cc. capsule shows that the volatile matter is practically all expelled at the end of the 7-min. period. The excessive increase in the 14-min. continuous heat with the 20-cc. crucible must be attributed to the high oxidation factor inherent to this type of apparatus.

It may also be noted that the losses in the intermittent

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[3] *8th Internat. Congr. Appl. Chem.*, 10, 139.

heat tests are somewhat greater than those for the same period of continuous heating, which can be ascribed to the oxidation resulting from air absorbed in the cooling of the intermittent tests. On this basis the correction factor as applied by Method II may be somewhat in excess of the actual, although the result thus corrected is more nearly the value estimated from the continuous and intermittent heats than the uncorrected figure.

V. C. M. uncorrected	4.0 per cent
V. C. M. estimated actual	3.6 per cent (difference on continuous and intermittent subtracted)
V. C. M. by Method II	3.5 per cent

Vanadium Compounds as Driers for Linseed Oil[1]

By F. H. Rhodes[2] and K. S. Chen

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Satisfactory driers for linseed oil may be prepared by heating ammonium metavanadate with rosin or linseed oil. The driers thus prepared, when used in amounts sufficient to give 0.2 per cent of vanadium in the oil, cause it to dry to a hard, tough, smooth film. Vanadium is superior to lead in drying power and gives smoother and tougher films than does manganese or cobalt. The principal objection to the use of vanadium driers is that they darken the oil somewhat.

The initial oxidation of linseed oil containing vanadium drier is much more rapid than that of oil containing an equivalent amount of lead drier, and the rapid absorption of oxygen continues for a much longer time; about 1.75 times as much oxygen is absorbed.

The vanadium driers described in the following paper possess certain advantages not shown by the lead, manganese, or cobalt driers in common use, and should prove very satisfactory in the preparation of certain types of paint and varnish.

THE use of vanadium as a drier for paint oils was suggested by Sabin,[3] who states that "the writer also made a vanadium compound which was a very efficient drier, but of course its cost prevented its use." The cost of the material is not, however, sufficient to prevent the use of vanadium if it were found that such driers were very much more efficient than driers made from the more common metals, or if the discovery of new sources of vanadium or the development of improved processes of recovery from the ore should decrease its cost.

Materials

The linseed oil used in this work was taken from a sample lot of "Superior Grade," pure, raw linseed oil presented to this laboratory by Spencer Kellogg and Sons. The lead, cobalt, and manganese driers which were used for comparison with the vanadium driers were presented by Harshaw, Fuller and Goodwin Company. Upon analysis, these driers were found to contain the following percentages of metal:

Lead linoleate	24.2
Lead resinate (precipitated)	22.5
Manganese linoleate	10.55
Manganese resinate (precipitate)	6.02
Cobalt linoleate	12.25
Cobalt resinate (precipitated)	2.33

Preparation of Vanadium Driers

The pure ammonium metavanadate used in the preparation of the vanadium driers was purchased from the Vanadium Corporation of America.

FROM IGNITED OXIDE—A mixture of 6 g. of vanadium pentoxide, prepared by ignition of ammonium metavanadate, and 100 g. of linseed oil was heated with constant stirring. The mass gradually thickened and became dark green in color. Even after heating to 350° C. for 2.5 hrs., however, a considerable amount of the solid oxide remained suspended in the viscous mass.

In an attempt to prepare the fused resinate from the vanadium pentoxide, 6 g. of the oxide were fused with 100 g. of rosin. Decomposition began at 250° C. and copious fumes were evolved. After 1 hr.'s heating there was obtained a dark green viscous mass which solidified on cooling to a brittle amorphous mass in which particles of unreacted oxide were still visible.

It was thought probable that the failure to obtain complete reaction in these cases was due largely to the fact that the ignited oxide is crystalline and, like many other ignited crystalline oxides, relatively inert. Attempts were made, therefore, to prepare driers by heating together ammonium metavanadate and rosin or linseed oil. Under these conditions the ammonium salt should decompose, evolving ammonia and giving amorphous vanadium oxide which should react readily with the oil or rosin.

FROM AMMONIUM METAVANADATE—Vanadium linoleate was prepared by heating 100 g. of linseed oil to 300° C. and adding 10 g. of ammonium metavanadate slowly and with constant stirring. At each addition of the vanadate, ammonia was evolved and the solid residue reacted readily with the oil. The mixture was heated and stirred for a short time after the addition of the last portion of the ammonium vanadate, and was then allowed to cool. The final product was a dark green waxy mass which showed no particles of unincorporated oxide or vanadate and which contained 3.15 per cent of vanadium by analysis. The rather low vanadium content is due to the fact that considerable "dusting" occurred during the addition of the vanadate.

In the same way, vanadium resinate was prepared by adding 10 g. of ammonium vanadate to 100 g. of rosin at a temperature of 250° C. This resinate was a dark olive-green amorphous solid containing 2.68 per cent of vanadium.

Preparation of Solutions

A series of concentrated drier solutions was prepared by dissolving the linoleates (or resinates) of lead, manganese, cobalt, and vanadium, respectively, in warm linseed oil. In each case the amounts of oil and drier were such as to make 100 g. of drier solution containing exactly 1 g. of the metallic element of the drier. From these solutions four series of solutions of drier in raw linseed oil were prepared, each series consisting of solutions containing, respectively, 0.1, 0.2, and 0.3 per cent of metal. In preparing each solution, the required amounts of raw oil and of concentrated drier solution were mixed and heated to 200° C. in order to secure thorough and uniform incorporation of the drier in the oil.

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[1] Received October 14, 1921.

[2] Professor of Industrial Chemistry.

[3] "Technology of Paint and Varnish," 2nd edition, 38.

Comparison of Driers

RELATIVE DRYING TIME—In a series of experiments made to determine the relative drying times of the oils containing the various driers, each sample was painted out in a thin film on a glass plate which was allowed to stand at room temperature until dry. The time required for each sample to "set" (*i. e.*, to dry until no longer sticky when touched lightly with the finger) and to "dry" (*i. e.*, to become hard enough to give no impression when pressed with the finger) was noted. For purposes of comparison, a similar test was made with raw linseed oil containing no drier. The results are shown in Table I.

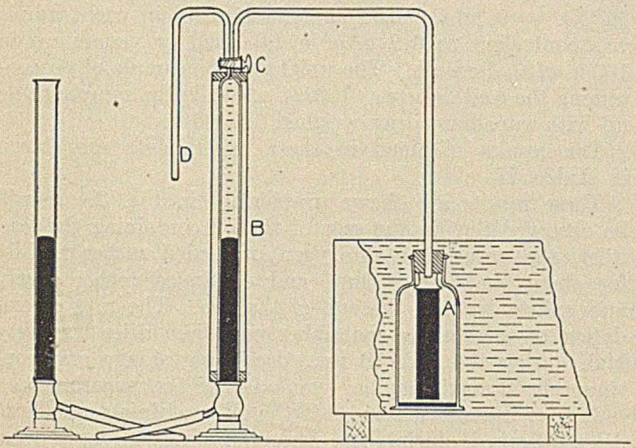

Fig. 1

Table I—"Setting" and "Drying" Times of Raw Linseed Oil with Various Driers

Drier		Amount	Hours to	
Metal	Type	Per cent	"Set"	"Dry"
Manganese	Resinate	0.1	12.5	14
Manganese	Resinate	0.2	15	17
Manganese	Resinate	0.3	17	18
Manganese	Linoleate	0.1	13	13.5
Manganese	Linoleate	0.2	15	17
Manganese	Linoleate	0.3	17	17
Cobalt	Resinate	0.1	4.5	5.5
Cobalt	Resinate	0.2	4.5	6
Cobalt	Resinate	0.3	5.5	8
Cobalt	Linoleate	0.1	5	6.5
Cobalt	Linoleate	0.2	4.5	6.5
Cobalt	Linoleate	0.3	4	5.5
Vanadium	Resinate	0.1	7	9
Vanadium	Resinate	0.2	6	8
Vanadium	Resinate	0.3	6	8.5
Vanadium	Linoleate	0.1	7	9.5
Vanadium	Linoleate	0.2	6	8.5
Vanadium	Linoleate	0.3	6	8.5
Lead	Resinate	0.1	38	42
Lead	Resinate	0.2	29	32
Lead	Resinate	0.3	28	31
Lead	Linoleate	0.1	38	42
Lead	Linoleate	0.2	29	32
Lead	Linoleate	0.3	27.5	31
Raw linseed oil	....	...	57	63

It will be observed that an increase in the concentration of manganese drier, either resinate or linoleate, causes an increase in both the setting time and the drying time. This is due to the fact that with the higher concentrations of manganese the oil film "casehardens," *i. e.*, a tough film forms rapidly at the surface and, by excluding the air from the lower part of the film, actually increases the drying time.

The results in Table I indicate that vanadium driers are much more efficient than lead or manganese driers. Oils containing vanadium driers dry about twice as rapidly as do oils containing an equivalent amount of manganese drier, and almost five times as rapidly as do oils containing an equivalent amount of lead drier. Vanadium driers are only slightly less efficient than cobalt driers.

CHARACTER OF FILM—Like cobalt, vanadium appears to cause the oil to dry uniformly throughout its mass. No tendency to the formation of surface films or "skins" was observed.

The films with manganese drier showed a distinctly wrinkled appearance after drying. Cobalt also caused some wrinkling. The oils made up with the lead or vanadium drier gave perfectly smooth films.

Each film was allowed to stand for 1 wk. after it was classed as "dry," and was then examined for toughness by scratching with the point of a knife. The films containing manganese were distinctly brittle, and broke away in small scales. Those made with cobalt drier were somewhat brittle, and broke in short strips from the edge of the knife. Films containing lead or vanadium were tough, coming away in long curling ribbons.

The oils containing vanadium driers were darker in color than the others, and gave brownish films. It is possible that this darkening might be decreased or eliminated by varying the procedure used in preparing the drier. In any case, the color would be objectionable only in the preparation of white paints or specially pale varnishes.

Comparison of Vanadium and Lead Driers

In order to obtain a more quantitative comparison of the drying properties of vanadium and of lead, a series of experiments was made to determine the effect of the respective driers upon the rate of absorption of oxygen by linseed oil.

The apparatus is shown in Fig. 1. The wide-mouthed bottle A was immersed in a thermostat, the temperature of which was constant to within 0.1° C. The bottle was closed by a tightly fitting rubber stopper, through which was inserted a glass tube connected to one outlet of a mercury-filled Hempel gas buret, B. The other outlet of the buret was connected, by tube D, with a tank of oxygen. Two duplicate pieces of apparatus were constructed, so that parallel tests on the two driers could be made at the same time and under as nearly as possible identical conditions.

PROCEDURE—A strip of cotton filter cloth, 10 in. long and 1 in. wide, was weighed, saturated with oil containing the desired amount of drier, and again weighed to determine the weight of the sample. One end of the strip was attached to a copper wire in such a manner that the cloth hung flat and free from folds, and wire and cloth were suspended in the bottle as shown. Before placing the sample in position the bottle was filled with oxygen at atmospheric pressure, and a small amount of concentrated sulfuric acid was placed in the bottom of the bottle to absorb any water vapor that might be formed during the oxidation of the oil. The stopper carrying the inlet tube and the wire from which the sample was suspended, was then inserted tightly. Exactly 100 cc. of dry oxygen at known (atmospheric) pressure and known temperature were drawn into the buret, the stopcock was so turned as to connect the buret with the bottle, and the apparatus was allowed to stand in this position. As the

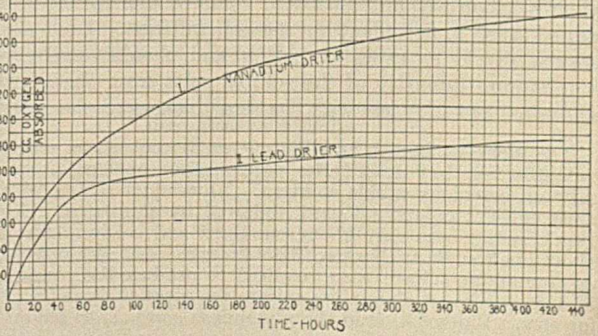

Fig. 2

TABLE II—OXYGEN ABSORBED BY LINSEED OIL WITH LEAD AND VANADIUM DRIERS

TIME Hrs.	Cc. Oxygen Absorbed Calc. to 0° C., 760 Mm. Hg Vanadium	Lead
1.5	50.1	4.17
3.5	70.4	12.9
5	81.8	24.4
6.5	91	29.9
9	97	43.5
11.4	112.4	51.1
23	141.5	93.8
27.5	154	104
30.5	157	116.6
33.5	162.5	121.5
35.5	170.5	128.1
46.5	205	155.8
54.5	221.3	159
73	240	169.5
81	251.5	174.7
94.5	272	183.5
104.5	285	191.6
128.5	311.2	196.2
153.5	333.4	203
179	348	208.7
203	363.9	214.5
247	383	219.8
286	406.5	232
382	435	247
430	444	252

oxygen was absorbed by the oil, the leveling tube of the buret was raised so as to maintain atmospheric pressure within the apparatus. At definite intervals readings were taken to determine the amount of oxygen absorbed by the oil. The experiment was continued until the rate of absorption of oxygen became very slow.

Duplicate runs were made with samples of linseed oil containing lead drier and vanadium drier, respectively. The temperature of the thermostat was kept constant at 30° C. ± 0.1° C. The amount of drier in each sample was equivalent to 0.2 g. of metal (lead or vanadium) in 100 g. of the sample. The weight of the sample of oil containing the lead drier was 1.0224 g., while the sample made up with vanadium drier weighed 1.0403 g.

The results obtained in these experiments are shown in Table II.

These results are shown graphically in Fig. 2. It will be observed that in the case of the oil containing the lead drier, the absorption of oxygen proceeded rather rapidly for about the first 80 hrs., and continued rather slowly and uniformly until the end of the run. The rate of oxidation of the sample containing vanadium drier was very high during the first 10 hrs., decreasing slowly and continuously throughout the remainder of the experiment.

It is of interest to note that the oil containing vanadium drier absorbed, during the period of observation, a total amount of oxygen equivalent to 1.76 times the amount of oxygen absorbed by the sample prepared with lead drier.

The Soil Solution[1]

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THE investigator of "alkali soils" often has difficulty in obtaining a clear filtrate because in the watery extract the degree of dispersion of the colloidal disperse phase is so great and in such a stable form that the solution may be kept for years[1,*] without flocculation. The particles of such a phase are so small that it is impossible to separate them by ordinary filtration. It is imperative, however, that the soil extract be free from colloidal particles; colored colloids interfere with sharpness of end reaction in colorimetric and some volumetric reactions, and where the colloid is of a proteinous nature, subsequent reduction may liberate nitrogen or ammonia which in the end reaction may be interpreted as nitric nitrogen. Furthermore, the colloids may actually combine with one or more of the reagents giving erroneous results. The ideal method of obtaining a clear, aqueous solution would be one which yielded a clear solution without filtration. This would necessitate the addition of a flocculent to the soil infusion. Such a substance should be rapid in action and should remove only a minimum quantity of the soluble salts from the solution, and must not interfere with the sensitiveness of the method.

The work of Linder and Picton[2] on flocculents is especially valuable, as they tested the precipitating powers of various salts on arsenious sulfide solution. Aluminium sulfate was the most efficient compound used, followed by aluminium chloride. Ferric sulfate was only about one-third and calcium salts only about one-fourth as effective; 3200 times as much sodium chloride as aluminium sulfate were required to produce the same effect. McGeorge[3] found aluminium sulfate the most efficient flocculent for clay. Wolkoff[4] found the aluminium compounds among the best flocculents, but there was a great variation, depending upon the soil. This is to be expected from Hardy's rule that the precipitating power of an electrolyte for a colloid depends on the valence of the ion which carries the electric charge opposite that of the dispersoid. The colloids found in the soil may be either the electronegative colloid—clay—or the positive or negative organic colloid.

Buhlert and Fickenday[5] recommended the addition of 2 per cent of sodium chloride, whereas King and Whitson[6] used potassium alum. The quantity of alum recommended, however, gave with some soils[7] a cloudy solution which had to be filtered before it could be compared in the colorimeter. Furthermore, in the presence of sulfates there is a loss of nitrates when the phenoldisulfonic acid method is used. Chamot[8] and co-workers found aluminium cream the best precipitating agent of several tested for organic matter, and that it occasioned no loss of nitrates. Lipman and Sharp[9] found potassium alum, aluminium cream, and boneblack all decidedly unreliable, inducing losses of nitrates in the phenoldisulfonic acid method. They found lime to be much more reliable, but it must not be used with chloroform because the double decomposition which takes place produces chlorides, which interfere with the accurate determination of nitrates.[10] One of us has used the Pasteur-Chamberland filter very extensively in his work[11] on soil nitrates. This gives a clear solution and occasions only slight losses of nitrates.[12]

COMPARISON OF CLARIFYING AGENTS

Sodium, potassium, and iron alum, ferric sulfate, lime, finely precipitated calcium carbonate, and talc, together with the centrifuge and the Pasteur-Chamberland filter, were tested on a number of soils rich in soluble salts and having a high clay or organic colloidal content. These agents could be arranged in a descending order of efficiency as follows: Pasteur-Chamberland filter, ferric alum, ferric sulfate, sodium alum, potassium alum, centrifuge, talc, calcium carbonate.

The centrifuge was run at a speed of 1200 r. p. m., and some solutions were not clear after 30 min. centrifuging. Many soil-water mixtures to which talc or calcium carbonate were added were not clear after several hours.

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[1] Received October 31, 1921.

[2] Chemist, Utah Agricultural Experiment Station.

[3] Associate Chemist.

[*] Numbers in text refer to Bibliography at end of paper.

The quantity of the specific salt recovered varied, depending upon the method used in clarifying the solution (Table I).

TABLE I—PERCENTAGES OF NITRATES, CHLORIDES, AND SULFATES RECOVERED FROM CLARIFIED SOLUTIONS

Method	Salt Recovered Nitrates Per cent	 Chloride Per cent	 Sulfates Per cent	Method	Nitrates Recovered Per cent
Filter..........	98.4	100.1	100.1	Ferric sulfate	96.5
Centrifuge......	97.0	...	...	Calcium oxide	96.5
Sodium alum...	99.2	100.0	...	Calcium carbonate	96.3
Potassium alum.	99.6	...	...	Talc	94.6
Ferric alum.....	93.7	...	...	....	..

Since neither calcium carbonate nor talc gave clear solutions, they can be discarded. Conclusive .evidence has been produced to show that when lime is used in the determination of nitric nitrogen by the phenoldisulfonic acid, the aluminium reduction,[13] or the Ulsch reduction methods,[14] low results are obtained. This is not due to the lime carrying out with the colloid some of the nitrate, for similar results are obtained when lime is added to a pure solution of sodium nitrate and the nitric nitrogen determined directly by the Ulsch method.

It therefore appears that the Pasteur-Chamberland filter, centrifuge, or sodium or potassium alum is best suited to use as a flocculent in the determination of nitric nitrogen in the soil. Moreover, the evidence is conclusive that the filter does not retain quantities of chlorides, sulfates, or nitrates sufficient to vitiate the results in soil analysis.[14] Only the filter or centrifuge can be used where sulfates are to be determined in the solution.

Five grams of alum may be added to a soil solution without its interfering with the recovery of nitrates or sulfates, but the writers have yet to find a soil which requires over 2 per cent to give clear filtrates. On the other hand, when lime is used as the flocculent the quantity of nitric nitrogen recovered is inversely proportional to the quantity of lime added to a soil-water mixture.

TIME OF EXTRACTION

The time necessary for water to dissolve the salts within a soil may vary greatly with the condition of the soil when the water is added, as well as the treatment given the mixture. If the water is not left in contact with the soil for a sufficient length of time some of the salts may be left unextracted, and if left too long denitrification may take place. Yet we find a large variation in the time recommended by different workers.[5,6,11,15,16,17]

In order to obtain more exact information on this subject, the writers extracted with 500 cc. of water for varying lengths of time 100-g. portions of various soils containing, in the case of nitrates and chlorides, 2 g. of alum. When sulfate was determined the alum was omitted. The samples, in 1000-cc. bottles, were agitated in a mechanical shaker for the time indicated and allowed to stand long enough to settle (not over 10 min.), and the nitrates, chlorides, and sulfates were determined by the Ulsch,[14] Volhard,[18] and gravimetric methods,[19] respectively. The average results for a number of determinations are given in Table II.

TABLE II—PERCENTAGES OF NITRATES, CHLORIDES, AND SULFATES EXTRACTED FROM SOIL IN VARYING LENGTHS OF TIME

SALT	Time of Shaking (Minutes) 5	 10	 15	 20	 30	 35	 40	 45
Nitric nitrogen..	100.4	100.4	98.5	...	101.3	101.3	98.1	...
Chlorides....	100.1	100.3	..	100.0	100.2	...	...	99.9
Sulfates.....	88.3	...	..	100.8	97.6	...	102.8	101.7

Inasmuch as these tests were made on finely powdered soil and the soil-water mixture was thoroughly agitated for the time indicated, they would not represent the condition where unpulverized soil was treated with water. So far as the nitrates and chlorides are concerned nothing is to be gained by shaking the soil longer than 5 min., but in the case of the sulfates equilibrium is not reached until they have been shaken 40 min.

These results were obtained from solutions not nearly saturated. For example, at 0° 100 g. of water will dissolve 26.9 g. of anhydrous magnesium sulfate, or 76.9 g. of the heptahydrate, or 4.8 and 55.59 g. of the corresponding salts of sodium. Under the present conditions there are present but 2.25 per cent of sulfates calculated as sulfuric acid (about half and half sodium and magnesium sulfates). If, as frequently happens, soils are rich in gypsum, much longer shaking will be necessary to attain equilibrium in any ratio of soil to water which we wish to use.

RATIO OF SOIL TO WATER

We find little regularity in the ratio of water to soil, used by different workers.[5,6,15,20,21,22] In the present investigation, the writers have made determinations of the various salts in soil and soil to which dried blood was added, varying only the ratio of water to soil. The average results for a number of determinations are given in Table III.

TABLE III—PERCENTAGES OF SALTS EXTRACTED WITH VARYING RATIO OF SOIL TO WATER

SALT	RATIO 1:5	 1:10	 1:15	 1:20	 1:25
Nitric nitrogen..................	99.8	98.6	97.2	97.8	100.0
Sodium chloride.................	99.9	100.0	99.5	99.9	...
Sulfates.........................	99.6	98.8	101.2	100.0	...

The difference found is only what could be attributed to experimental error. Hence, we may conclude that the ratio of soil to water is immaterial, provided the soil does not contain sufficient salt to give a saturated solution. However, the water in the sample must be taken into consideration. The facts that the same quantity of salt is extracted with the varying quantities of water and that nearly 100 per cent is recovered in the various experiments reported in this work make it very doubtful if Allen and Bonazzi's[23] contentions are justified, that the determination of the nitric nitrogen in the water extract does not give a determination of the nitric nitrogen in the soil.

USE OF AN ANTISEPTIC

Most workers assume that if the soil is to stand in contact with the water any length of time and nitrates are to be determined, an antiseptic should be added; yet, we have no definite information as to its quantity. In many cases the quantity added may actually accelerate the biological transformations going on in the soil. Moreover, it is not immaterial what antiseptic be used, for chloroform[10] used in the presence of lime with the phenoldisulfonic acid method gives inconsistent results.

In order to determine the error due to the standing of the soil solution, 100-g. portions of a rich garden soil were treated with water and varying quantities of nitric nitrogen and the quantity of nitric nitrogen present was determined after varying lengths of time. The average results are given in Table IV.

TABLE IV—MILLIGRAMS OF NITRIC NITROGEN RECOVERED FROM SOIL AFTER VARYING LENGTHS OF TIME

Hours	Nitrogen Recovered in 100 G. Soil	 100 G. Soil + 20 Mg. N. N.	 100 G. Soil + 40 Mg. N. N.
0	36.85	53.35	72.85
24	36.53	53.44	72.23
48	34.00	55.28	70.00
120	26.00	50.40	67.20
144	19.90	46.24	53.95

After the first 24 hrs. there was a gradual increase in loss. This indicates that the loss where the solutions are to stand some time may be appreciable. However, considerable quantities of nitric nitrogen disappear from a mixture of soil and fresh horse manure. This is often considerable during the first 24 hrs., even in the presence of 2 per cent of sodium alum. Repeated tests of water extracts of ordinary fertile soils kept at 24° C. for 24 hrs. showed no loss of nitric nitrogen, and even after 48 hrs. the loss was always very small.

It is evident, therefore, that where the soil-water mixture, or the soil extract, is to stand some time precautions must be taken to prevent a loss of nitrogen. The antiseptics which have been used are lime, alum, chloroform, and thymol. Lime interferes with the determination of nitric nitrogen and can be discarded. The results from tests on the other three are given in Table V.

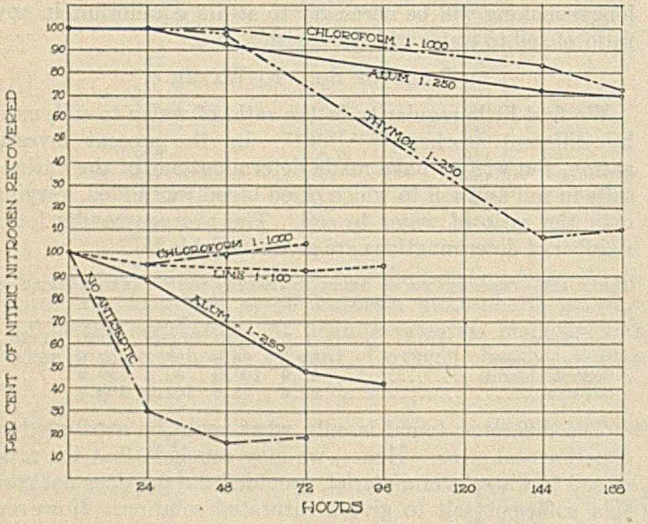

Fig. 1

Table V—Milligrams of Nitric Nitrogen in Soil after Varying Lengths of Time with Antiseptic

Treatment	At First	After 24 Hrs.	After 48 Hrs.	After 144 Hrs.	After 168 Hrs.
Soil + 2 g. alum	48.00	47.63	45.20	35.00	33.60
Soil + 2 g. alum + 20 mg. nitric nitrogen	67.96	67.26	65.44	58.14	55.34
Soil + 2 g. alum + 40 mg. nitric nitrogen	89.68	87.28	84.34	77.01	72.85
Soil + 2 g. alum + thymol	49.04	49.00	48.30	4.00	5.00
Soil + 2 g. alum + thymol + 20 mg. nitric nitrogen	69.36	67.68	67.96	4.40	4.00
Soil + 2 g. alum + thymol + 40 mg. nitric nitrogen	89.26	88.36	8.26	1.40	4.00
Soil + chloroform	51.80	51.80	51.30	43.40	37.80
Soil + chloroform + 20 mg. nitric nitrogen	71.94	71.87	71.46	60.66	57.55
Soil + chloroform + 40 mg. nitric nitrogen	88.46	91.06	88.26	80.84	72.86

Similar data are illustrated graphically in Fig. 1, in which the upper graphs give results obtained on a rich greenhouse soil, while those at the bottom are from a soil-manure mixture.

Table VI—Milligrams of Nitric Nitrogen from Soil and Manure after Varying Lengths of Time

Treatment	Nitric Nitrogen Found			
	At First	After 24 Hrs.	After 48 Hrs.	After 72 Hrs.
Soil, no antiseptic	3.064	0.826	0.49	0.56
Soil + 2 g. alum	3.117	2.732	2.59	1.96
Soil + 2 g. alum + 0.5 cc. $CHCl_3$	3.067	2.980	3.06	3.22
Soil + 2 g. alum + 1.0 cc. $CHCl_3$	2.956	2.840	2.90	2.91
Soil + 2 g. alum + 2.0 cc. $CHCl_3$	2.800	3.010	2.90	2.89
Soil + 2 g. alum + 3.0 cc. $CHCl_3$	2.790	2.910	2.93	3.16

It is evident from the results reported in Table VI that nothing is to be gained by adding over 0.5 cc. of chloroform to 100 cc. of the soil-water mixture. Moreover, as these results clearly show, more concordant results are obtained when analyses are made immediately and the authors dispense with an antiseptic.

The losses of nitrogen reported in most of this work are maxima and probably would never be duplicated in regular work, because the soil contained such large quantities of nitrates and fresh horse manure. Moreover, the solutions were kept in an incubator at 24° C. during various intervals. It would appear that under ordinary conditions, where the time in which the soil is in the water is short and the temperature comparatively low, no loss would result with ordinary soil where the 2 g. of alum had been added.

Summary

Clear soil extracts may be obtained by adding 2 g. of lime, ferric sulfate, ferric alum, sodium alum, or potassium alum to the soil-water mixture, by filtering through the Pasteur-Chamberland filter, or by centrifuging. The last three procedures give a clear solution with a minimum loss of salt. Lime, ferric sulfate, and ferric alum cause a considerable loss of nitrates.

In the determination of chlorides and nitrates nothing is to be gained by agitating the soil and water for more than 5 min., provided the soil is finely divided and the solution vigorously shaken. A longer time of agitation is required to reach equilibrium in a soil solution in which sulfates are to be determined. This time will depend upon the quantity and quality of sulfates present.

Usually a ratio of one part of soil to five of water is sufficiently wide, but this also will depend upon the quantity and kind of sulfates present.

Where nitrates are to be determined in the soil solution and alum is used as the flocculent, no other antiseptic is necessary; where alum is not used and the solutions are to stand for some time it is well to add 0.5 cc. of chloroform to each sample.

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Composition Basis for Considering Water Requirements of Plants[1,2]

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The results of field and greenhouse experiments recorded in the following paper indicate that fertilization of a soil which responds to direct or indirect fertilizer treatment allows the plants to make their growth on a smaller amount of water and to have a different composition from what they otherwise would.

The same effect is produced by cultivation, which by opening up the soil increases bacterial activity, which in turn gives increased concentration of the soil solution.

Proper fertilization and cultivation minimize dangers to crops from drought injury in humid regions of the United States by having the plant go into the drought period with an accumulative reserve of soil moisture.

This work opens up the study of fertilization from the basis of water requirement.

THERE is hardly a plant for which one cannot find wide ranges in the published analyses. Different experiment stations have tried to produce high protein corn or to raise the content of some valued constituent in another crop. This question of variation in analysis is so mixed up with food chemistry that the writer has thought it worth while to search for reasons for this variation.

Some investigators have analyzed plants to find out what fertilizer constituents they contain, and have attributed the variations in analysis to lack of fertilizer constituents in the soil. In accordance with Liebig's theories, they have added plant food to the soil in quantities equal to those taken out by the crop. Another method of study of plant growth has been to try to determine directly from the soil analysis what is lacking, and how to fertilize for increased crops. The writer has worked out a rather novel method of attacking the problem, namely, the application of different fertilizer materials to the soil, and a study of the variation in plant composition and water requirements caused by these fertilizer treatments.

FIELD EXPERIMENTS

In some experiments made in 1914 in orchards where cultivation was the largest variable, the writer found large differences in the moisture content of the soil at only one period of the year. The data in Table I show conditions in this young orchard. The results show that differences in soil management gave entirely different trees, as indicated by circumference gains, average weight of leaf, and per cent nitrogen in leaves. The importance of cultivation, by which air is let down into the soil and chemical reactions allowed to take place, is clearly shown in this table.

The two plots where the trees made the greater growth have much larger nitrate contents and have lost relatively much less water up to the height of the growing season. Records on rainfall have been kept, and study of the relative absorption and retention of water by this soil under the different systems of management has shown very little difference under the cultural treatments in the absorptive capacities of the surface with prevailing rates of rainfall. It appears, then, that the immense differences in the changes of relative weights of water in the soil must have something to do with the water utilization by the plants.

Kiesselbach of Nebraska makes the following statement:[3] "Up to an optimum soil productivity the amount of water transpired per pound of dry matter reduces with an increase in available nutrients." Again he says:[4]

> 21—The water requirement per pound of dry matter is much larger in an infertile soil than in a fertile soil. Increasing the fertility of the soil reduces the water requirement for grain production and for total dry matter. An application of manure has a much greater effect upon an infertile than upon a fertile soil. Thus, as an average for 2 yrs., equal applications of sheep manure to infertile, intermediate, and fertile soils reduced the water requirements for ear corn production 42.6, 25.4, and 10.5 per cent, respectively. For total dry matter these water requirements were reduced 28.9, 17.1, and 8.1 per cent, respectively. However, the total water requirement per plant was increased by an application of manure to infertile, intermediate, and fertile soil, respectively, 106.7, 42.6, and 28.7 per cent. From these figures it is apparent that increasing the fertility does not reduce but rather greatly increases the total amount of water necessary per plant. This is due to increased plant growth. The reduction in water requirement per pound of dry matter is due, not to some effect of a denser soil solution upon the need for a rapid transpiration rate, but, rather, simply to a more thrifty and vigorous growth of the plant, resulting from a more favorable supply of food materials. It appears to be more a matter of nutrition than of transpiration.
>
> 23—The average water requirement per pound of dry matter of two varieties of corn which had been grown for many years under the humid conditions of New York was approximately the same as the average for two varieties which had been grown continuously under the relatively dry conditions of western Nebraska.

TABLE I—ORCHARD MANAGEMENT INVESTIGATIONS

(Data under Different Systems of Soil Management)

	Clean Culture Cover Crop	Accumulative Straw Mulch	Sod for Several Years
Average circumference gains of trees 1911–1916, cm.	25.5	25.9	17.1
Average weight per leaf, grams	1.18	1.49	1.08
Nitrogen in leaves, per cent	2.31	2.36	1.71
Average nitrate content of soil during growing season	57.5[1]	47.0[1]	14.5[1]
Relative wts. water in soil at start of growing season, lbs.	11.40[2]	11.56[2]	11.86[2]
Relative wts. of water in soil at height of growing season, lbs.	8.45[2]	11.27[2]	3.78[2]
Change in relative wts. of water in soil, lbs.	2.95[2]	0.29[2]	8.08[2]

[1] Parts NO_3 per million parts of dry soil.

[2] Areas of surface 12 in. by 12 in. by 9 in. in depth.

Kiesselbach's field work was largely under relatively dry conditions throughout the growing season. It is the writer's observation that in most of the humid regions of the United States periods of water deficiency are relatively short; therefore the decrease in relative water requirements of variously fertilized plants will let those under better conditions go through the drought on an *accumulative water reserve.* Moisture determinations made for several years in the orchard reported on in Table I show that variations in moisture were not accounted for by relative differences in the water absorbing and evaporating powers of the soils of the different plots. Ample water was always present during drought periods on those plots where increased fer-

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[1] Presented before the Division of Agricultural and Food Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] The basis for this work consists largely of data secured by the author or under his direction while in the employ of Purdue University Agricultural Experiment Station.

[3] Letter to the author.

[4] Nebraska Agr. Expt. Sta., *Research Bulletin* **6**, 15

tility was shown by leaf weight, nitrogen content of leaves, and relatively higher growth characteristics.

On the basis of these facts and certain other observations, the writer considered that soils of humid regions contain ample moisture, under all systems of treatment, at the start of the growing season. The moisture differences at the height of the season were so large when different plots were compared (during so-called drought periods) that the conclusions drawn in the introductory paragraphs seem tenable.

GREENHOUSE EXPERIMENTS

Greenhouse experiments were organized on the basis of this field work, according to most careful and approved methods, with variations in fertilization, to see if the use of water by plants bears any direct relation to plant composition. The moisture content of the soil was kept uniform in all cases and the cultural pots were so rotated that differences of light and other factors of the greenhouse would be overcome.[5]

TABLE II—VARIATIONS IN WATER REQUIREMENTS AND PLANT COMPOSITION DUE TO DIFFERENT FERTILIZER TREATMENTS OF *Capsicum Annuum Abbreviatum*

	Check[1]	One Application of Limestone	Two Applications of Limestone	Three Applications of Limestone and Phosphorus Fert.	Three Applications of Limestone and Nitrogen Fert.
Water requirement per unit dry matter	1785	1415	1402	1323	1215
Height of plants at maturity, cm.	25.3	24.2	26.9	29.4	34.5
Wt. of peppers harvested, grams	160	182	212	258	418
Dry weight of four plants, grams	43.1	42.7	43.8	51.8	80.5
Nitrogen in plants, per cent	1.33	1.30	1.30	1.32	1.53
Ash of plants, per cent	7.12	7.00	7.08	6.53	5.79

[1] Soil was Sioux silt loam taken from the experimental field at the Indiana Agricultural Experiment Station.

Table II shows a decrease in water requirement due to fertilization, which varies inversely as the weight of peppers produced and as the dry weight of the plants themselves. The per cent of nitrogen in the plants bears an inverse relation to the water requirement and a direct relation to the per cent ash. These experiments are taken as proof that the water requirement of a plant is decreased by fertilization when the plant is grown on a soil which responds to fertilization.

TABLE III—VARIATION IN WATER REQUIREMENTS AND PLANT COMPOSITION DUE TO DIFFERENT FERTILIZER TREATMENTS OF HEAD LETTUCE

	Check[1]	5 Ton Dry Manure[2]	NPK[3]	10 Ton Dry Manure	Double NPK	5 Ton Dry Manure and NPK
Water requirement per plant as harvested	37.9	24.3	21.9	22.3	16.0	16.1
Green weight, grams	20.7	34.1	66.4	57.5	115.5	80.3
Moisture content of plants, per cent	87.9	89.8	92.1	91.8	92.3	93.1
Nitrogen in tops of plants, per cent	1.48	1.75	2.21	2.08	2.44	2.58
Nitrogen in roots of plants, per cent	0.87	0.84	0.93	0.81	0.96	1.07
Phosphorus in ash of plants (tops), per cent	0.25	0.36	0.40	0.36	0.67	0.69
Calcium in ash of plants (tops), per cent	1.84	2.74	3.06	1.96	2.81	2.08

[1] An open sandy soil was used.
[2] Well rotted horse manure containing 65 per cent moisture used.
[3] NPK from dried blood, banner bone, and muriate of potash in quantities of each element equal to one-third the nitrogen in 5-ton dry manure.

The data given in Table III are confirmatory of those presented in Table II, although obtained on a different soil and with a different plant.

Table III shows that:

1—The 5-ton manure with complete fertilizer has decreased the units of water required to produce one part of green weight by over one-half.

2—The weight of plants grown show a variation of nearly 400 per cent based on the check.

3—The changes in water requirement through a study of moisture content of the plants, the per cent nitrogen in tops, the per cent nitrogen in roots, the phosphorus content of plant ash, and the calcium content of plant ash are evidence that plant composition and water requirement bear a relation.

This work shows the fallacy of the old statement that "fertilization burns out the soil."

There is a common saying, "Cultivate to conserve soil moisture and you will have larger crops." The author believes that "cultivate to let air into the soil, thereby increasing bacterial activities which in turn cause the plants to get more plant food and grow larger on less moisture," would be nearer the truth.

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[5] *Botan. Gaz.*, **66** (1918), 364.

Eastman Pure Organic Chemicals

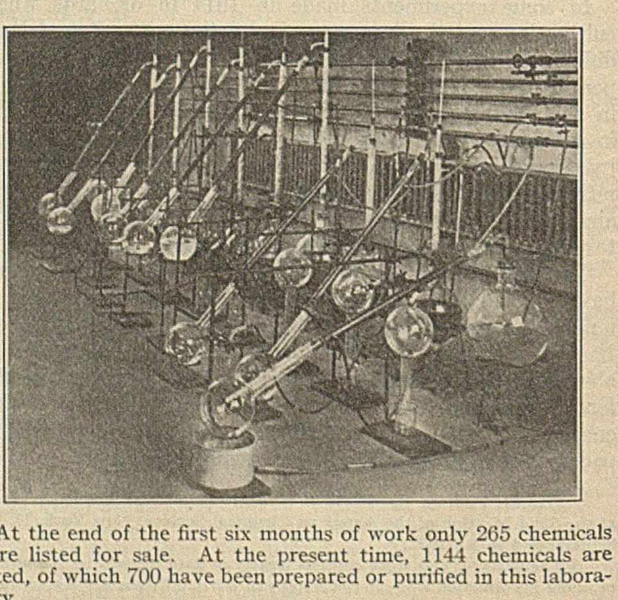
The lecture by C. E. K. Mees and H. T. Clarke on "The Preparation of Synthetic Organic Chemicals at Rochester," which was delivered at the Montreal Meeting of the Society of Chemical Industry last August, is being distributed in pamphlet form by the Eastman Kodak Company.

After discussing the war crisis which necessitated the manufacture in this country of pure chemicals for use in research, the authors describe in interesting detail the laboratories of the Eastman Company which are devoted to this work.

Laboratories and equipment differ in many respects from the research laboratory and from the industrial laboratory. On account of the large number of products required in small amounts, it is not feasible to instal large-scale apparatus suitable for one process only. On the other hand, operating on the laboratory scale is very expensive. The problem is, therefore, to operate with apparatus applicable to as many processes as possible, and to work on as large a scale as this limitation permits.

As an example of the modifications, the cement floors are bounded by open gutters, while supply pipes for water, gas, compressed air, vacuum, steam, and electricity run along the walls. A great deal of work can thus be carried out on the floors, with economy of space and other advantages. The accompanying photograph illustrates such a set-up for fractional distillation.

The pamphlet is abundantly illustrated with photographs of modified laboratory equipment.



At the end of the first six months of work only 265 chemicals were listed for sale. At the present time, 1144 chemicals are listed, of which 700 have been prepared or purified in this laboratory.

The Physiological Principles Governing Ventilation When the Air Is Contaminated with Carbon Monoxide[1,2]

By Yandell Henderson and Howard W. Haggard

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VITIATION of the atmosphere by the products of combustion and especially of incomplete combustion is recognized as one of the most important industrial conditions affecting health. Progress in this field has, however, dealt chiefly with the effects of high concentration of the gases concerned; that is, with conditions verging on asphyxia. Thus the investigations carried out heretofore for the United States Bureau of Mines have had chiefly in view estimations of such conditions as the amount of exhaust gas from traction engines which would be distinctly dangerous to coal miners, and the concentration of carbon monoxide which, after an explosion, would incapacitate the men from escaping. But in regard to the effects of small amounts of carbon monoxide and related gases, and the dependence of these effects, especially decrease of mental and physical efficiency, upon duration of exposure, there have not been collected data upon which definite standards could be based.

The plan to construct tunnels under the Hudson River between New York and Jersey City for the use principally of motor vehicles has therefore raised several problems which have previously never been extensively investigated. Whereas the conditions in coal mines and about gas producer plants apply only to healthy men, the conditions which will prevail in the tunnel under the Hudson River will affect the general public, not only healthy adults but children and even invalids. The amount of traffic is likely to be large, even from the beginning, and is likely to increase in a few years to the maximum capacity of the roadway. The total amount of exhaust gas discharged from passenger cars and trucks will therefore be considerable. The distance between the ventilating shafts at the pier heads on the two sides of the river will be somewhat more than 3300 feet—a distance greater than in any existing tunnel used by motor vehicles—and the total length of the tunnel about 8500 feet between portals. The ventilation must, therefore, be ample to prevent not only danger, but even slight discomfort, and must be managed in such a fashion as to avoid excessive wind velocities. The cost of installing ventilating fans will, in any case, be an appreciable item in the initial construction, and the maintenance of artificial ventilation during the operation of the tunnel is likely to be one of the largest single items of continuing expense.

Accordingly, the commissions of the states of New York and New Jersey through their Chief Engineer, Mr. Clifford M. Holland, contracted with the Bureau of Mines to undertake on their behalf the investigation of these basic problems:

1—The amount and character of the exhaust gas produced by various types and sizes of passenger cars and trucks.

2—The nature of the toxic substances in exhaust gas, and their allowable concentration—that is, the extent to which the gas must be diluted with air to become practically harmless.

3—The movements of air in ducts.

4—A synthesis of all these and related matters on a practical working scale in a vehicular tunnel constructed for this purpose in the experimental coal mine of the Bureau of Mines near Pittsburgh.

The results of these investigations will together afford the data upon which plans and designs for the ventilation of the tunnel may be intelligently based.

Problem 1 was placed in charge of Mr. A. C. Fieldner,[16,*] supervising chemist of the Bureau of Mines Experiment Station, Pittsburgh. Problem 2, of which the results are here to be summarized, was assigned to Professor Yandell Henderson of Yale University, consulting physiologist of the Bureau of Mines. The work was carried out with the collaboration of Howard W. Haggard, A. L. Prince, M. C. Teague, and R. M. Wunderlich in the Physiological Laboratory at Yale University. Problem 3 was investigated by Professor A. C. Willard of the University of Illinois. Problem 4 was supervised by Mr. A. C. Fieldner with the advice and collaboration of all concerned.

FUNDAMENTAL CONSIDERATIONS

Although carbon monoxide is the cause of more deaths than the total due to all other gases, apart from a single reaction it is a physiologically inert and nonpoisonous substance. This reaction is its combination with hemoglobin, the red coloring matter and oxygen-carrying element of the blood. To whatever extent hemoglobin is so combined, it is rendered incapable of transporting oxygen from the lungs to the tissues and organs of the body, until the carbon monoxide is again displaced. It is highly probable that all of the results of inhalation of carbon monoxide are due directly or indirectly to oxygen deficiency. Even when other toxic substances are present—as in smoke, in fumes from explosives, and in other incomplete combustions—carbon monoxide is usually the chief cause of injury or death. It acts wholly through asphyxia.

The body of an adult man of average weight contains enough hemoglobin to hold about 600 cc. of oxygen. If completely saturated, it would hold the same amount of carbon monoxide, one molecule of carbon monoxide replacing one molecule of oxygen in the blood. The absorption of 6 cc. of carbon monoxide from the lungs produces, then, 1 per cent of saturation and abolishes 1 per cent of the oxygen capacity.

The unit in which various concentrations of carbon monoxide are commonly measured and expressed for purposes of ventilation is one "part," or a certain number of "parts" of this gas mixed with 10,000 times as much air. A "part" is a hundredth of 1 per cent of an atmosphere. A man at rest breathes about 8000 cc. of air per minute, of which about 6000 cc. reach his lungs, or 60 liters in 10 minutes. Let us suppose that this air contains one part of carbon monoxide, or 6 cc. in 60 liters, and that all of this 6 cc. is absorbed. The blood would then become saturated at the rate of 1 per cent every 10 minutes per "part" of carbon monoxide in the air. Evidently the duration of exposure is a limiting factor in the amount absorbed, for one cannot absorb more than one inhales.

It appears that when a man begins breathing any low concentration of carbon monoxide mixed with air, absorption at very nearly this rate does occur, but only at first. Then the rate becomes slower. Even if the exposure is prolonged, carbon monoxide merely displaces oxygen from the blood up to a point

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[1] Received December 24, 1921.

[2] An abbreviation of a report to the Chief Engineer of the New York and New Jersey Tunnel Commissions. State of New York 1921, Legislative Document **64**. Published here by permission of the Director of the U. S. Bureau of Mines and of the Chief Engineer of the Tunnel Commissions. For a more extended discussion of features of hygienic importance, see Henderson, Haggard, Teague, Prince, and Wunderlich, *J. Ind. Hgy.*, **3** (1921), 79, 137.

[*] Numbers in text refer to Bibliography.

of equilibrium depending upon the relative amounts, or mass actions, of carbon monoxide and oxygen in the air breathed and the intensity of the affinities of the two gases for hemoglobin. If thereafter the pressure of oxygen is high enough and that of carbon monoxide is low, or absent as in pure air, oxygen can likewise displace carbon monoxide and thus completely restore the oxygen-carrying power of the hemoglobin. The blood is neither directly changed nor injured by the process.

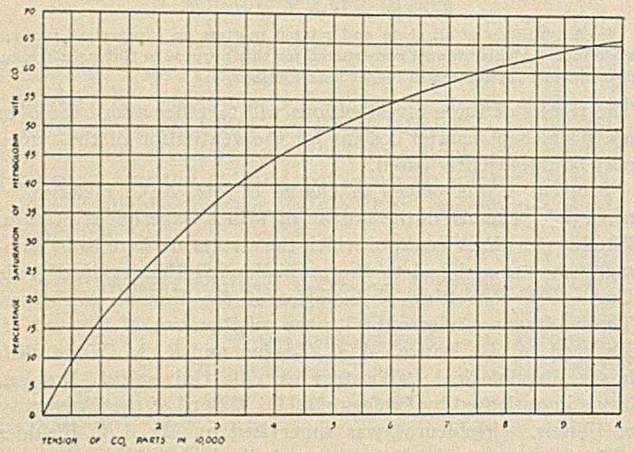

Fig. 1—Final or Equilibrium Distribution of Hemoglobin between Carbon Monoxide and Oxygen When Various Low Concentrations of Carbon Monoxide in Air Are Inhaled for an Indefinitely Long Time. (After Haldane)

Hemoglobin attracts carbon monoxide about 300 times as strongly as it does oxygen. Thus, if P_{O_2} and P_{CO} are the pressures of oxygen and carbon monoxide, and Hb_{O_2} and Hb_{CO} the amounts of oxyhemoglobin and carbon monoxide hemoglobin in the blood, the relations are expressed by the formula:

$$\frac{P_{O_2}}{P_{CO} \times 300} = \frac{Hb_{O_2}}{Hb_{CO}}, \quad \text{or}$$

$$\text{percentage } Hb_{CO} = \frac{P_{CO} \times 300}{P_{O_2} + (P_{CO} \times 300)};$$

or more specifically, if there are 1500 parts of oxygen and 2 of carbon monoxide, the formula works out to:

$$\frac{2 \times 300}{1500 + (2 \times 300)} = 28.5 \text{ per cent saturation with carbon monoxide.}$$

The air in the lungs contains about 1500 parts of oxygen in 10,000. (It is actually somewhat less than 15 per cent of oxygen. The affinity of hemoglobin for carbon monoxide may also be less, or more, than 300. We are here using round numbers merely to illustrate the principle without attempting mathematical precision.) We may calculate the blood equilibrium for any concentration of carbon monoxide in the air, and from such data we may obtain the carbon monoxide dissociation curve of the blood (as shown in Fig. 1—an expression of the fundamental relations established by the investigations of J. S. Haldane).[3,4,5,6,15]

This curve indicates that, if air containing 2 parts of carbon monoxide in 10,000 is breathed for a time long enough to attain equilibrium, the blood should become about 28 per cent saturated; with 4 parts, 44 per cent; with 6 parts, 54 per cent; and so on. In the curve it is to be seen that, for instance, the equilibrium value for 10 parts of carbon monoxide in 10,000 of air is 66.6 per cent saturation, which is a sufficient degree of saturation to render a man unconscious and totally helpless. If continued, the asphyxia might lead to serious permanent injury or even death.

The question of greatest practical importance is: How long a time would be required to attain this or any other definite percentage of saturation? In other words, what is the physiological law defining the rate of absorption of carbon monoxide into the blood? From the simple calculation, given previously, regarding the oxygen capacity of the body and the volume of air drawn into the lungs, it appears that a man breathing 10 parts of carbon monoxide would inhale enough of the gas to become 66.6 per cent saturated in 66.6 minutes. But, as already indicated, the more carbon monoxide the blood contains, the greater becomes the force with which this gas tends to diffuse out again into the air. The more nearly this tendency equals and counterbalances the pressure of the gaseous carbon monoxide in the lungs, the slower the absorption of more carbon monoxide becomes. Thus to attain a condition of complete blood equilibrium many hours would be actually required; indeed, the time is indeterminate. Doubtless other factors also play a part in retarding and stopping absorption.

It appeared to us, however, that *a definite quantity for determination would be the time required for attainment of percentage saturations of one-half the equilibrium values.* Thus, in an atmosphere containing 2 parts of carbon monoxide, for which the blood equilibrium is about 28 per cent, how long a time would be required for the blood to become 14 per cent saturated? How long with 4 parts and an equilibrium value of 44, to attain 22 per cent saturation; or with 6 parts and an equilibrium of 54 to reach 27 per cent? The answer to this question is the principal practical contribution to knowledge which we have to make—namely, that *the time for attainment of half equilibrium for persons sitting at rest and breathing concentrations of carbon monoxide up to 7 parts is never considerably less than one hour.* This fact is, we believe, of fundamental importance for ventilation engineering. We have established it purely experimentally. It might easily be correlated with the oxygen consumption and the carbon dioxide elimination, but we have not thought this to be of practical importance to the immediate object of this report. It does not, nor does it aim to, express what the average person does under the conditions, for many of our subjects fell much below this rate of absorption. None exceeded it. The value of the rule is that it expresses the worst attainable, or, so to speak, the "maximum load."

We may here conveniently consider the question, often raised, of possible extreme individual susceptibility. Such susceptibility might conceivably arise: (1) from anemia, that is, a subnormal amount of hemoglobin; (2) from an unusual avidity of the individual's hemoglobin for carbon monoxide; (3) from unusual susceptibility to the ill effects of oxygen deficiency; or (4) from a volume of breathing much above the ordinary. The first is unimportant practically, inasmuch as anemics need not spend long periods in ill-ventilated garages, nor ride through tunnels on slow moving trucks. If, however, they are transported at the speed of a passenger car or an ambulance through a two-mile tunnel containing the average concentration of carbon monoxide here to be proposed, the time of exposure will be too brief to allow an absorption sufficient for any considerable ill effects. The second possibility has been investigated by us, but has not been found to occur. (Owing to their highly technical and space-consuming character, these studies are omitted here, but appear in the full report.)

There is reason to believe that there are individual differences in the degree of the ill effects induced by considerable oxygen deficiency. Aviators and mountain climbers exhibit such differences, and in our more extreme tests headache has occurred in some persons at a somewhat lower percentage saturation of the blood than in others. We have, however, found no one who experienced this effect—the first sign of oxygen deficiency—under the conditions of the standards we shall propose.

The volume of breathing is by far the most important element in the rate of absorption of carbon monoxide and thus in the individual variations in the ill effects of inhalation of this gas. In general, the expired air of a healthy man contains 4 or 5 per cent of an atmosphere less oxygen than the inspired air, and this percentage deficit is nearly the same during rest with a breathing of 8 liters and under physical exertion with a respiration several times as large. In other words, the volume of breathing is roughly proportional to the amount of the oxidation and energy liberation occurring in the body. In our observations, persons of vigorous physique and large breathing rates have absorbed carbon monoxide much more rapidly, as measured in percentage blood saturation, than those of more sedentary habit and delicate physique. As the standard which we shall propose is one adjusted to protect even the strong, it will therefore afford an extra safeguard to the weak and sick, who breathe little (except in febrile cases) and who would, accordingly, absorb carbon monoxide comparatively slowly. Only in the case of children, whose active vitality involves a relatively large food and oxygen consumption and a corresponding volume of breathing, will this rule probably not hold. But even for the most active child, a period of exposure of only 10 or 15 minutes to the concentration of carbon monoxide here approved will not be long enough for any considerable absorption of the gas.

The particular problem before us—that of a standard for the ventilation of the proposed vehicular tunnels under the Hudson River—may, therefore, be thus simply expressed: What percentage saturations of the blood with carbon monoxide cause appreciable discomfort in healthy men sitting at rest, and what percentage saturations do not? The answer to this question, the probable duration of exposure of passengers through the tunnel, and the law of carbon monoxide absorption as above stated, are the three considerations on which any sound standard must be based.

In view of the foregoing discussion it is, we trust, clear that standards of concentrations, which will adequately protect men exposed for the greater part of an hour, will afford an enormous factor of safety for persons inhaling the vitiated air for only 10 or 15 minutes. We are informed by the engineers that all traffic through the tunnels will be in two distinct classes—namely, passenger cars, which will make the trip in 10 or 12 minutes, and trucks which may take as long as 35 or 40 minutes. The standards which we set ourselves to work out are such as will afford not only absolute safety but also complete freedom from any trace of discomfort for healthy and vigorous adults exposed for periods of 45 to 60 minutes.

Experiments on Men in Six Cubic Meter Chamber

The method of studying the effects of various concentrations of carbon monoxide upon which we have chiefly relied for establishing our standard is illustrated in Fig. 2. It involves a chamber of 6.4 cubic meters (226 cubic feet) capacity, the walls and door of which are covered with galvanized sheet iron with soldered joints. The door is easily made gastight by placing long strips of broad (2-inch) adhesive plaster over the cracks along lintel, jambs, and sill. The chamber holds any concentration of gas for a day without appreciable loss from diffusion through undiscovered leaks. A small hole in the door, covered by a piece of adhesive plaster, allows the hand of the subject to be thrust outside for the withdrawal of blood.

Into this chamber are introduced measured amounts of pure carbon monoxide, made by dripping formic acid into strong sulfuric acid and distilling it by gentle heat into a large bottle filled with water, which the gas displaces. The concentration of gas desired in the chamber is obtained by running into the bottle 640 cc. of water per part of carbon monoxide desired, and thus displacing this volume of gas from the bottle into the chamber. An electric fan in the chamber insures immediate and complete mixing. In our experiments, two checks on the concentration of gas in the chamber were obtained: (1) By analysis of the carbon monoxide, before it was introduced, by means of a modified Orsat apparatus, and ignition with an electrically heated platinum spiral; and (2) by analysis of a mixed sample of the air from the chamber by the iodine pentoxide method, or by means of diluted blood. (For a description of these analytical methods, see bibliographical references 1, 2, 3.)

In this chamber, in turn, the members of the staff of this investigation and a few other persons spent periods of one hour after amounts of carbon monoxide from 2 to 8 parts, and in one case, 10 parts, had been introduced. While the subjects sat and read most of the time, there were a sufficient number of acts—such as turning on the electric fan, standing up to look out of the window for a moment, opening and closing flasks to take air samples for later analysis, etc.—to correspond fairly well with the activity of the driver of a car. When we speak of the absorption of carbon monoxide by a person "sitting at rest," the condition must, therefore, be understood as only such moderate rest as this.

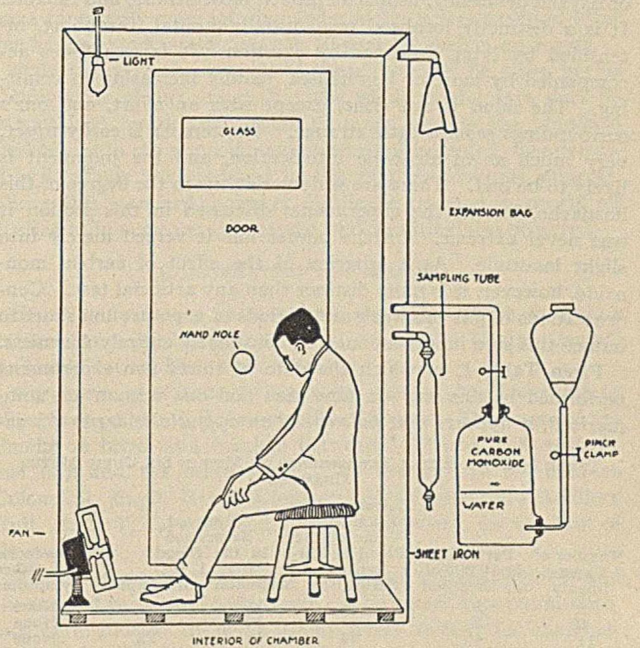

Fig. 2—Six Cubic Meter Chamber and Apparatus for Introducing Measured Amounts of Carbon Monoxide

Blood, to the amount of twenty or thirty drops, was drawn from a finger before the subject entered the chamber; and 0.02 cc. was drawn at the middle of the period and at the end, and usually once or twice during the next 3 hours. These blood samples were analyzed for carbon monoxide by the carmine titration method.[3]

After the subject had been out of the chamber for a few minutes, the tension of carbon monoxide in his lungs, supposedly in equilibrium with the blood, was determined by breathing back and forth several times, during 20 to 30 seconds into a rubber bag. Football, or basket ball, "bladders" were used for this purpose. (A series of check determinations on four subjects showed that the maximum concentration of carbon monoxide from these bags was reached in five rebreathings during 30 seconds.) This air was then analyzed for carbon monoxide by the iodine pentoxide method, or the blood carmine method. The subject's volume of resting breathing was determined either in or outside of the chamber by means of a mouth-piece, nose clip, double valves, Douglas bag, or gas meter; and the volume per minute was calculated.

In some experiments the respiration was increased by exercise, and the increase was measured and correlated with the correspondingly greater absorption of carbon monoxide. In these experiments the subjects did "stationary" walking or running in the chamber by lifting the feet and stamping. The exertion involved is considerable, but with care it can be kept quite uniform for half an hour at a time. The pulse was counted in the chamber, and before and after the test. The effects on the pulse and respiration of running up and down four flights of stairs, each 12 feet vertically, were also determined before and after the period in the chamber.

In a few cases the retinal fields were determined and plotted. With the degrees of anoxemia occurring in these experiments, however, the effects on vision in this respect were unimportant. The Romberg test, the ability to stand erect with eyes closed without wavering, was also used. In some cases after an hour in eight parts of carbon monoxide, it showed marked loss of equilibrium.

But of all signs and tests, both in the experiments in the small chamber here under discussion and in those that are to be described in the next section, the typical carbon monoxide, or oxygen deficiency, headache proved most definite and reliable. It is a distinctly localized pain, usually frontal, throbbing, intensified by lying down or by exertion. It is sometimes accompanied by more or less nausea, readily increasing to vomiting. The mind is not clear, except with an effort, and one's surroundings seem a little strange. The temper is easily upset, very much as in alcoholic intoxication, and the judgment is likely to be bad. There are wide variations in the degree of this headache, but in the experiments discussed in this section it was never extreme. On the border line it verged merely into slight lassitude. As a criterion of the effect of carbon monoxide, however, it is more distinct than any artificial test. Concentrations of gas too weak and periods of exposure too short to induce this sign in anyone may be considered entirely harmless.

From Table I, in which the data of thirty-two experiments performed in this way on nine men and one woman are summarized, it appears that *no one had an appreciable degree of headache after a period of 1 hour in the chamber with 4 parts of carbon monoxide* or less, and that with 6 parts the effect, if any, was usually very slight. With 8 parts there was decided discomfort for some hours, although not enough to interfere with efficient work in the laboratory or at the desk. After an hour in 10 parts even an unusually resistant subject (Y. H.) was decidedly miserable and averse to work for 5 or 6 hours, and could still recognize the effects after 12 hours. Examination of these data enables us to reach a working rule regarding the rate of absorption of carbon monoxide, for we find that up to and including concentrations of 6 parts of carbon monoxide in 10,000 of air the figures in Column 5 of Table I do not exceed values of about one-half those for complete equilibrium given in Column 3 and drawn from Fig. 1.

TABLE I—SUMMARIZING EXPERIMENTS ON MEN IN SIX CUBIC METER CHAMBER

Number of Experiments	Parts CO in 10,000 of Air Breathed	Corresponding Equilibrium Value of the Blood in Percentage Saturation	Observed Saturation in the Blood after 1 Hr.		Headache and Other Symptoms
			Minimum	Maximum	
2	2	28	11	12	None
3	3	37	10	14	None
11	4	44	14	22	None
9	6	55	18	26	None in 7 Slight in 2
4	8	62	26	32	Marked in all 4
1	10	67	38	..	Severe

In other words, during one hour sitting at rest in such atmospheres, a man's blood never absorbs appreciably more than half the amount of carbon monoxide which it would take up if he stayed in the atmosphere indefinitely. Inactive and small breathing persons absorb less. At concentrations of 8 and 10 parts of carbon monoxide the figures deviate slightly from this rule, but the rule of half saturation appears to be safe and convenient up to 7 parts. From the experiments in which work (stationary walking) was performed in the chamber it appears that a man who exercises sufficiently to double the volume of breathing absorbs as much carbon monoxide in half an hour as he does at rest in one hour. We have found in other experiments, that when walking fast a man breathes about twice as much air (with a corresponding energy expenditure and oxygen consumption) as when sitting still, and that when hurrying or doing rather heavy manual labor he breathes about three times as much, and under exertion even more. These figures may be directly applied to conditions as they occur in regard to absorption of carbon monoxide. The estimation of the time required for half equilibrium must be shortened accordingly.

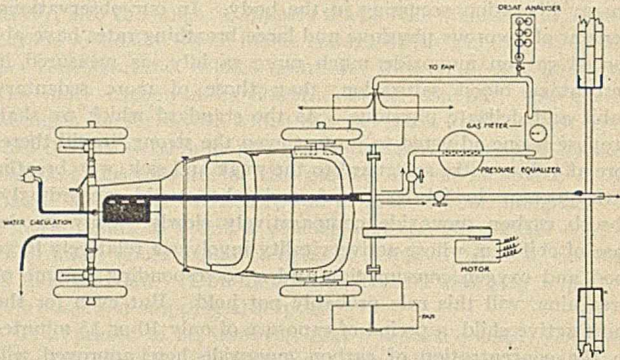

FIG. 3—APPARATUS IN LARGE GASSING CHAMBER FOR PRODUCING EXHAUST GAS UNDER CONDITIONS SIMULATING THOSE IN A VEHICULAR TUNNEL

ELIMINATION OF CARBON MONOXIDE—As regards the elimination of carbon monoxide after gassing, our data show that the process is not complete until one or two hours, or even longer, after return to fresh air. Roughly, the rate of elimination is 30 to 50 per cent per hour, depending doubtless on bodily activity and the volume of fresh air breathed.

OBSERVATIONS IN LARGE GASSING CHAMBER

The experiments above described involve exact, but rather artificial conditions. Exhaust gas is not pure carbon monoxide and the number of persons who could be tested in the 6 cubic meter chamber was quite limited. It appeared essential, therefore, to obtain confirmatory observations under as nearly real conditions and on as many persons as possible. For this purpose a brick building, 30 feet square, with walls 12 feet high at the side, and a hip roof, was erected. Its cubic capacity was approximately 12,000 cubic feet of air, which is about the volume of a section of the vehicular tunnel which will contain one car when the traffic is active.

A Ford car was installed (as shown in Fig. 3) near the middle of this chamber, with a continuous stream of water running into and out of its radiator to prevent overheating. The axles were supported on a wooden framework so that the rear wheels turned clear of the ground. Against them were pressed two large wooden pulley wheels on a piece of heavy shafting, at the ends of which were wooden paddle wheels. The engine of the car, therefore, ran with a fair load, and the power was expended in mixing the air in the chamber. The paddle wheels did this so effectively that in a number of tests practically uniform concentrations of exhaust gas were found simultaneously in all parts of the chamber.

The exhaust of the car was connected to a 2-inch iron pipe with a T and two valves. From one valve a pipe led to a gas meter, and discharged close to one of the paddle wheels, which drew in and distributed the gas. The pipe from the other valve led outside of the building. Thus, by adjusting the valves, all or any part of the exhaust gas could be discharged into the chamber, and this volume read on the meter. Samples of the exhaust gas unmixed with air were analyzed for carbon monoxide in an Orsat apparatus, with ammoniacal cuprous chloride as the absorbent. The percentage ranged between 5.5 and 6.8 per cent with an average of about 6 per cent. The engine discharged a total of about 25 cubic feet of exhaust gas per minute, from which we calculated that approximately 1.5 cubic feet of carbon monoxide were produced by the car per minute.

Diffusion from the chamber through the walls and roof, and through cracks around the doors and windows, was considerable. Whenever the engine was stopped, there was thus a drop of about one-third of the concentration of carbon monoxide in 15 minutes. Usually the entire exhaust of the engine was discharged through the meter into the chamber until the desired concentration of carbon monoxide was approximately reached. Thereafter, a part of the gas was discharged out of doors, and only enough was passed into the chamber through the meter to compensate for loss by diffusion. Samples of the air in the chamber were taken at intervals during the period of exposure, and the amount of carbon monoxide determined either by means of iodine pentoxide (with a correction for vaporized gasoline) or by the blood carmine method, or in both ways. Some discrepancies occurred in the analytical data, but it must be kept in mind that the methods were difficult and the amounts of the substance were minute far beyond the range of ordinary gas analysis.

With practice, considerable facility in controlling the concentration of carbon monoxide in the chamber was attained. The experimental conditions were quite realistic. The car was old and had had rough treatment, and the engine was somewhat irregular in action. The exhaust gas was, therefore, contaminated with at least as much gasoline, oil and soot, and other substances, in addition to water vapor, carbon monoxide, and carbon dioxide, as may be met with in any well-regulated vehicular tunnel. Owing to the fact that vaporized gasoline and other constituents of exhaust gas beside carbon monoxide act upon iodine pentoxide (the condensation of these vapors by means of liquid air had not then been worked out), the figure 0.6 was determined as the factor by which it was necessary to multiply the iodine liberated in analysis of chamber air for the estimation of the carbon monoxide.

Two Typical Experiments in Large Gassing Chamber

Protocol 1

The atmosphere in the chamber gave on analysis 4 parts of CO in 10,000 of air over the entire period of 1 hour. Eight subjects were exposed to this for the full hour. For the most part they were seated. The approximate percentage saturation of the blood with carbon monoxide (per cent HbCO) was determined indirectly from analysis of the alveolar air from the lungs, obtained by breathing back and forth several times from and into a small rubber bag.

Subjects	Sex	Per cent HbCO	Headache and Other Symptoms
C. P.	Male	18	None
E. S.	Male	17	None
E. W.	Male	21	None
M. H.	Female	20	None
M. B.	Female	20	None
E. H.	Male	18	None
E. L.	Male	17	None
M. S.	Male	20	None

Protocol 2

The atmosphere in the chamber gave on analysis an average of 9 parts of CO in 10,000 of air. Seventeen subjects were exposed to this for the full hour. For the most part they were actively walking about. The percentage saturation of the blood with CO was estimated as in the previous protocol.

Subject	Sex	Per cent HbCO	Headache and Other Symptoms (as Reported by Subjects)
E. G.	Male	35	Dizziness, headache, and some nausea
A. V.	Male	37	Throbbing headache, general lethargy for 24 hrs.
A. D.	Male	30	Headache, nausea, and chills
J. O.	Male	29	Short period of dizziness, severe headache for 9 hrs.
L. P.	Male	27	Throbbing headache for 9 hrs.
M. O'C.	Male	37	Severe headache for 6 hrs.
J. F.	Male	35	Severe headache, vomited, in bed 5 hrs.
E. W.	Male	35	Severe headache for 20 hrs.
M. G.	Male	35	Severe headache for 5 hrs.
H. F.	Male	29	Severe headache for 8 hrs.
E. T.	Male	33	Nausea and severe headache for 7 hrs.
E. S.	Male	28	Headache for 8 hrs.
H. B.	Male	30	Severe headache and some nausea for 6 hrs.
H. L.	Female	30	Nausea and violent headache for 48 hrs.
E. W.	Male	27	Headache for several hours
A. W.	Male	28	Headache and some nausea
P. S.	Male	30	Severe headache and vomiting
J. S.	Male	28	Severe headache for 72 hrs.

In this chamber groups of a dozen or more persons at a time sat or moved about for periods of one hour. In addition to the staff of this investigation a number of students of the Yale Medical School served as subjects. We take this opportunity to recognize the intelligent and valuable service rendered by these young men and women.

After the tests the general condition and feelings of the subjects, particularly the occurrence or absence of headache, were noted. When the subjects had breathed fresh air for 5 minutes after leaving the chamber, samples of lung air, obtained by having them rebreathe repeatedly into a small rubber bag, were analyzed for carbon monoxide. In such analyses the gas found is that which has diffused out of the blood into the lung air, and the analytical data indicate, therefore, the tension (partial pressure) of the carbon monoxide in the blood. The effect of running up and down four flights of stairs was also noted, as exercise markedly intensifies asphyxial symptoms. We have repeatedly seen fainting induced by a less exertion after one hour of moderate activity in 10 parts of carbon monoxide.

Only two typical protocols of these tests can be given in this abbreviation of our report, but the whole of the data may be summarized by the statement that, so long as the standard worked out in the previous section was not exceeded, no appreciable ill effects were induced in any of the numerous subjects. Above this standard, however, headache resulted in nearly all cases, and in some persons nausea and vomiting also occurred.

Confirmatory Experiments

Some confirmatory observations were also made in public garages, and in the taxicab stand under the Grand Central Railroad Station, New York City.

EXPOSURE OF HORSES TO EXHAUST GAS—A few observations were made on two U. S. Army artillery horses. They were of the Percheron breed and weighed between 1400 and 1800 pounds, one bay and the other white. We are greatly indebted to Colonel R. E. D. Hoyle, Commanding Officer, Field Artillery Unit, R. O. T. C., stationed at Yale University, for the loan of the animals.

The car was taken outside of the tunnel gassing chamber and the exhaust gas piped to the inside. The horses were not hitched, but were allowed to move about freely inside the chamber. In each experiment a blood sample was drawn from the ear before and after gassing. The results obtained corresponded fairly closely with those on man.

The Rule of Half Equilibrium Value in One Hour

From well-established theory, as discussed above, and from the foregoing experiments, we have these data:

1—A curve (Fig. 1), which expresses the equilibrium relations between the partial pressure of CO in air and the percentage saturation of the hemoglobin of blood freely exposed to such air.

2—The rule that one hour may be used as the (minimum) period for attainment of one-half the equilibrium degree of blood saturation for a person at rest.

3—The fact that this period varies inversely as the energy expenditure and corresponding volume of air breathed.

4—The fact that for an exposure of one hour, 18 per cent saturation of the blood does not produce even a slight headache. For exposures of several hours, we have adopted for various reasons 12 per cent saturation (full equilibrium to 0.6 part per 10,000 of air) as the figure which would produce no appreciable decrease of comfort or efficiency.

These data are combined in Fig. 4. The two scales at the left show the corresponding values for CO in blood and CO in air, the ordinates and abscissae, respectively, of Fig. 1. The curves show the rate at which, as calculated from the half saturation rule, the blood would absorb CO when a man at rest breathes atmospheres of this gas of 1 to 7 parts in 10,000 of air. The time element is indicated below the abscissa in three scales according as the subject is sitting, walking, or working moderately. Horizontal dotted lines have been drawn at the levels of freedom from discomfort for exposures of one hour, and for exposures of several hours.

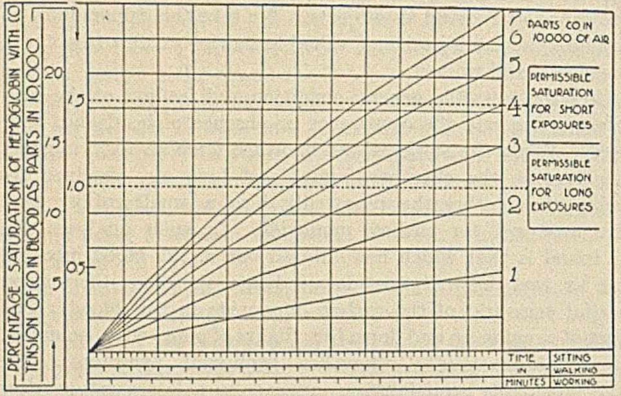

FIG. 4—CURVES SHOWING MAXIMUM RATE OF ABSORPTION OF CARBON MONOXIDE BY THE BLOOD IN PERSONS EXPOSED TO CONCENTRATIONS UP TO SEVEN PARTS OF CARBON MONOXIDE IN 10,000 OF AIR, FOR PERIODS UP TO 1 HOUR, DURING REST (SITTING), AND FOR SHORTER PERIODS OF WALKING AND WORKING. FOR DISCUSSION SEE TEXT

The way in which this diagram may be used is illustrated in Fig. 5. It is here supposed that the subject walks with the air current for 35 minutes while the CO increases gradually up to 7 parts per 10,000 of air. The small triangles show the increments of CO absorbed by the blood each in 5-minute intervals, and the total which might be reached. If the subject were sitting at rest in a car the triangles would be correspondingly smaller. If he were working hard they would be larger. If he were traveling against the air current the absorption and triangles would be largest at first and then progressively smaller. It is to be noted that the time element is the sum of all the bases of all the triangles, and not merely the abscissa of the highest concentration reached.

It is evident from this diagram that if at any point the concentration exceeds 6 parts of monoxide in 10,000 of air, men doing hard work for even a short time will be unfavorably affected. On the other hand, the curves show that passengers in cars going through the tunnel in 10 or 15 minutes will absorb very little carbon monoxide—a factor of safety which is, we believe, sufficient to afford ample protection for children and invalids. *The standard which we propose for exposures of 45 minutes—4 parts in 10,000 or its equivalent in an average of concentrations from 0 up to 6 in 10,000—affords, in the light of our experiments, not only complete safety but also an assurance of freedom from disagreeable effects.* Risk of considerable discomfort would begin at 8 to 10 parts of carbon monoxide in 10,000 of air in periods of one hour during rest and for shorter periods during exertion. Actual danger would begin with concentrations not very much higher and periods not very much longer. The point should be emphasized, however, that we are dealing only with a standard of chemical purity of the air. Other features of tunnel ventilation as, for example, wind velocity, moisture, temperature, etc., are not included in the standard here defined, nor is comfort in these respects assured by it.

The whole matter may be even more simply summed up in an expression involving the time measured in hours, the concentration of carbon monoxide in the air in parts in 10,000, and a constant for each degree of physiological effect. The physiological effects of all concentrations and times (within reasonable limits, that is, a few hours) may be then defined as follows:

1—Time × concentration = 3, no perceptible effect.
2—Time × concentration = 6, a just perceptible effect.
3—Time × concentration = 9, headache and nausea.
4—Time × concentration = 15, dangerous.

Physical exertion and increased breathing would reduce the constant in the first equation from 3 to 2, or 1, or even less, and would affect the other equations correspondingly.

CONCORDANCE OF THE STANDARD HERE PROPOSED WITH THE OBSERVATIONS OF OTHER INVESTIGATORS

The standard defined in Fig. 4 may seem, from the work of others, especially that of Haldane, unduly high, if one fixes attention upon the concentration of carbon monoxide in the air breathed; or it may appear unnecessarily low, if stated in terms of the maximum percentage saturation, *i. e.*, complete equilibrium of the blood and the corresponding tension. The work of Haldane is so preëminent in this field, alike in amount, thoroughness, and practicality, that discordance between the conclusions drawn from his investigations and the standard here proposed would require elaborate explanation and defense. In fact, however, we believe that when all aspects of the question are taken into consideration, our observations, and conclusions, although differing in detail, are essentially concordant with those of Haldane.[4,5] Briefly stated, his principal conclusions were as follows:

> The symptoms caused by carbon monoxide depend upon the extent to which the hemoglobin has been saturated. The symptoms are due solely to the deficiency of the oxygen percentage in the blood.
>
> When air containing carbon monoxide is breathed, about half of the carbon monoxide actually inhaled is absorbed, except toward the end of the process when absorption is coming to a standstill.
>
> The rate of absorption and time required for symptoms to appear is proportional to the respiratory exchange and may be very much shortened by the increased breathing of exercise.
>
> The symptoms do not become appreciable during rest until the blood is about a third saturated. An individual in this condition suffers from palpitation and throbbing in the head and is liable to become faint or dizzy on any exertion, such as that of ascending stairs, or on sudden exposure to cold air.

In experiments on himself Haldane[6] found that, when 50 per cent saturated, he could scarcely stand and could not walk alone without falling down. There was giddiness, dullness of the senses, distinct shortness of breath, and labored breathing. In the course of 2 or 3 hours after leaving the contaminated air he found that nearly all of the carbon monoxide disappeared from the blood, which had then returned to its normal condition. Headache lasting for some hours was likely to ensue from the exposure if the latter were sufficiently long.

In reporting on the conditions which should be maintained in the Underground Metropolitan Railways of London,[7] he said:

> Roughly speaking, the probable action on a healthy person of varying percentages of carbon monoxide in the air may be stated as follows: 2.5 volumes per 10,000 would suffice after a sufficient time (after an hour and a half during rest, but very much less during even slight exertion) to cause symptoms just distinctly appreciable on exertion. Five volumes per 10,000 would cause marked dizziness or fainting on exertion, 9 volumes would cause inability to walk, and about 15 volumes might produce death. * * * * Considering the enormous number of people in various states of health who use the railway, * * * * it seems desirable that not more than one volume per 10,000 of this gas should be present in the air.

To these statements may be added the fact that Burrell[8] found that after breathing air containing 25 parts of carbon monoxide per 10,000 of air for 20 minutes he had at first only a slight headache, but later became ill. The illness lasted for several hours and was accompanied by nausea and headache.

Obviously when Haldane recommended a standard of 1 : 10,000 he had in mind prolonged exposure. If, however, we turn to the more fundamental physiological conditions—namely, that of the percentage saturation of the blood—the apparent discrepancy between his recommendation (1 : 10,000) and ours (4 : 10,000) disappears. Thus, a glance at Fig. 4 shows that 50 minutes, a much longer time than any one will be exposed in passing through the Hudson River Tunnel, in an atmosphere containing 4 parts of carbon monoxide in 10,000 could induce only 16 per cent blood saturation. Now, from Fig. 1, blood which is 16 per cent saturated would be in full equilibrium with about 1 part of carbon monoxide in 10,000 of air. In other words, a stay of many hours in an atmosphere of 1 part of carbon monoxide in 10,000 of air would involve the same percentage saturation as a stay of 50 minutes in 4 parts per 10,000. Indeed, as the development of symptoms from carbon monoxide is wholly a question of oxygen deprivation, it is safe to assert that even a somewhat greater saturation of the blood lasting for only a short period would involve less physiological ill effect than a prolonged period, involving nearly full equilibrium, in 1 part per 10,000 of air.

Finally, we may here quote from a letter received from Dr. Haldane, which was in answer to a letter from us stating the general trend of our observations and findings, and in which Dr. Haldane says:

> In the report on the Underground Railway the chemical standard which I recommended if steam traction was continued was 0.15 per cent of carbon dioxide, and I pointed out that this would contain about 0.01 per cent carbon monoxide. But the standard was not based primarily on the carbon monoxide, but on the general unpleasantness of the air. There was no definite evidence of people being upset by the carbon monoxide, though there was often 0.03 to 0.05 per cent at certain parts of the tunnel and stations; and I even found 0.066 per cent of carbon monoxide (with 0.89 per cent of carbon dioxide) on the platform of Gower Street Station (near University College). Passengers were never exposed long enough for ill effect and the men at the stations were probably more or less acclimatized.* * * *
>
> What I should now say is that with long exposures of several hours anything more than 0.02 per cent should be avoided. For exposures of less than an hour 0.05 per cent would not be really objectionable. As regards gases from motors, however, the smoke and smell might possibly be worse than the carbon monoxide. On this point I have no experience, though I have run across cases of poisoning where there does not seem to have been much smoke or smell.
>
> You will probably see from the above that my ideas about carbon monoxide coincide very closely with what your experiments point to.* * *

Comparative Toxicity of Pure Carbon Monoxide, Illuminating Gas, Exhaust Gas from Gasoline, Exhaust Gas from Coal Distillate, and Gasoline Vapor

The general agreement between the experiments with pure carbon monoxide mixed with air in the small chamber and the results with exhaust gas in the large chamber indicates strongly that in the concentrations occurring in the latter (and thus in any garage or tunnel) carbon monoxide may be taken as the only substance of sufficient toxicity, and present in sufficient amount, to have any considerable physiological effect. All of the data in both of these series of experiments were, however, based upon low concentrations of the gas and the deductions from them might not apply equally to high and lethal concentrations.

We have, therefore, thought it well to check these results by means of observations on animals in high concentrations of gas. For this purpose dogs were used. The animal in each case was placed in a cube-shaped plate glass chamber measuring about 3 feet on a side. The gas to be tested was mixed with air in a gasometer of several hundred liters capacity, so that the carbon monoxide concentration was about 0.3 to 0.4 per cent, or 30 to 40 parts in 10,000. From the gasometer the gas mixture was passed into the chamber through a tube by a small electrically driven air blower. Another tube from the chamber led outdoors. Usually the gas was run in at such a rate that the animal was at the point of death in 30 to 35 minutes. The animal was then removed from the chamber and a sample of blood was drawn, and analyzed by the carmine titration method.

EXPERIMENTS WITH PURE CARBON MONOXIDE MIXED WITH AIR—In this atmosphere the animals became unconscious with no more apparent discomfort than if anesthetized with ether. The blood of five dogs at the point of death contained the following percentages of carbon monoxide: 87, 82, 84, 79, 88; average, 84.

EXPERIMENTS WITH ILLUMINATING GAS, FATTENED WATER GAS, MIXED WITH AIR—In such an atmosphere the symptoms during intoxication differed in some respects from the preceding group. There occurred in all cases more rapid collapse and distinctly greater respiratory excitement. Nausea and vomiting, which were lacking in the experiments with pure carbon monoxide, occurred in all the animals of this second group. These observations and the fact that death ensued with a lower percentage of carbon monoxide in the blood indicate that illuminating gas contains some substance or substances which render it distinctly more toxic than an equal amount of pure carbon monoxide. The blood of the five dogs used in these experiments contained at the point of death the following percentages of carbon monoxide: 74, 67, 76, 71; average, 72.

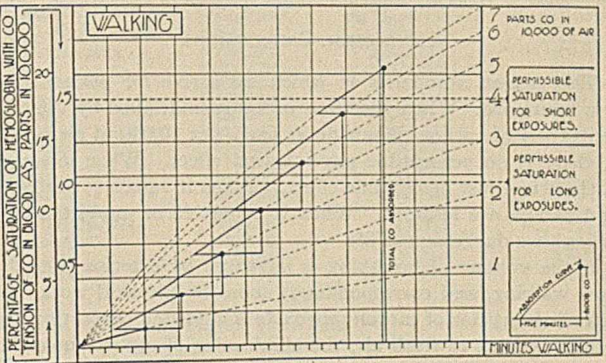

Fig. 5—Illustration of Method for Applying Absorption Curves to Specific Conditions Arising in a Vehicular Tunnel. Longitudinal Ventilation. Subject Walking in Direction of Air Current

EXPERIMENTS WITH EXHAUST GAS FROM A CAR USING GASOLINE—For these tests the three commonest varieties of gasoline sold locally were used successively. A large rubber bag was attached to the exhaust of a car (one in good condition, with an efficient and smooth running engine), while it was standing with the engine running "idle." This gas was analyzed for carbon monoxide by means of an Orsat apparatus in the usual way. The gas was then mixed with air in the large gasometer to approximately the same concentration of carbon monoxide as in the previous experiments and was then administered to animals in the glass chamber. In these experiments the animals were at the point of death in approximately the same time as in the first series of experiments. The symptoms were similar to those from pure carbon monoxide and unlike those from illuminating gas. The percentages of carbon monoxide in the blood were also similar to the first series, but higher than the second. Evidently carbon monoxide was here practically the only toxic substance. The blood of the five dogs in this group of experiments contained at the point of death the following percentages of carbon monoxide: 84, 86, 83, 81, 81; average, 83.

EXPERIMENTS WITH EXHAUST GAS FROM A CAR USING COAL DISTILLATE—Two dogs were exposed to this gas, exactly as the animals had been exposed in the previous experiments to exhaust gas from gasoline, and died with symptoms like, but more marked than, those of the dogs poisoned with illuminating gas. The blood of these two animals had a decided brownish tinge indicating a marked destructive influence upon the hemoglobin of the blood. It is known that benzene has such an effect.

The composition of the coal distillate, according to figures kindly furnished by the chemist of the Gas Company, was:

	Per cent
Benzene	69.0
Toluene	15.5
Solvent naphtha	13.5
Heavy naphtha	2.0
TOTAL	100.0

The blood of the two dogs used in these experiments contained at the point of death the following percentages of carbon monoxide: 60, 64; average, 62.

EXPERIMENTS WITH GASOLINE VAPOR[9]—In order to determine the possible part which unburned gasoline vapor might play as a toxic constituent of exhaust gas, dogs were exposed to the vapor of carefully controlled concentrations. It was found that 100 parts of gasoline vapor in 10,000 of air caused convulsions and 250 parts resulted in death. Obviously unburned gasoline is not an appreciable factor in the effects of exhaust gas, but the vapor contained in a tank from which gasoline has been drawn, and even after considerable ventilation, would be highly toxic—as the practical experience of the industry fully confirms.

PRINCIPAL CONCLUSIONS

The general standards at which we arrive for periods of a few hours are: When the time in hours multiplied by the concentration of carbon monoxide in parts per 10,000 of air equals 3, there is no perceptible physiological effect. When it equals 6, there is a just perceptible effect. When it equals 9, headache and nausea are induced. When it equals 15 or more, the conditions are dangerous to life.

If the volume of breathing is increased by exercise (even by slow walking, and correspondingly more by physical work) the rate of absorption of carbon monoxide is increased proportionally.

After return to fresh air, the elimination of carbon monoxide through the lungs proceeds at a rate of 30 to 60 per cent reduction of the blood saturation per hour.

In the exhaust gas from gasoline, carbon monoxide is the only considerable toxic constituent. In the exhaust gas from coal distillate (benzene, etc.), and in illuminating gas, there are present accessory toxic substances.

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A. C. S. Lecturers at West Point and Annapolis

From the data submitted to the authorities, the following speakers have been selected to address the United States Military Academy and the United States Naval Academy on the dates mentioned:

U. S. MILITARY ACADEMY

April 5—"Chemical Agents in Battle," MAJOR E. J. ATKISSON, Chemical Warfare Service, Edgewood Arsenal, Md.

April 12—"The Manufacture, Chemistry, and Uses of Rubber Goods," MR. W. C. GEER, Vice President, B. F. Goodrich Co., Akron, Ohio.

April 19—"Motor Fuels Ten Years Hence," PROF. RALPH H. MCKEE, Columbia University, New York, N. Y.

April 26—"Helium, Its History, Properties, and Use in Aeronautics," DR. R. B. MOORE, Chief Chemist, Bureau of Mines, Washington, D. C.

May 3—"The Role Played by Cellulose in the Late War," PROF. HAROLD HIBBERT, Yale University, New Haven, Conn.

U. S. NAVAL ACADEMY

February 25—"Nitrogen Fixation and Its Relation to the Production of Food and Explosives," DR. ALFRED H. WHITE, Professor of Chemical Engineering, University of Michigan, Ann Arbor, Mich.

March 11—"Chemical Agents in Battle," MAJOR E. J. ATKISSON, Chemical Warfare Service, Edgewood Arsenal, Md.

April 1—"Fuels," PROF. S. W. PARR, University of Illinois, Urbana, Ill.

April 15—"Motor Fuels Ten Years Hence," PROF. RALPH H. MCKEE, Columbia University, New York, N. Y.

April 29—"Helium, Its History, Properties, and Use in Aeronautics," DR. R. B. MOORE, Chief Chemist, Bureau of Mines, Washington, D. C.

May 13—"The Role Played by Cellulose in the Late War," PROF. HAROLD HIBBERT, Yale University, New Haven, Conn.

Platinum Theft

Attention is called to the fact that on the night of February 6, 1922, platinum to the amount of 100 grams was stolen from the office of F. A. Richmond, Chemical Laboratory, Elmira College, Elmira, N. Y.

Industrial Notes

For the purpose of encouraging research work on glass, the Research Committee of the Glass Division of the American Ceramic Society has made arrangements for providing glass of desired composition and desired form for investigators in this field. The material will be supplied free of charge and no limitations as to the nature of the research will be imposed. The recipients of the material will be under no obligations except that of publication of the results of their investigations, the committee requesting only that wherever possible the *Journal of the American Ceramic Society* be given preference in reporting the results. Inquiries from interested persons may be addressed to one of the following members of the Committee on Research: E. C. Sullivan, Corning Glass Works, Corning, N. Y.; E. W. Washburn, University of Illinois, Urbana, Ill.; R. B. Sosman, Geophysical Laboratory, Washington, D. C.

The statistics for imports of chemicals, drugs, dyes, and medicines for the year 1921 show a decrease in value of 54.8 per cent as compared with 1920. The loss in value for the entire import trade was 52.5 per cent. Receipts of chemical products for recent years are as follows:

1914	$ 88,039,120
1918	151,832,065
1919	126,048,538
1920	211,528,099
1921	85,603,912

In nearly every case the drop from the 1920 figures is due to a general fall in prices, and not to a decrease in volume of imports.

Investment in Chemical Education in the United States, 1920–1921

(Compiled by Research Information Service, National Research Council)

By Clarence J. West and Callie Hull

At the request of the Chemical Foundation of New York City the Research Information Service of the National Research Council has compiled a series of tables showing the investment in chemical education in the United States for the collegiate year 1920–1921. This information was secured by sending questionnaires to the 600 universities and colleges listed in the Educational Directory of the U. S. Bureau of Education. Reports were received from about 450 institutions. This number, therefore, represents approximately three-fourths of all the colleges and universities in the United States. It represents, however, a much larger proportion of the amount of money invested, as practically all of the large colleges and universities responded. In nine states returns were complete; in practically all of the other states returns varied between two-thirds and three-fourths of the institutions listed.

The information was tabulated first by university or college grouped under the individual state, but on account of the length of these tables, the statistics have been summarized by state in Table I. The ten states leading in investment in chemical education for this period are listed in Table II. These figures include not only the actual money invested, but also the appropriations for new buildings and equipment under construction at this time. This latter amount, $7,553,300, is divided between 17 states and 27 institutions. Of these institutions Cornell leads with $2,000,000 and Yale is next with $1,866,900. The sums reported by the other institutions vary between $5000 for Howard College, Alabama, and $465,000 for the University of Minnesota. Twelve institutions reported a total of about $2,000,000 worth of building under consideration.

TABLE II—TEN STATES LEADING IN INVESTMENT IN CHEMICAL EDUCATION, 1920–1921

New York	$ 6,790,015	Minnesota	$ 2,351,210
Massachusetts	4,146,917	Illinois	1,868,983
Ohio	3,196,204	California	1,490,587
Connecticut	2,786,495	Michigan	1,390,850
Pennsylvania	2,404,521	Indiana	1,098,726

Those states having over $500,000 invested in buildings and equipment are shown in Table III. The cost of maintenance and the number of students are also given. From these figures one may roughly approximate the cost per student per year in the states listed.

TABLE III—STATES HAVING OVER $500,000 INVESTED IN BUILDINGS AND EQUIPMENT FOR CHEMISTRY

State	Approximate Valuation of Buildings and Equipment	Cost of Maintenance of Chemical and Chemical Engineering Departments	Total Number of Students
New York	$ 3,973,459	$ 805,556	16,453
Massachusetts	2,793,873	1,345,571	5,954
Ohio	2,014,679	503,825	8,571
Pennsylvania	1,854,852	464,269	6,444
Minnesota	1,515,972	168,447	5,823
Illinois	1,490,272	370,782	7,779
California	1,217,045	271,192	3,869
Michigan	840,499	276,901	4,862
Oklahoma	773,000	88,800	1,786
Indiana	745,000	152,226	3,667
Texas	659,495	204,706	3,393
Connecticut	618,500	151,095	1,351
New Hampshire	605,000	43,500	711
Wisconsin	569,710	236,774	3,361
Missouri	550,105	135,044	2,932
Colorado	546,750	102,462	2,102

TABLE I—INVESTMENT IN CHEMICAL EDUCATION IN THE UNITED STATES, 1920–1921

STATE	Number of Institutions Reporting	Approximate Valuation of Buildings and Equipment	Valuation of New Buildings under Construction and Their Equipment	Funds Received for Chemical Endowment during Year	Cost of Maintenance of Chemical and Chemical Engineering Departments (Salaries, Chemicals, Supplies, Services, etc.)	Total Number of Students in Chemistry (All Courses)		Total Number of Students in Chemical Engineering (where Separate Department Is Maintained)	
						Graduate	Undergraduate	Graduate	Undergraduate
Alabama	8	$ 191,044	$ 5,000	$ 600	$ 39,436	8	901	1	41
Arizona	1	60,000	....	....	17,500	3	250	...	...
Arkansas	5	45,500	....	....	22,000	8	514	...	...
California	12	1,217,045	....	2,350	271,192	44	3,825	14	67
Colorado	8	546,750	....	350	102,462	24	2,078	...	54
Connecticut	5	618,500	2,016,900	....	151,095	47	1,304	...	...
Delaware	1	75,000	....	....	11,682	...	156	...	37
Dist. of Columbia	6	410,233	....	....	121,443	70	1,258	12	133
Florida	3	97,000	....	....	28,450	2	536	...	...
Georgia	8	169,650	....	....	56,543	...	1,255	...	44
Idaho	1	21,000	....	....	18,315	...	291	...	...
Illinois	23	1,490,272	....	7,929	370,782	1,093	6,686	16	342
Indiana	11	745,000	....	201,500	152,226	42	3,625	3	101
Iowa	15	444,210	400,000	....	133,545	19	2,720	2	31
Kansas	14	385,971	82,500	4,000	101,103	44	2,406	...	155
Kentucky	7	100,940	....	75,800	34,929	17	786	...	...
Louisiana	5	374,630	....	....	75,114	23	1,157	5	111
Maine	4	329,679	....	....	49,210	2	563	2	81
Maryland	9	343,489	....	....	97,725	48	1,713	...	...
Massachusetts	16	2,793,873	....	7,473	1,345,571	178	5,776	52	273
Michigan	9	840,499	265,000	8,450	276,901	114	4,748	39	1,435
Minnesota	9	1,515,972	665,000	1,800	168,447	132	5,691	32	132
Mississippi	5	451,000	275,000	22,000	48,650	12	1,165	...	...
Missouri	10	550,105	150,000	1,300	135,044	33	2,899	...	343
Montana	2	220,000	250,000	12,000	28,655	2	400	...	30
Nebraska	8	496,820	50,000	14,000	87,906	13	1,808	...	...
Nevada	1	30,000	....	....	11,800	1	120	...	...
New Hampshire	2	605,000	....	....	43,500	2	709	...	66
New Jersey	3	275,000	....	....	64,309	4	1,028	...	...
New Mexico	3	120,000	....	....	14,600	...	178	...	...
New York	31	3,973,459	2,009,000	2,000	805,556	1,089	15,364	89	744
North Carolina	14	358,000	50,000	2,000	81,300	16	1,690	...	...
North Dakota	4	130,000	....	....	34,258	2	508	...	4
Ohio	31	2,014,679	675,000	2,700	503,825	139	8,432	9	292
Oklahoma	5	773,000	....	....	88,800	10	1,776	...	150
Oregon	5	59,600	....	....	33,423	5	1,047	...	...
Pennsylvania	33	1,854,852	79,900	5,500	464,269	112	6,332	11	257
Rhode Island	2	100,000	450,000	....	36,006	20	833	...	14
South Carolina	11	323,620	....	400	58,780	5	1,141	...	...
South Dakota	6	161,000	....	....	45,276	12	653	...	...
Tennessee	13	450,700	....	....	87,294	60	2,274	...	19
Texas	11	659,495	....	1,000	204,706	36	3,357	6	67
Utah	2	196,093	....	....	20,780	6	714	...	..
Vermont	4	298,675	....	100,000	39,234	2	782	...	...
Virginia	15	436,750	....	52,000	116,501	28	3,101	1	138
Washington	4	263,969	....	....	108,777	18	1,031	...	218
West Virginia	3	43,000	100,000	....	11,750	...	199	...	...
Wisconsin	8	569,710	30,000	716	236,774	98	3,263	8	206
Wyoming	1	....	....	....	6,500	...	85	...	...
TOTAL	417	$28,230,784	$7,553,300	$525,868	$7,739,970	3,643	109,128	302	5,585

SCIENTIFIC SOCIETIES

The Birmingham Meeting

Plans for the Birmingham Meeting, April 4 to 7, are progressing rapidly. Headquarters will be at the Tutwiler Hotel, where the banquet will also be held.

Six special addresses will be given at the General Meeting, including the following:

Van H. Manning, "The Pioneer's Field in Petroleum Research."
Charles L. Reese, "Informational Needs in Science and Technology."
W. C. Geer, "Recent Developments of the Chemistry of Rubber."

Excursions to the steel, by-products, coke, and other industries are planned for Friday and Saturday of the meeting week.

Excursion to Kingsport, Chattanooga, and Muscle Shoals via Special Train to Birmingham

Through a committee, C. L. Parsons, *Chairman*, the Washington Section is arranging for a special train of Pullman cars leaving Washington at 6 P. M., March 30, spending Friday, March 31, at Kingsport, Tenn., and the Clinchfield region; Saturday, April 1, at Chattanooga; Sunday, April 2, at Muscle Shoals; and reaching Birmingham Monday, April 3.

The train is contingent upon 125 *guaranteed* fares. Early application should be made to secure Pullman accommodations desired.

Tickets should be bought from point of departure, via Washington, traveling over Southern and Norfolk & Western Railroads, direct to Birmingham. If 350 people purchasing tickets by certificate plan are present in Birmingham at the meeting a return ticket *via same route* may be purchased at one-half the regular fare. Extra tickets for side trips and for Pullman accommodations must be purchased in advance and check for same (made out to Charles L. Parsons) must accompany application. No application for space will be considered unless accompanied by remittance.

Extra railroad charges for side trips Johnson City to Kingsport and return and Chattanooga to Muscle Shoals will be $10.87.

Pullman fares all four days:

Upper berth	$13.20
Lower berth	16.50
Drawing room (2 or 3 persons)	58.00

The above charges for Pullman are made to cover necessary guarantees. If Pullman cars are filled, there will be rebate of any excess fare paid. Application for space must be made on or before March 20.

If 125 applications accompanied by full remittance for extra fare and Pullman are not received by that date, the train will be abandoned and all remittances returned. If the train runs, no remittances will be returned for any cause as they are part of the guarantee. Regular straight ticket must be purchased from point of departure and certificate taken to secure reduction on return fare. Special train will be given up at Birmingham and party will return as individuals via Chattanooga, Knoxville, Roanoke, and Lynchburg to Washington, and home. This train is normally open to members north of Washington and east of Pittsburgh as these points ticket south through Washington. Any members living further west who can buy tickets via East Radford, Va., and are willing to return *via same route*, will be gladly received on the train there or at Johnson City, but same extra fare and Pullman rates will apply. Suggestions are being made to western local sections that they arrange for special cars via Muscle Shoals to be attached to train there. These cars cannot be a part of the Kingsport and Chattanooga trip on account of the basic requirement of the railroad that return tickets be sold at a reduced price only over the route for which certificate is issued.

Permission has been obtained to visit the nitrate plant and water power development at Muscle Shoals. *This permission is limited to American citizens and to those who have no personal connection with or financial interest in the manufacture of cyanamide.*

Ladies and personal guests may accompany members.

Detailed plans have not yet been made for the entertainment at Kingsport, Tenn., and at Muscle Shoals, but we have been promised a hospitable reception at both places. Saturday will be spent either at Knoxville or at Chattanooga, probably at the latter city. The region around Kingsport, Tenn., has become an interesting industrial center and large plants, such as the Clinchfield Portland Cement Plant, the extract plant and tannery of the Grant Leather Corporation, a large face brick plant, the wood distillation plant of the Tennessee Eastman Corporation, are in operation. An immense leather working plant of the Simmons Hardware Company and the new plant of the Corning Glass Company are ready for operation, but are at present closed down. The Union Dye and Chemical plant has ceased operations. The plants which are in operation, however, are sufficient to give a very interesting day for members, and it may be possible to extend the trip to South Clinchfield to view the Carbo-coal process of the International Coal Products Company, which is the only going concern making use of processes of low temperature distillation of coal combined with the production of briquetted solid fuel. The possibility of visiting this plant appears to be entirely a question of time. If visited, there will be a slight addition to the railroad fare. At Chattanooga there are important industrial plants, such as by-product coke plants, electric furnace manufacture of ferroalloys, cottonseed and peanut oil refining, hydrogenation of oils, alum plant, etc. Details of the trip are being arranged.

All are familiar with the immense fixed nitrogen development made by the Government at Muscle Shoals, the partly developed water power, and the proposition for the purchase of the same from the Government which is now before Congress. Permission to visit the plants has been granted with the limitation above cited. The people of the immediate locality will arrange a special entertainment for the Society.

Committees

Honorary Chairman: George Gordon Crawford.

Executive Committee: J. F. Carle, Theodore Swan, C. N. Wiley, Max Kuniansky, James T. MacKenzie, J. R. Harris, H. S. Geismer, Alden K. Boor.

Finance Committee: Theodore Swan, *Chairman*, Erskine Ramsey, Frank Miller.

Hotels, Publicity and Meeting Places: C. N. Wiley, *Chairman*, F. G. Cutler, Henry Burn.

Registration and Information: Max Kuniansky, *Chairman*, R. T. Pittman, R. W. Allen.

Banquets: J. T. MacKenzie, *Chairman*, J. H. Adkins, J. W. Moore.

Excursions: J. R. Harris, *Chairman*, Theodore Swan, K. Landgrebe, A. G. Overton, G. St. J. Perrot.

Smokers: Alden K. Boor, *Chairman*, T. S. Bissell, C. W. Hogg.

Transportation: H. S. Geismer, *Chairman*, W. E. Mitchell, R. H. Cunningham.

Ladies' Entertainment: Mrs. Eugenia B. Dabney, *Chairman*.

Papers: Dr. A. C. Montgomery, *Chairman*.

Reports on the Progress of Applied Chemistry

In order that the Annual Reports on the Progress of Applied Chemistry issued by the Society of Chemical Industry may be more widely known in this country, the Society is offering Volume VI (to be published in March) at the reduced price of 10s. post-free, to members of the American Chemical Society. This is the price charged to its own members.

Orders, with remittance, should be sent to Dr. J. P. Longstaff, Journal of the Society of Chemical Industry, Central House, 46 & 47, Finsbury Sq., London, E. C. 2, England.

Calendar of Meetings

American Chemical Society—63rd Meeting, Birmingham, Ala., April 4 to 7, 1922.

American Electrochemical Society—Spring Meeting, Baltimore, Md., April 27 to 29, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, week of June 19, 1922.

American Society for Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 26 to July 1, 1922.

Officers of Local Sections, A. C. S.

The 1922 officers of the New Haven Section are:

President: MILO C. BURT
Vice President: TREAT B. JOHNSON
Treasurer: JOHN L. CHRISTIE
Secretary: BLAIR SAXTON
Councilor: HAROLD HIBBERT

The 1922 officers of the Georgia Section are:

Chairman: C. A. BUTT, Atlanta.
Vice Chairman: Dr. J. F. SELLERS, Atlanta.
Secretary-Treasurer: L. B. LOCKHART, $33^{1}/_{2}$ Auburn Ave., Atlanta
Councilor: W. P. HEATH, Atlanta.

American Institute of Chemical Engineers

The American Institute of Chemical Engineers will meet in Niagara Falls, Ontario, at the Hotel Clifton, beginning June 19, 1922. One day will be spent at Buffalo, and one devoted to a boat trip to Toronto with visits to industries there.

The feature of the program will be a symposium on the manufacture of the heavy acids. The Secretary, Dr. J. C. Olsen, Brooklyn Polytechnic Institute, Brooklyn, N. Y., will be glad to correspond with any who may be interested, whether members of the Institute or not.

NOTES AND CORRESPONDENCE

The Outlook in Europe

Editor of the Journal of Industrial and Engineering Chemistry:

It was my privilege to visit England, France, Belgium, and Germany during the months of October and November 1921, and my general impression of the conditions is such that I cannot put my finger on any one particular thing that would restore some of these countries to even a seminormal condition.

BRITISH TARIFF CONDITIONS

England has always been a free trade country, but since the war she has seen her industries slipping, with every indication of going under, and has enacted a general tariff bill, called the "Safeguarding of the Industries Act" in which a duty of $33^{1}/_{3}$ per cent has been placed on all industries which need protection, such as optical glass and optical instruments; scientific glassware; laboratory porcelain; synthetic colors, rare earths, and chemicals. In addition, an Anti-Dumping Act has been enacted, which became a law on October 1, 1921. I can quote only Part 2, Section B, of the Anti-Dumping Act of England, which relates to the depreciation in value of foreign currency, which we would do well to follow:

> Evidence as to price at which similar goods can be profitably manufactured in the United Kingdom.
>
> Evidence to show that the depreciation in relation to sterling of the currency of the country of manufacture is responsible for the fact that the prices at which the goods are sold or offered for sale in the United Kingdom are below the prices at which similar goods can be profitably manufactured in the United Kingdom.

In addition to this, England has protected her dye and synthetic chemical industry by means of embargoes and prohibitions, which prevent some foreign chemicals from coming into the country.

FRANCE AND BELGIUM

The condition in France is still more interesting, for France has enacted a tariff, known as the Law of September 1921, which is composed of four distinct types of tariff. They are known as the "old tariff," "new tariff," "favored nation tariff," and the "coefficient."

The "old tariff" is the one which existed prior to that date, and applies to some materials not made in France, and others not indigenous to France. The "new tariff," generally speaking, is a very high tariff on certain chemicals and manufactured articles. The "favored nations tariff"—from which the United States is conspicuously absent—favors those countries which France has chosen; but the most important and interesting part is the "coefficient." This is a number 2, 3, 4, or more in the fourth column of the Tariff Act, which in every instance is used as a multiple of the duty assessed. In other words, precipitated barium sulfate is assessed at 2 francs per 100 kilos, and includes the coefficient 5; therefore, it is dutiable at 10 francs per 221 lbs.

France has no unemployed men at present; the entire country looks very prosperous.

Belgium is in the same condition, and has a high protective tariff, but I am not in possession of the latest laws on the subject.

THE ECONOMIC CONDITION OF GERMANY

The condition in Germany is exceedingly interesting in view of the fact that by far the largest part of the plants in Germany are working nights. There is no unemployment, as there is no foreign competition. As I pointed out to the Treasury Department last summer (in June 1921), Germany, in addition to her high tariffs, has a list of embargoes which precludes the importation of any material which can be made in Germany out of German raw material. If we wished to retaliate by shipping 1000 tons of barium peroxide to Germany at five cents per ton it could not be done, because the material could not enter any of the customs ports of Germany.

The man who goes to Berlin, lives at a fine hotel, and orders the best wine for a few cents a bottle in our money, and then comes back talking about how prosperous Germany is, is not acquainted with the facts. It is true that Germany is working very hard, and that one passes hundreds of factories brilliantly illuminated at night, particularly in the iron district near Essen, but the workman is being paid in a currency that is continually depreciating, and the savings which he had put aside last year, when the mark was worth 1.6 cents, have depreciated until now their purchasing power is far less than it was a year ago, and their international value has fallen to half a cent. Such a condition is not wholesome, and I feel sure that unless Germany receives a gold loan from the Allies and the United States she may soon find herself in the same deplorable condition as Austria and Poland. Germany is running her railroads at a tremendous loss (approximately thirteen billion marks this year); her post-office shows a deficit of two billion marks, and, while she has neither army nor navy, she is supporting the foreign army on her soil at a cost, equal to, if not greater than, that of France. Another pernicious defect of the financial condition in Germany is the fact that many of her merchants have opened accounts in Holland, England, the United States, and South America, and when they export goods to these countries, they deposit the funds in the gold of that country. The consequence is that raw and manufactured material has been exported, but the money has never been returned to Germany.

Another very depressing effect upon the Germans, particularly in relation to their reparation payments, has been the decision of the Allies in regard to Upper Silesia. It is expected that Germany will pay the indemnity either in gold or in kind, in accordance with Article 175 of the Treaty. It was agreed that Upper Silesia should decide by plebiscite whether it should become a part of Germany or a suzerainty of Poland. The vote was overwhelmingly for Germany, but a little rider at the end of Article 175 states that even if the plebiscite shall decide in favor of one country or the other, the Commission may reverse this decision if they so see fit. It is a long time since I read this particular article and I am not sure I am correct in quoting Article 175, and I know I am not correct as to the exact verbiage used, but such at least was the intent of that paragraph.

I happened to be in Germany at the time that this decision was made, and it had a very depressing effect, not only upon the people but upon the mark; and, while I hold no brief for Germany, my sense of fair play rebelled, for I felt France is encouraging future wars instead of preventing them.

Germany has not the slightest desire for another war, she has not the money, and she has not the men, and, in my opinion, what she wants is to be left alone to work out her own salvation. France would be infinitely better off if she reduced her army of 800,000 men and utilized them for the rebuilding of the devastated zone. Of course, if you go through the battle area as I did from the Ostend coast to Rheims, you feel that no punishment is too great to visit upon Germany, but it is a dangerous thing to allow your passions to get the better of your prudence. Universal peace would not be so far off if the Tammany politicians of France, of which she unfortunately has many, were superseded by safe and sane statesmen.

Mr. Frank A. Vanderlip once stated "You cannot milk a cow and cut its throat at the same time," and that, it strikes me, is what is being done to Germany, in addition to what Germany is doing to herself.

Czechoslovakia ought to be taken for an example, for they are working gladly and peacefully; they have stopped printing money; their internal organization is on a paying basis, and the chances are that that country will come out ahead of all the other Central empires.

As far as stocks of raw materials and finished products in Germany are concerned, Germany will soon come to the end of her tether in the matter of textiles, for, with their depreciating mark, they are unable to buy cotton, wool, and silk at competitive prices. As far as chemicals are concerned, Germany has enough raw material to undersell the world for many years.

MAXIMILIAN TOCH

NEW YORK, N. Y.
December 20, 1921

"The Fire and Explosion Hazards of Commercial Oils"

Editor of the Journal of Industrial and Engineering Chemistry:

In the interest of accuracy, we desire to call attention to a number of errors in the chapter on coal-tar oils in a book by Vlachos entitled "The Fire and Explosion Hazards of Commercial Oils," published by Vlachos & Co., 1921. This book is intended for the enlightenment of fire underwriters. Its object is, therefore, praiseworthy, for underwriters are generally deficient in exact information concerning the complex and highly specialized materials of the oil industries. Unfortunately, the authors themselves do not appear to have exercised sufficient care in presenting the subject of coal-tar oils and this chapter contains a number of statements which can only be described as grossly inaccurate.

Turning to the opening paragraphs of Chapter 16, Page 229, we find the flash point of "about 16° F. below zero" attributed to coal tar. The flash point of crude tar is very difficult to ascertain as the tar always contains considerable moisture and the water vapors practically eliminate any true flash point. It is safe to say that crude coal tar will never flash at temperatures below 180° F. Distilled or dehydrated tars necessarily have the light oils removed during the process of dehydration and the residual tar will flash only at temperatures well above 200° F. The flash point of 16° F. below zero attributed to coal tar by the authors is probably intended to refer to benzene, as will be readily seen by reference to the chapter title and subtitles. Nevertheless, the opening words of the chapter explicitly refer to coal tar as a crude material derived from the by-product coke ovens and gas works.

In the second and third paragraphs of this chapter, the temperature of production of coal tar from coke ovens and gas works is given as 1100° F. and 1500° F., respectively. While carbonization temperatures vary, the temperature in by-product ovens is usually 1800° F., never as low as 1100°, and the temperature in gas retorts is approximately 2000° F. True these temperatures are of no particular significance or interest to the fire underwriters, but if given at all should be stated with some degree of accuracy.

In the next paragraph the authors state that coal tar flashes readily. It does not at ordinary temperatures as expressed above. "When stored in large steel tanks with steel roofs it is an acceptable risk." Steel roofs on coal-tar storage tanks are distinctly unsafe, owing to the corrosive action of the ammoniacal impurities in the liquor which always separates out on the top of coal tar in storage tanks. It is universal practice in the industry to use wooden roofs covered with pitch and felt surfaced with gravel or slag. These roofs will last as long as the tank itself. The steel roofs would not last five years and are always an element of danger by reason of the rapid corrosion. Crude coal tar in storage invariably has a layer of water on top from a few inches to several feet in depth. It is about as free from incidental fire hazard or even conflagration risk as any liquid material could be.

On page 231, we find "the modern coal-tar stills are vertical and the older stills are horizontal." Vertical tar stills are almost unknown in American practice. The horizontal still is standard for discontinuous distillation. This is probably unimportant as direct fired stills are not ordinarily insured. The authors appear to have inspected some very extraordinary installations: *viz.*, continuous stills which are gravity fed; large open tank agitators in which benzene was treated with crude sulfuric acid, etc.

In the last page of this section on benzene, we find the interesting statement that the authors have personally witnessed the violent explosion of creosoted wood and they deplore the use of creosoted wooden floors in "so-called fireproof industrial buildings." In view of the remarkable showing made by creosoted wooden block pavements in the Baltimore conflagration some years ago as compared with the brick and stone pavements, this statement will be regarded with considerable interest by the wood-preserving industry. The explosion of a piece of creosoted wood is unique. The authors should by all means give us the full details concerning this fascinating phenomenon.

We have not read the rest of the book. Doubtless, it may be quite free from the unfortunate errors which we have noticed in the chapter on coal-tar oils, but in turning the pages we did observe what is evidently only a typographical error on page 33 where the boiling point of water is given as 220° F.

Too literal interpretation by fire underwriters of these pronouncements may lead them into some interesting arguments with oil chemists.

S. R. Church

40 Rector St.
New York, N. Y.
February 6, 1922

The International Trade Situation

The January 7, 1922, issue of *The Chemical Age* (London) contains an interview with Brigadier General Sir William Alexander on the international trade situation, and especially on British industrial problems in relation to those of other nations. Sir William recently made a tour of the United States and Canada, closely concerned with the future of the dyestuffs industry, and is therefore especially well qualified to speak on this problem.

He points out that though the surplus capacity for dyestuff manufacture, for instance, developed during the war may mean a peace-time war of elimination, Great Britain and America have every chance of pulling through since they are uniquely and satisfactorily placed for all the raw materials, if application and determination be added. Britain can maintain her plants in operation provided that British Empire consumers support their own industries, that her chemists and engineers responsible for running plants concentrate toward maximum efficiency, that labor recognize that maximum production per unit of labor or plant is the greatest security for regular and good wages and low cost of living, that the government continue to assist British industries to fight against depreciated currencies and other handicaps to fair trading on equitable terms, and that the government realize that its consuls and trade commissioners overseas should be competent, commercially, to pioneer, advertise and assist in the development of British trade.

> The reconstruction of Europe is all-important to Great Britain as an exporting nation, and no opportunity on the part of such solvent countries as Great Britain and America to assist in reconstruction on sound lines to the extent of such finances as can be safely extended should be missed, but the greatest and most enduring assistance will be in the direction of encouraging poor nations to help themselves. Nations whose currencies have fallen so low as to have little or no purchasing values will require to go hungry until they reorganize their internal economies and industries by producing or taking out of the ground the equivalent of currency to balance imports by exports.***** Such a policy is the only permanent and reliable method of stabilizing exchanges.
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> * * * *
>
> This doctrine carries little encouragement toward a speedy revival of trade in Great Britain, but*****in our present state of reduced circumstances we must not trade beyond our means. *****We shall retrieve our own prosperity more quickly and surely by concentrated development of trade within the Empire, adding such outside business as exhibits a fair commercial risk, rather than retard reconstruction on normal lines by the encouragement of trading with insolvent nations against phantom credits.******
>
> America has recovered from the general depression to a greater degree than any other nation because about 80 per cent of her trade is within her own boundaries, because she has nursed and protected her industries.
>
> * * * *
>
> In the peace-time war for commercial supremacy there will be no room for middlemen. Let us make certain that we do not drift into a position of being neither producers or merchants.
>
> Best interests will be served by a trade recovery that is gradual and not spasmodic. The interregnum of restricted trade should be utilized to the fullest extent in perfecting plant, processes, and production efficiencies for all classes of manufactures for which the country is advantageously placed. Chemicals and dyestuffs, with unlimited sources of coal and coal-tar products, limestone, salt, etc., should form two of the most extensive. When reconstruction and reëstablishment of confidence bring demand we should then be in a position to command a fair share of the world's trade against any fair competition.
>
> * * * *
>
> Consultation between manufacturers and close coöperation between employers and employed should be encouraged to the utmost, with the object of obtaining maximum output, from a minimum of plant, at a minimum cost, and also that we may compete for world trade more collectively as a nation and less as isolated members with no common interests.

The American Potash Industry

Editor of the Journal of Industrial and Engineering Chemistry:

There is a quite justifiable general opinion opposed to a tariff on any material for protective purposes and particularly opposed to any such protective tariff on a material of which the farmers are to a large extent the ultimate consumers. However, the situation as to the tariff on potash proposed in the bill under consideration, in Paragraphs 75 and 1635, is such as to make it actually to the financial interest of consumers to have those paragraphs retained in the tariff bill when finally passed.

Except for the periods from 1915 until 1919, and 1919 to date, the production of potash salts has been a German monopoly because the first developed deposits of soluble potash salts were in Germany and the business was so conducted as to keep it under German control by artificial conditions imposed by the German government.

Prior to 1909 this monopoly had maintained high prices of potash salts, around $38.00 per ton of 80 per cent muriate. In 1909 the German syndicate was broken for a few months and during that time American interests bought potash mines and under the Schmidtman contracts gave those particular mines the large tonnage of the American market, cutting the price to $21.00 per ton of 80 per cent muriate.

With this low price, little more than the cross-country freight on California potash to the eastern United States, the American-owned German mines made the largest profits in their history.

The re-forming of the German syndicate was followed by the famous German 100 per cent export potash tax applied to product of mines which did not belong to the syndicate or which shipped more than half their product out of Germany; this put the American price higher than it was before. The celebrated Hill-Taft settlement followed, putting the price back to $38.00 per ton, and there it stayed until the European war stopped potash coming out of Germany.

Opponents of tariff protection for potash make much of the assertion that, if five years of the sort of embargo that so effectively kept potash out of this country during 1915 to 1919, with the enormous prices that were paid by consumers, did not establish an American potash industry capable of competing with Germany, certainly the protection provided by the paragraphs in the present bill cannot do so and can result only in that much increased cost to the American consumers, the greatest number of whom are the already sadly overburdened farmers.

A careful analysis of the situation, however, will quickly relieve the mind of the erroneous impression thus given by a casual survey.

All the forces of the enormous German potash propaganda had been at work for many years in directing as far as possible all search for American potash to the far western regions from which the freight alone across the country would nearly equal the prices at which Germany could lay down potash on our eastern seaboard, and, as was proved by the Schmidtman contracts above referred to, at an enormous profit to German mines if allowed to operate on large production.

The widespread feldspar and greensand potash deposits of the East were prevented from exploitation by the secret forces of the same propaganda frightening proverbially timid capital away from the enormous investments required in plants and machinery for operation of necessary processes to change this insoluble potash to soluble form.

The hidden deposits of soluble potash that must of necessity exist in the salt fields of the eastern United States could not be accidentally discovered as they had been by hundreds of years of shaft and stope mining for rock salt in the salt fields of Germany, for the very good reason that salt mining in the United States has been entirely developed in the last seventy-five years and confined entirely to the purest veins of sodium salt, where there could not of course be any potash, and this same propaganda exploited to the fullest extent the idea that an all-wise Providence had confined potash deposits to the German salt fields alone.

The European war embargo on German potash therefore found this country totally unprepared to develop quickly any potash production within the limits to which capital could be obtained, except in the salt lakes and deserts of the far West, and only the high prices obtainable justified the costly work of recovery on the comparatively small scale permitted by the limited capital which could be interested. No man who invested a dollar in potash plants during the war period was ever sure of having six months in which to operate without being again subjected to German competition. Consequently investments were made as far as possible with the idea of getting in and getting out quickly with a profit if possible.

After three or four years' record of reasonable profits, some companies actually did get economical operations established, so that with reasonable protection afforded, they can even now produce potash salts at less than double the old German prices.

The exploitation of the several processes for extraction of the insoluble feldspar and greensand potash in the East has gone on slowly and steadily as capital could be secured, and with the protection afforded by the bill in question one plant now almost completed and several more under way will get into operation and will not be hampered by heavy freight from western deposits.

If the present bill had been a law any time before or during the war, American potash production would in less than five years have been on such a scale of magnitude that prices far lower than even the Schmidtman contracts would give handsome profits.

It is a fact well proved by history that whenever American manufacturers are sure of no competition which can have any advantages of foreign cheap labor or foreign government protection, they go into the intensive development of a product on large-scale production with labor-saving mechanical ingenuity that always results in cheapening of that product to a point where foreign competition is left far behind.

With the passage of the bill in question it is a foregone conclusion that capital will be ready and eager to go forward with the developments now so well under way, and in a very short time American quantity production, with the results of the wonderful research work that has been carried out by American chemists for the past five years, will totally destroy Germany's domination of the potash industry of the world. Without this protection, the industry is doomed and German domination will be permanent and complete.

Notwithstanding the fact that the recent German and French potash contracts have been made with American fertilizer companies (three of the principal companies still own large interests in German potash mines), at about the old price ($37.00 per ton of 80 per cent muriate), the price charged the good old American farmer is $52.00 per ton or only a little below the price at which American producers were already offering their American-made potash.

The actual difference to the farmer, therefore, will be but very few dollars and the profit will go to the importer who is sending good American dollars out of this country, instead of to the American mine and factory whose every expense benefits the sadly unemployed ranks of American labor and brains.

H. D. RUHM

136 LIBERTY ST.
NEW YORK, N. Y.
January 20, 1922

Fire at Heyden Chemical Plant

Editor of the Journal of Industrial and Engineering Chemistry:

We have noted in the January issue of the JOURNAL a statement with reference to our fire which is grossly exaggerated.

The plant of the Heyden Chemical Company of America, Inc., Garfield, N. J., was visited by a serious fire on the afternoon of December 12, in the refined salicylic acid section. The fire loss, including use and occupancy insurance, is estimated to be between $550,000 and $600,000.

The conflagration started at 2:45 P. M. in the middle sublimer of a set of three. Two employees were cleaning the hot air chamber. One of them left the chamber and upon returning tripped over a flexible extension cord connected with a properly protected electric light bulb. The lamp fell to the iron grating at the bottom of the hot air chamber, knocking off the guard and breaking the bulb, and the terminal wires came in contact with the iron which caused a short-circuit. The flash ignited the refined salicylic acid in the chamber. The operators endeavored to put out the fire with buckets of water, which failed, and they then closed all dampers, enclosing the flame in the hot air chamber. The sides of the chamber were bulged out by the gas generated from this small fire, which caused the flame to spread instantly to the dust in the room and then to the salicylic acid which had just been removed from the sublimer. The company's fire department had a hose stream playing on the burning sublimer at about the time the dust ignited, which caused a "puff," blowing out the end wall of the building, and the wind carried the flames around the fire protection walls, separating each of the sublimers, and the other sublimers caught fire, causing the destruction of the refined section of the salicylic acid, sodium salicylate and acetylsalicylic acid departments.

The capacity of the destroyed refined salicylic acid section of the plant was approximately 225,000 lbs. of U. S. P. acid per month. The crude equipment is intact.

Of the five men who were burned, four of them have reported back at work and the fifth, the foreman who was most seriously burned, it is expected will be discharged from the hospital early in February. The foreman, who was the most seriously burned, received his injuries through his efforts to turn on the valve controlling the carbon dioxide gas, with which all sublimers were equipped to prevent the possibility of serious fire. He was caught in the "puff" which took place just as he was entering the sublimer room.

F. H. CHAMBERLAIN, *President*

HEYDEN CHEMICAL COMPANY OF AMERICA, INC.
GARFIELD, N. J.
January 18, 1922

The Formula Index

Editor of the Journal of Industrial and Engineering Chemistry:

The work that *Chemical Abstracts* has been doing and is doing for the chemists of America and elsewhere is of the utmost importance. This work has been developing without a backward step from its start in 1907, until just recently. However, the action of the directors of the SOCIETY in stopping work upon the formula index to *Chemical Abstracts* for 1921 is very much to be deplored, as it curtails the usefulness of the journal.

I wish to take this occasion to protest against this action and to ask other chemists interested to file a similar protest. The reasons which lead to my opinion are the following:

The heart of any abstract journal is its index. Chemistry is now so complex that it is utterly impossible to have a simple index. Those responsible for *Chemical Abstracts* realized this and, beginning with the Decennial Index, evolved the most scientific nomenclature yet proposed for such an index. This index is a very excellent one but neither it nor any other complete word index can be used without considerable study and experience with the principles involved.

On the other hand, a formula index especially for organic compounds is extraordinarily simple to use. It furthermore gives more accurate and quicker information as to the presence of a given compound in an index than will a word index.

I trust that some way will be found to restore the formula index to *Chemical Abstracts*. It would be very much better to increase the dues of the SOCIETY or to economize in other directions rather than to drop this formula index. As a matter of fact, a formula index ought to be prepared as a supplement to the Decennial Index, as soon as possible.

R. NORRIS SHREVE

43 FIFTH AVE.
NEW YORK, N. Y.
January 18, 1922

Permanence of the Grignard Reagent

[PRELIMINARY NOTE]

In connection with a series of quantitative studies on the Grignard reagent, particularly the determination of the optimum condition for the formation of this reagent, it was considered desirable to undertake investigations which it is hoped will extend the general usefulness of the reagent, more especially where reasonably large quantities are used.

The Grignard reagent is generally prepared by adding a solution of the appropriate RX compound in absolute ether to magnesium turnings. The RMgX compound so formed is quite sensitive to air, a small amount of moisture, in particular, decomposing a relatively large amount of the reagent. Partly for this reason and the uncertainty concerning its stability, the reagent is very conveniently used directly after preparation. One rarely hears of "stock" Grignard reagent.

It has been found that ethyl magnesium bromide in ether and phenyl magnesium bromide in ether, when protected from the air, are stable after a period of two months. Parallel experiments with ethyl magnesium bromide in the light and in the dark have shown that daylight is without influence on the strength of the solution. The investigation is being extended to a variety of typical RMgX compounds, some in highly concentrated ethereal solutions, over a longer time period.

A study is also being made of pastes, of so-called "individual" compounds, and of solvents other than ether, with the intention of decreasing the fire hazard and the comparatively large expense attendant on the use of ether as a medium.

HENRY GILMAN
CHARLES H. MEYERS

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE, AMES, IOWA
December 23, 1921

Contamination by Aluminium in Analytical Work

Editor of the Journal of Industrial and Engineering Chemistry:

Considerable trouble has been met in the courses in qualitative analysis at the University of Illinois on account of the appearance of decidedly appreciable amounts of aluminium during the course of the procedure. It was found to come from two rather unexpected sources.

One source was the filter papers used. These papers were purchased for the usual "qualitative" grade, and behaved very satisfactorily so far as holding fine precipitates was concerned. Upon filtering acid solutions, however, enough aluminium was leached out to give decided tests for this element. Sulfates and traces of iron were also detected. Quantitative examination showed that, as an average of several determinations, a 10-cm. paper contained 3 mg. of aluminium and iron (computed as Al_2O_3 and Fe_2O_3), to say nothing of considerable amounts of acid-soluble silica. The source of this contamination can only be conjectured. The presence of the aluminium and sulfate suggested alum, which might have come by the use for filter stock of trimmings from paper mills and binderies, which would contain alum as sizing. The acid-soluble silica, on the other hand, indicates clay, which is sometimes used as a filler for "weighting" paper.

A second source of aluminium was found in the porcelain evaporating dishes used. Digesting acid solutions in the brand of dish which has been used in this laboratory for the past two or three years results in the solution of various amounts of aluminium and silica, particularly if the glaze has been broken by previous use. It was found that more than 50 per cent of the dishes in the student cupboards would show a mark if a graphite pencil were drawn across their interior surfaces. As an extreme example, one badly pitted dish lost 6.9 mg. upon boiling 6 *N* HCl in it for 15 min. As a substitute for these dishes, the classes in qualitative analysis have been using small beakers, which approximate the familiar "Pyrex" cooking vessels in composition. These were found very satisfactory, and it may be interesting to note that the indications are that the breakage accounts of the students will be reduced somewhat by their use.

These experiences are passed along to the rest of the chemical brotherhood "for the good of the order."

J. H. REEDY

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
November 16, 1921

Holland's Tariff Situation

Editor of the Journal of Industrial and Engineering Chemistry:

In reading Mr. Watson Davis' interesting article on conditions in Europe [THIS JOURNAL, **14** (1922), 73], I note certain somewhat erroneous statements.

It is true, as Mr. Davis states, that Switzerland and Holland, as neutral border states, have to face severe competition. What Switzerland may have done to overcome this drawback I do not know, but so far Holland has not "raised stringent tariff barriers to prevent a flood of goods from Germany, Austria, and other low-wage-plane countries." Many people in Holland are of the opinion that only such a barrier, in the form of a protective tariff bill, can save our trade and industry from gradual economic starvation. It is not my intention to discuss this question here, but simply to call attention to a misunderstanding of our condition. In my opinion, Holland's economic breakdown as a consequence of Germany's industrial and financial policy toward her is not a mere phantom, but a real fact.

H. BAUCKE

KONING & BIENFAIT
DA COSTAKADE 104, AMSTERDAM, HOLLAND
January 19, 1922

Ramsay Memorial Fellowship

The Trustees of the Ramsay Memorial Fund have requested the National Research Council to nominate a Fellow to devote his whole time to research in chemistry in some English university upon a stipend of 250 pounds sterling per year, with an additional allowance of 50 pounds for apparatus. The National Research Council has appointed a nominating committee consisting of F. G. Cottrell, Chairman of the Division of Chemistry and Chemical Technology, National Research Council, Washington, D. C.; E. B. Mathews, Chairman of the Division of Geology and Geography, National Research Council, Washington, D. C., and Professor of Mineralogy and Petrography, Johns Hopkins University, Baltimore, Md.; and W. E. Tisdale, Secretary of the Division of Physical Sciences, National Research Council, Washington, D. C.

This Committee is willing to receive applications from any American chemists who have taken a degree with distinction in chemistry in a university or college within the United States, and who are now connected with a university or college, or have recently been graduated therefrom.

The appointment will be for the academic year 1922–1923. Under the general regulations of the Ramsay Memorial Fund, Fellows are eligible for reappointment.

Applicants should furnish:

1—Certificates or other satisfactory evidence of birth, health, character, and academic or other distinctions.

2—A written application stating:

(*a*) Education and employment to date, and particularly the nature, extent, and place or places of his academic studies and research.

(*b*) Particulars of the work and place of work proposed; and

(*c*) The names and addresses of not more than three references well acquainted (one or other of them) with the health, character, capacity, and career of the applicant, without, however, any written testimonials from them or others. One of the references should be a teacher under whom the candidate has studied, or a high official of his university, college, or other place of education.

These Fellowships are open in chemistry, either pure or applied, and work may be carried on at any university, college, or other place of higher education, or an industrial laboratory within the British Empire. Their object in this instance has, in addition to the stimulation of research, the special earnest wish on the part of English scientists to cultivate the wider acquaintance and good fellowship which is so much to be desired between scientific men of the world.

The Ramsay Memorial Fund for research in chemistry within the British Empire was founded in 1920 to commemorate the services to chemistry of Professor Sir William Ramsay, K.C.B., F.R.S., with an initial endowment of £14,000. Since that time several special endowments have established additions to this Fund, and special Fellowships with appropriate regulations are granted under: The Glasgow Special Fund; Royal Hellenic Government Special Fund; Federal Government of Switzerland and of Swiss Subscribers Special Fund; Royal Italian Government Fund; Fund of the Honorary Advisory Council for Scientific and Industrial Research, Canada; Royal Swedish Government Special Fund.

Applications should be mailed before April 15 to W. E. Tisdale, Secretary, 1701 Massachusetts Ave., Washington, D. C.

American-Made Chemicals

Editor of the Journal of Industrial and Engineering Chemistry:

We have received recently from two large American universities requests for quotations on chemicals in which the description of the chemicals with comments on them is *written in German*, in several cases chemicals of German origin being specified which are available from American sources in the United States.

It is, of course, not likely that an American university supported by American funds and whose students hope eventually to find positions in the American chemical industries would really intend to exclude American-made chemicals and to accept only chemicals of foreign origin.

From the manufacturer's point of view, however, it is important that orders be in English because the naming of chemicals in German might prevent a supply house from supplying American chemicals, even though they had the latter in stock and would prefer to quote on them under other conditions.

I venture to suggest that when such documents are received written in German from American sources they be sent back with a request that they be translated into English.

C. E. K. MEES

EASTMAN KODAK CO.
ROCHESTER, N. Y.
January 26, 1922

Protecting Metallic Laboratory Hardware and Utensils from Corrosion

Editor of the Journal of Industrial and Engineering Chemistry:

In most laboratories there are acid fumes and in all there are metal burners, ring-stands, tripods, and similar tools. This means that unless much pains are taken there is often considerable trouble from corrosion. The writer has found that to sand-blast and paraffin-dip all such utensils effectively preserves them even from the fumes of strong acids in hoods and enclosed places. The objection to enamel baked on such tools is that it chips off and exposes the metal, but the rough surface holds the softer paraffin in place in spite of much handling. Incidentally this method is quite inexpensive. A steel vise so treated and in daily use for over two years shows little or no corrosion in a laboratory where there are acid fumes continually.

W. G. BULLARD

CHEMICAL LABORATORY
UNITED SHOE MACHINERY CO.
BEVERLY, MASS.
December 6, 1921

An Experimental Study of the Significance of "Lignin" Color Reactions

(Correction)

In my paper of the above title, published in THIS JOURNAL, 13 (1921), 625, the following errors on page 626 escaped correction:

Column 1, 4th line from bottom, "light transmission" should read "light absorption."

Column 2, line 2, "bands of highest transmission (minima of absorption)" should read "bands of absorption."

Column 2, line 4, "11.30 for safrol" should be "13.35 for safrol."

Column 2, line 5, "minimum" should read "maximum."

Column 2, line 8, "minima" should read "maxima."

ERNEST C. CROCKER

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
January 9, 1922

A Revision of the Optical Method for Analyzing Mixtures of Sucrose and Raffinose

(Correction)

Three typographical errors are to be noted in the paper by C. A. Browne and C. A. Gamble [THIS JOURNAL, 13 (1921), 793].

On page 795, Formulas 11 and 13 and the formula for N should contain plus signs instead of multiplication signs.

WASHINGTON NOTES

Muscle Shoals

On February 2 the Secretary of War sent the Henry Ford Muscle Shoals offer to Congress, accompanied by his report and appended documents, which included a detailed analysis of the offer by the Chief of Engineers and by the Chief of Ordnance, and on February 6 he transmitted similar data to the Senate. The House referred the matter to the Committee on Military Affairs and that committee started its public hearings on February 8, the Secretary of War being the first witness to appear before the committee. He stated that he preferred a 50-year lease but that he was perfectly willing to waive this personal preference if the committee preferred the 100-year period. He did not understand that the production of nitrates by Mr. Ford at Nitrate Plant No. 2 would be sufficient in amount to affect the market throughout the whole country, as he estimated Mr. Ford's output would not be more than one-thirtieth or one-fortieth of all of the fertilizer used in the country. He felt that while there was no reason whatever to doubt Mr. Ford's sincerity, there was nothing in the agreement to prevent his successors from abandoning the operation of the plant if they saw fit and hence he thought that there should be some guarantee in the contract that the lessee would continue to manufacture nitrates and fertilizers and suggested that this might best be accomplished by the formation of a company so that the contract would be with the company rather than with Mr. Ford personally.

Major General Williams, Chief of Ordnance, followed the Secretary of War and occupied the greater part of one day's sessions in explaining valuations of properties involved in the Ford offer. He stated that it had cost the Government about $88,000,000 to construct Nitrate Plants Nos. 1 and 2, the steam power plant at Muscle Shoals, the Waco Lime Quarry, and the Gorgas Warrior plant and the transmission lines. The present value of these plants he estimated at $16,000,000 and their scrap value at $8,000,000.

Major General Lansing H. Beach, Chief of Army Engineers, was then called before the committee. He said there are certain features in the 100-year lease which should receive consideration because of the slowness in the development in the market for power in that locality. He also felt that another feature of the award to Mr. Ford which deserved consideration was the fact that the Tennessee River possesses an immense potentiality with regard to water power development. He stated that there is no stream in the country, considering the amount of water which it carries and the steepness of its slope, which will furnish the amount of water power that the Tennessee River does, except perhaps the St. Lawrence.

Colonel Hull, Acting Judge Advocate General, was the next witness and answered questions relative to the legal aspect of the Ford proposal.

Mr. Ford did not appear before the committee, but was represented by Mr. W. B. Mayo, engineer, who stated that Mr. Ford was not willing to modify his proposal in any way except to clarify the language and that he would not consider a 50-year proposal. It is his plan to use Nitrate Plant No. 1 to make the raw materials that go into the manufacture of automobiles and Nitrate Plant No. 2 for the manufacture of fertilizers. He further intends to use all the power developed at the various Muscle Shoals plants for his own purposes.

The Senate has referred the Ford proposal to the Committee of Agriculture and Forestry, and the committee will hold its first public hearings on February 16. The proponents of the Ford measure feel that their cause is in the hands of friends with this committee and those opposed to the Ford proposal feel that they will be well taken care of in the House Committee on Military Affairs.

The Dye Probe

The subcommittee of the Judiciary, appointed to investigate the dye and chemical industry, has been completed with Senator Shortridge of California as chairman. The other members of the committee are Senator Reed of Missouri and Senator Ernst of Kentucky. The support of chemical manufacturers throughout the country has been pledged to the committee by Dr. Chas. H. Herty in his capacity as President of the Synthetic Organic Chemical Manufacturers Association, and R. C. Jeffcott, President of the American Dyes Institute, has written to the committee offering to coöperate with them and facilitate their labors in every way. The public hearings began February 20.

Patent Office Relief

On February 14 the Senate passed, without amendment, the Patent Office relief bill. It begins to look as if the bill will become a law before This Journal issues and that a measure of relief is in sight for the Patent Office which now has on hand 62,000 applications for patents aside from 6000 applications for trademarks and designs—more work than was received in that office for any entire year up to 1909 and enough work to keep the Patent Office busy if it closed its doors and did not do any new work for the rest of the year.

Standardization of Glassware

At the request of the Section of Physics and Chemistry of the Association of Scientific Apparatus Makers of the United States of America, the Bureau of Standards called a conference of manufacturers of chemical glassware and representatives of users and dealers to consider the standardization of sizes and shapes of beakers, flasks, and other lines of apparatus. The conference opened at the Bureau of Standards at 10 o'clock on January 28 and later adjourned to the Shoreham Hotel.

The manufacturers expressed a willingness to coöperate in the unification and standardization of sizes and shapes along the lines of the recommendations of the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society which have previously been published in This Journal, **13** (1921), 1070, and a subcommittee was appointed by the conference to work out the details of this standardization. The working committee consists of representatives of the Corning Glass Works, the Kimble Glass Co., the Vineland Flint Glass Co., and Whitall Tatum. Mr. Walter Eimer was authorized to serve as executive officer.

Metric System Referendum

At a meeting of the National Council of the Chamber of Commerce of the United States on the afternoon of February 9, at the Washington Hotel, Washington, D. C., the question "Shall there be legislation for the compulsory adoption of the metric system?" was discussed. The report to the Board of Directors by the Special Committee on the Metric System was read by Mr. Edmund D. Fisher, chairman of the committee. This report favored the taking of a referendum throughout the country on the question of the adoption of the metric system, and suggested the wording of the question substantially in accord with the Ladd bill now before Congress. After addresses on the advantages of the metric system by Howard Richards, Jr., Secretary of the American Metric Association, and on the disadvantages of the system by W. C. Wilson, Assistant to the President of the American Institute of Weights and Measures, a lively discussion took place during the course of which both sides were presented in detail. At the close of the discussion, the Council passed a resolution recommending the postponement of the referendum to a more fitting time.

Recovery of Potash Lost in Washing Wool

A small wool washer made for recovering potash from fleeces in a solution of sufficient concentration to make the recovery of the potash profitable has been designed and is being tried out by the Bureau of Chemistry. It is said that the average fleece contains about 4 per cent of potash by weight, but in the ordinary method of washing wool it comes out in such dilute solution that it does not pay to recover the salt.

About 600,000,000 lbs. of wool are scoured in the United States each year, and if only 3 per cent of potash are recovered it would amount to 18,000,000 lbs. of actual potash that would be available for use in fertilizers. Some nitrogen is also recovered from wool along with the potash.

The United States Tariff Commission has expanded its census of dyes and coal-tar chemicals to include other synthetic organic chemicals. The prompt return of the schedules by the manufacturers it is hoped will insure earlier publication of the census than has heretofore been possible.

The National Agricultural Conference which assembled in Washington at the call of Secretary of Agriculture Wallace adjourned on January 28 after adopting a resolution favoring the acceptance of the Henry Ford offer for Muscle Shoals.

February 14, 1922

LONDON LETTER

By Stephen Miall, 157 Haverstock Hill, N. W. 3, Hampstead, England

I have heard no regrets that the year 1921 has now come to a close. It has been the worst year for chemical industry in history. There may have been in the middle ages worse years from the point of view of the progress and well-being of mankind, but in those early days applied chemistry, as such, did not exist.

We seem here—it may be a delusion—but we seem to have passed the worst of the depression. The textile industries are a little better than they were, the engineering industries are no worse; they hardly could be. The home markets are on the whole not quite so stagnant as they were six months ago, and the export business seems to be a little brighter. Of the manufacturers of chemicals, no large firm has gone into liquidation, and of the merchants very few. The soap industry seems now to be blessed by a number of orders and in some other branches of industry the outlook is brighter. No reasonable man here expects good trade in 1922 but almost all think it will be better than during the last few months. The political horizon has undoubtedly cleared even in Europe, where fears and animosities dating back a few centuries are apt to flare up at intervals because some sentiment of nationality or something equally unsubstantial has been aroused. It happens that this continent is at the moment fairly peaceably inclined and it is quite possible that in the course of the current year some of the old antagonisms will die down. It is, of course, hopeless to expect the Prussians to be friendly with the French or the Turks with the Greeks, but we may get to the stage where they can do business together.

Sometimes in the English papers we read of developments in applied chemistry but when they are closely investigated they turn out to be waiting for further capital or something of that sort. This is the fate of the Claude process for synthetic ammonia here and of other means of getting rich beyond the dreams of avarice.

I have after a good deal of search come across one development actually in being—not an epoch-making one, certainly, but of interest for all that—an improved method of making sodium silicate. Instead of dissolving the lumps of crude sodium silicate obtained by roasting together soda-ash and sand, and then evaporating the aqueous solution to a sirup, the new method introduces into a ball-mill a limited quantity of water and the lumps of crude silicate, which are ground up together until a mass is obtained which sets to a solid on cooling and contains 75 per cent of silicate. The new process is operating on a considerable scale in South Yorkshire and is said to be successful. The owners of the works claim a very considerable saving by eliminating the usual dissolving and evaporation. Probably the process with some modifications is capable of being adapted to other varieties of manufacture.

Those engaged in low-temperature carbonization of coal continue to speak with confidence of the satisfactory working of the plant at Barnsley, and they promise to disclose some new features a month or two hence. If these claims are well founded I hope to visit the works again and to give a detailed description of the novel features.

January 9, 1922

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Patent Reform

French inventors are under the law of 1844 in the matter of industrial ownership. This legislation has been recognized as superannuated for a long time, and a campaign for its reform is now being conducted. The chemists, who are the inventors most frequently involved, are specially active in this campaign.

For instance, a scientific communication made by the Académie des Sciences or in one of the chemical societies becomes public property, by this very fact, especially if a patent has not been taken out at the same time. Furthermore, it may happen that a scientific communication may not contain patentable material, though it may possess the highest technical interest; it does not always constitute a novelty, but frequently it may involve a condition of reaction which may lead to a great industrial improvement. Also, certain chemists take out patents but do not immediately find manufacturers and financiers to make possible their development; patent fees are paid for some years; then the chemist becomes discouraged and stops these payments. Some time later he is surprised to see his patents and processes put into operation.

All these gaps would need to be filled by creating what the *Syndicat des Inventeurs*, who are at the head of the movement, call "*le droit de suite*," a right which would obviously be limited to a certain period, fifty years, for example. There would be an almost complete fusion between this *droit* and what we French call "*le droit d'auteur*." Scientific treatises would be deposited, just as models or machines, and to this depot the *droit d'auteur* would be paid by the concessionaire.

Chemists differ on the question of how to know whether or not a new compound should be patented, and after a long discussion at the Congress of Industrial Chemistry it was decided that a new chemical compound could be patented as a new industrial product, but that the holder of the patent would be obliged to grant a license to any inventor who found a better method of preparation for this product. The conditions of this license would be settled by agreement of those interested or fixed by the authorities.

Further, the vote was passed that patents of chemical products could be expropriated by the State for public use.

Proposed Research Council

The French Senate is now considering a first draft of a law organizing an "Office national des recherches scientifiques, industrielles et agricoles." This organization is modeled on the National Research Council in the United States.

This plan has been fought from the first by Parliament, who see in it a duplication of the laboratories of the big teaching establishments of the state. It has been decided that the part of the new office would be one of coördination between the different laboratories, not only of the state but also of private industry. There have been established in France some laboratories analogous to the Mellon Institute, and these organizations would coöperate in the work of this office.

American Degrees for Sale

An ill-worded announcement which appeared in a French chemical paper has disturbed a number of our American friends. Individuals without authority have been offering to secure advanced degrees in American universities upon payment of a sum of money. I, who have seen many of your universities and laboratories, know that a degree can be obtained only by serious research work. The activity of the numerous American chemical societies and their many publications are still further witnesses that students at the universities are forwarding science and that the diplomas are the fruit of their labor. It is no less true that many French chemists have received from America circulars offering to secure these diplomas.

In France, we are publishing notices discrediting this, but it would also be well if the foreign ambassadors of the United States would publish an advertisement in order to avoid such attempted trickery in the future.

January 8, 1922

OBITUARIES

Charles Baskerville

Charles Baskerville, chemist, cultured gentleman, and loyal friend, died of pneumonia on the night of January 28 at his home in New York City. For nearly four weeks he had fought a brave but losing fight for his life. The news of his death has brought sadness and a deep sense of personal loss to his friends in many states of the Union and to those outside its bounds who had learned to esteem him and to value his friendship. The mere outline of his life and scientific achievements can tell but part of the story to those who knew him best and were nearest to him.

Underwood & Underwood

Charles Baskerville

Dr. Charles Baskerville was born in Mississippi June 18, 1870. Entering the University of Mississippi at sixteen years of age, he completed two years of academic study there. Later he spent a year at Vanderbilt University and further pursued his studies at the University of Virginia, devoting himself especially to the study of chemistry under Mallet. In 1891, he came to the University of North Carolina as part-time assistant in chemistry and, on completing the requirements, in 1894 received the Ph.D. degree. While on leave of absence for part of 1893 he studied under Hofmann at the University of Berlin.

During the fourteen years of his connection with the University of North Carolina he advanced from assistant to assistant professor, associate professor, professor, and, from 1900 to 1904, head of the department of chemistry. He proved himself an able teacher and kept in close touch with his students, showing a keen and sympathetic interest in all that concerned them, especially in their athletic sports where he acted as adviser and friend.

From the beginning of his graduate career he entered with zealous energy upon scientific investigation. His special interest lay in the field of the rare earths and many articles were contributed by him to the Society's *Journal*.

He became a member of the American Chemical Society in 1894 and later, as councilor and chairman of important committees, rendered much valuable service. He was one of the most constant attendants upon the annual meetings, effectively laboring for the best interests of the Society. He was also a Fellow of the London Chemical Society; a member of the Society of Chemical Industry; of the American Electrochemical Society; of the New York Academy of Sciences; of the Franklin Institute; and of the American Association for the Advancement of Science.

In 1904 he became professor of chemistry and director of the laboratory at the College of the City of New York, designing and supervising the erection of the new laboratory. His interest in research continued, tending more and more to the technical or applied side of chemistry, and this at last practically occupied his attention. In this connection may be mentioned his work on anesthetics, fats, oils, paper recovery, and other important matters. Several books have been published by him, including a text for schools, several for college classes, an account of the investigations upon the radioactive substances, and a volume on anesthetics.

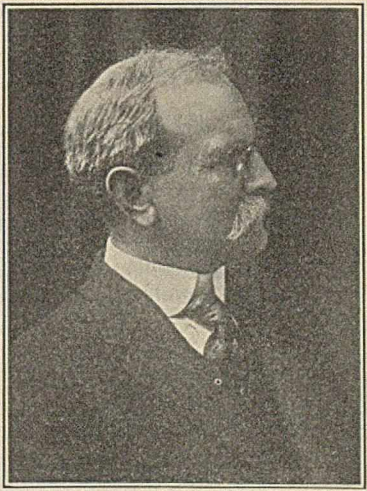
This necessarily brief outline reveals but little of the indomitable energy of the man, his multifarious activities, and the fine service rendered to the communities of which he was at any time a member. Bright, cheery, with most attractive personal characteristics and gifted in many ways, he will be greatly missed and his memory will be kept fresh by his many associates and friends.

F. P. Venable

William Frear

In the early morning hours of January 7, 1922, William Frear died from an apoplectic stroke, suddenly, at his home in State College, Pa. Chemistry lost an indefatigable worker, one of the pioneers of the science as applied to agriculture, in general, and to food production and legal regulation, in particular. His associates lost a zealous and inspiring co-worker, a patient thinker, a prudent counselor, and a true friend.

He was born March 24, 1860, at Reading, Pa., the son of the Rev. George Frear and Malvina (Rowland) Frear. After preparation in the public schools, he studied at Bucknell University (B.A. 1881), Harvard University, and Illinois Wesleyan University (Ph.D. 1883).



William Frear

On completion of these studies, Dr. Frear immediately entered the government service under the newly appointed Chief Chemist, Dr. H. W. Wiley. In 1885, he received the appointment of Assistant Professor of Agricultural Chemistry at the Pennsylvania State College where he was soon recognized as a leader in his subject, both in the College and in the State Experiment Station. He maintained, however, official and active association with the Federal service, doing notable pioneer work in the formative period of the enactment of Food and Drug laws, both State and Federal. As fundamental to and preparatory for this legislation, the Committee on Food Standards was appointed. As chairman of this Committee, it was Dr. Frear's duty to conduct a voluminous correspondence, make extensive literature searches, hold hearings at which antagonistic interests were in action, sift the evidence judicially, and draw a conclusion. The industry, care, thought, and tact which he displayed in this work is probably known only to the very few who were closely associated with him. The point of view and method of the scientific investigator is also too generally overlooked in this work. His services were again called for when in 1914 there was established the Joint Committee on Definitions and Standards, of which he was chairman at the time of his death.

As a true pioneer in agricultural college teaching and experiment station work, the scope of his interest and of his scientific production was wide, including meteorology, lime production and use, tobacco culture, soiling crops, composition of foods and feeds, including forage plants, laws to control the production and sale of fertilizers, foods and drugs, and kindred subjects.

The list of scientific societies of which he was a member and the positions of honor and responsibility, which he held in these societies and in his official life, testify to a life of remarkable breadth and high endeavor.

His social and civic activities were equally broad, keeping him engaged continually for his family, his neighbor, his church, his town, his state, and his country. He well fulfilled the specification of Phillips Brooks for a "four-square man."

Isaac King Phelps

Personals

Charles A. Roos, president of the firm of Charles A. Roos, Inc., 429 East 91st Street, New York, N. Y., manufacturers of copper chemical equipment, died suddenly of heart disease on the afternoon of Wednesday, January 11, 1922, in the New York Athletic Club, of which he had been a member for more than twenty years. Mr. Roos collapsed just as he was about to enter the water of the swimming pool.

Mr. Roos, who was sixty-three years old, was born in New York and was widely known through his various business interests. His firm not only manufactured much of the copper chemical equipment used in synthetic organic chemical manufacturing plants around New York City, but also produced a large amount of the copper equipment used by the large breweries in this vicinity. It is understood that the business will be carried on under the direction of his son, Mr. Charles A. Roos, Jr., who has been general manager of the concern for some years.

Frank R. Eldred, for many years chief chemist and director of the scientific division of Eli Lilly & Co., and **Frederick C. Atkinson**, chemical director of the American Hominy Co., manufacturers of cereal products, vegetable oils, sugars, and sirups, have organized the firm of Eldred and Atkinson, consulting chemists and engineers, with offices at 48 East 41st St., New York City, and 1857 Gent Ave., Indianapolis. Mr. Eldred will have charge of the New York office while Mr. Atkinson will remain in Indianapolis.

Mr. W. S. Frisbie recently resigned his position as Chief of the Bureau of Food, Drugs and Oil, State Department of Agriculture of Nebraska, to accept an appointment as Chemist in Charge of the Office of Coöperation, Bureau of Chemistry, Washington, D. C.

Mr. Jerome Alexander has recovered from his lengthy illness and has become president of the Uniform Adhesive Co., Inc., Brooklyn, N. Y., manufacturers of glues, gums, pastes, and adhesives.

Mr. Ernest W. Dean of the Bureau of Mines Experiment Station, Pittsburgh, Pa., has resigned from the Bureau, and is now with The Standard Oil Company of New Jersey.

Dr. Paul E. Klopsteg, formerly with the Leeds & Northrup Co., Philadelphia, Pa., is now with the Central Scientific Co., Chicago, Ill.

Mr. John P. Harris, chemical engineer for the Allbright-Nell Co., formerly of New York, is now located at 829 New York Life Building, Kansas City, where he will represent the Allbright-Nell Company in the southwest.

Dr. W. W. Skinner, Assistant Chief of the Bureau of Chemistry, has been elected chairman of the Joint Committee on Definitions and Standards to succeed Dr. William Frear, deceased. **Mr. E. M. Bailey**, Agricultural Experiment Station, New Haven, Conn., has been appointed as the representative of the Association of Official Agricultural Chemists on this committee to fill the vacancy caused by the death of Dr. Frear.

Mr. John Helfrich, who for the past four years served as manager of the Information Bureau of the Chemical Catalog Co., Inc., and who was in charge of the Service Department of This Journal, has resigned to establish an office at the Chemists' Club Building, New York City, as a consulting chemist specializing in the development of products that find an application in the leather industry. Prior to his association with the Chemical Catalog Co., Mr. Helfrich was engaged in the leather industry as chemist and assistant plant superintendent.

Industrials

The Bethlehem Laboratories, Inc., a $5,000,000 corporation, has been organized in Pittsburgh to manufacture a new antiseptic, known as hyclorite, which is said to possess 175 times the germicidal strength of hydrogen peroxide. Among the incorporators are Homer D. Williams, president, Carnegie Steel Co.; Taylor Allerdice, vice president, National Tube Co.; and Dr. J. J. Reilly, U S. Shipping Board. The plans of the corporation include the construction of a modern chemical plant in Pittsburgh.

At the annual meeting of the stockholders of Monsanto Chemical Works, the following directors were elected: John F. Queeny, Gaston DuBois, Edgar M. Queeny, Theodore Rassieur, H. O. McDonough, J. D. Lumaghi, and J. R. Goodall. The following officers have been elected for the year 1922: John F. Queeny, chairman of the board; Gaston DuBois, president; H. O. McDonough, vice president; W. R. Phemister, treasurer; Edgar M. Queeny, secretary; C. A. Zacher, assistant secretary.

The Commonwealth Edison Company of Chicago has opened a new $10,000,000 power plant, which when completed will generate 250,000 h. p. It is planned later to build another 250,000 h.-p. station on the shores of Lake Michigan at Waukegan, which will fit into a scheme of electric superpower development of Wisconsin, Illinois, and Indiana. The Chicago system has become the hub of a network of interconnected electric transmission lines in the upper Mississippi Valley which spreads nearly to Minneapolis on the north, southwest to the Mississippi River, and south to the coal fields of Kentucky.

The Drug and Chemical Section of the New York Board of Trade and Transportation has elected Frank C. Starr, Sharp & Dohme, chairman; August Wasserschied, Mallinckrodt Chemical Works, vice chairman; William A. Hamann, Roessler & Hasslacher Chemical Co., treasurer; William F. McConnell, secretary; Clement C. Speiden, Innis Speiden & Co., representative of the Section in the Board of Trade and Transportation.

E. L. Pierce, president of the Solvay Process Co., Syracuse, N. Y., has resigned, and will be succeeded by E. D. Winkworth, president and executive vice president of the Semet-Solvay Company. Mr. Pierce has also resigned his position as vice president and director of the Allied Chemical and Dye Corporation.

The Dyestuff Department of E. I. du Pont de Nemours & Co., Inc., has recently been reorganized with a view to the better handling of the technical and commercial problems of the industry. F. W. Pickard, vice president, has been relieved of his duties on the executive committee to become general manager, with W. F. Harrington as assistant. C. A. Meade, vice president and former general manager, and M. R. Poucher, former director of sales, have been made executive staff officials. Both are directors of the company. Cesare Protto, formerly assistant to Mr. Poucher, has been made director of sales.

The Combustion Engineering Corporation has opened a branch office at 806 First National Bank Building, Pittsburgh, Pa., in charge of Mr. W. C. Stripe, formerly manager of the Philadelphia office.

The National Aniline & Chemical Co., Inc., has announced the production of two new dyes, National wool green S and National quinoline yellow.

The Argentine Army has just placed its first order for American ammunition with E. I. du Pont de Nemours & Co. Previously a large part of the army's ammunition was purchased through German concerns.

BOOK REVIEWS

The Vitamins. By H. C. Sherman, Professor of Food Chemistry, Columbia University, and S. L. Smith, Specialist in Biological and Food Chemistry, U. S. Department of Agriculture. American Chemical Society Monograph Series. 260 pp. Book Department, The Chemical Catalog Company, Inc., New York, 1922. Price, $4.25.

Barely a decade has elapsed since the word "vitamin" was originated; yet to-day it is found not only in contributions to scientific journals but also in the pages of the popular magazines and newspapers and on the billboards by the highways. After all, it is not utterly surprising that the vitamins have become something to conjure with. Anyone who has actually followed the demonstrations of the unique physiologic potencies of these hitherto unidentified factors in nutrition—substances which promote well-being not by furnishing energy in measurable calories or foodstuffs in grams but rather by contributing some "little item" in food that spells nutritive success—can better appreciate the unanticipated significance of their discovery.

Quite naturally there has been and still is much confusion and misunderstanding about vitamins, what they are, where they occur, and how they function. Most contributions to science that lend themselves readily to popular exposition experience a similar history. There is at present an insistent demand for information that shall not be merely guesswork or superficial compilation. The intelligent interpretation of a scientific subject still in the making, yet already comprising results recorded in a thousand or more contributions to technical journals, requires an expert who is more than a mere abstractor. It is, indeed, fortunate that Professor Sherman and his colleague, experienced in the investigation of vitamins and related aspects of nutrition, have undertaken the timely task of preparing this monograph for the American Chemical Society's series. The contribution is comprehensive without being too diffuse. It reviews the history of the subject, the properties and distribution of the three now recognized specific vitamins, their relation to certain "deficiency diseases," and the place of vitamins in the problem of the food supply. The review of the successive discoveries which led to the development of the vitamin hypothesis is singularly accurate and intelligently discriminating. In this respect it quite surpasses in quality most of the stuff which has been purveyed as history of an interesting phase of scientific progress. In fact, the book gives the impression of first-hand information on every page. Here is a volume from which the nontechnical reader can derive instruction in readable form regarding the occurrence of vitamins in foods and their significance in nutrition, and "make possible an intelligent use of food so as to provide adequately for our vitamin needs along with our other nutritional requirement, and without going beyond the range of our ordinary staple articles of food." The trained investigator, on the other hand, will find the limitations of knowledge undisguised and the unsolved problems for research brought to his attention by the critical form of the review.

The elaborate bibliography itself guarantees that the new monograph will become the vade mecum of the rapidly growing numbers of persons who are curious, scientifically or otherwise, about vitamins.

Lafayette B. Mendel

The Physics and Chemistry of Colloids and Their Bearing on Industrial Questions. 190 pp. Published by His Majesty's Stationery Office, London, 1921. Price, 2s. 6d. net.

A prefatory note by the Department of Scientific and Industrial Research upon whose advice this pamphlet was published, says:

> In view of the growing industrial importance of colloidal physics and chemistry and with the intention of surveying critically the present state of knowledge as an aid to future development, the Councils of the Faraday Society and the Physical Society arranged a joint Conference on the subject which was held on the 25th of Oct. 1920........It must be understood that in these circumstances the Department of Scientific and Industrial Research accepts no responsibility for the statements of opinion or fact contained in this report.

The remark and the discussion following each section are indicative of the fact that there is not yet complete unanimity of opinion on many points of colloid chemistry. The science is in a state of flux, of constant criticism, experiment, and search for further light; it has the vitality of youth and growth.

Many well-known names are included among those who presented papers or took part in the discussion. Following an introductory survey by Svedberg is a paper on the general structure of colloids by W. Pauli. Then follow papers on *Emulsions and Emulsification* by Donnan, Clayton and Bhatnagar; on *The Physical Properties of Elastic Gels* by Hatschek, H. R. Proctor, Bradford, Barratt and Zsigmondy; on *Glass and Pyrosols* by Sir H. Jackson and M. W. Travers; on *Nonaqueous Colloidal Systems* by Sir Robert Robertson (nitrocellulose), Barr and Bircumshaw (cellulose acetate), F. Sproxton, B. D. Porritt (rubber), and Wolfgang Ostwald; on *Precipitation of the Disperse Systems*, by Willows, J. N. Mukherjee, W. Harrison, Wm. Clayton, Chatterji and Dhar, A. G. Lowndes (lead azide), and W. E. Hughes (electrodeposition of metals); on *Electric Endosmosis and Cataphoresis* by A. W. Porter, W. R. Ormandy, and H. Freundlich.

Appendix I is Jacques Loeb's paper on "The Proteins and Colloid Chemistry" (familiar to readers of *Science* and the *Journal of General Physiology*), where the author concludes that the behavior of the proteins contradicts the idea that the chemistry of colloids differs from the chemistry of crystalloids—though long before Graham's time, and surely ever since, it has been recognized that certain wide differences exist between the two.

Appendix II is a very valuable and interesting Inaugural Dissertation by H. Kneebone Tompkins, which since 1896 had lain unpublished at the University of London. Much important and time-saving work is undoubtedly thus buried in oubliettes. While Tompkins' work dealt mostly with rubber, he drew some very interesting analogies between vulcanized caoutchouc and other substances, notably metals, *which he regarded as colloids.*

Although many of the papers presented had already been published in the journals of the societies, and also in the *Kolloid Zeitschrift*, the Committee is to be thanked for rendering them all accessible in one volume, with discussion. This pamphlet will be in the library of chemists interested in colloids, and will arouse the interest of those who are not. Chemists cannot be like the Bourbons, who "learn nothing and forget nothing." Research demolishes old ideas so rapidly that often our textbooks are teaching theories and even "facts" which are recognized as erroneous.

Jerome Alexander

The Fire and Explosion Hazards of Commercial Oils.[1] By WILLIAM VLACHOS AND C. A. VLACHOS. xvii + 292 pp. Copyright by Vlachos & Co., 1921. Price, $5.00.

This book relates primarily to the fire hazard of the animal, vegetable, and mineral oils of commerce, together with the commercial processes of their manufacture and refining. The common solvents used for extracting oils are included. Essential oils are not referred to. There are chapters relating to hydrogenation, sulfonation, vulcanization, nitration, fuel oil burning systems, casinghead gasoline plants, ethyl and wood alcohol, and fire causes in the petroleum industry. In addition an oil schedule is presented which includes flashing points, iodine values, volatility, and what is referred to as the "fermentation value." Numerical values representing the comparative fire hazard are assigned to the oils and solvents of which there are fifty-five. This rating is referred to as the "Vlachos Grading."

The subject matter presented is based largely on the experience of Vlachos & Co., Philadelphia Inspectors, and on available technical literature. The field covered in the limited space of the book is too large to include much detail, and the information given is general in character, but the more important hazards are not neglected. The subjects are treated in a nontechnical manner and in a free conversational style from the standpoint of the underwriters' practical inspector. The book is of value to the inspector, the busy underwriter, and the chemist or chemical engineer requiring information on the above phase of the subject rather than on the chemical phases or the chemical and physical fundamentals involved.

The first eight chapters on animal and vegetable oils appear to represent the best part of the book. The chapters on sulfonation, vulcanization, and nitration appear to be too brief. The Vlachos Grading is similar in form to Underwriters' Laboratories classification of the hazardous properties of liquids, (better known as the National Fire Protection Association method), except that in the Vlachos Grading the iodine value is employed. In the opinion of the reviewer it would have been of assistance to the reader to include a brief reference to and comparison of the Vlachos Grading with other methods of classification of hazards. It is also thought that a bibliography referring to the technical literature on the subject would add to the value of the book.

A. H. NUCKOLLS

Contemporary Science. By BENJAMIN HARROW. 17 x 11 cm. 253 pp. Boni and Liveright, New York, 1921. Price, $0.95 net.

The subdivisions are: Introduction, by Benjamin Harrow; Modern Physics, by R. A. Millikan; The Structure of Atoms and Its Bearing on Chemical Valence, by Irving Langmuir; Engineering before and after the War, by Sir Charles Parsons; Methods of Gas Warfare, by S. J. M. Auld; What Are Enzymes, by Benjamin Harrow; Natural Death and the Duration of Life, by Jacques Loeb; The Physiology of the Aviator, by Yandell Henderson; Twenty-five Years of Bacteriology, by Simon Flexner; Before and after Lister, by W. W. Keen; The Measurement and Utilization of Brain Power in the Army, by R. M. Yerkes; Conceptions and Misconceptions in Psychoanalysis, by Trigant Burrow; Einstein's Law of Gravitation, by J. S. Ames.

Millikan cites the following as the ten most important advances in physics of the last twenty years: the verification of the atomic and kinetic theories; the divisibility of the atom; radioactivity; the atomicity of electricity; the electrical origin of mass; the nucleus atom; the nature of X-rays; crystal structure; the atomic numbers; the quantum relations.

Langmuir discusses the octet theory and concludes that:

> In the past the term valence has been used to cover what we may now recognize as three different types of valence, as follows:
>
> 1—Positive valence: the number of electrons an atom can give up.
> 2—Negative valence: the number of electrons an atom can take up.
> 3—Covalence: the number of pairs of electrons which an atom can share with its neighbors.
>
> It is recommended that only for valences of the covalence type should definite bonds be indicated in chemical formulas. One of the particular advantages of the present theory is that it becomes easy to distinguish between covalence and the other types, and thus to predict with certainty in what way electrolytic dissociation will occur, if at all.

Sir Charles Parsons lists the development of aircraft and of sound ranging and listening devices as the two big engineering achievements during the war and the development of the steam turbine and of electrical distribution as the pre-war achievements. Col. Auld's paper on gas warfare is already familiar to the chemists. Harrow advocates the view that an enzyme is a salt in the broad sense adsorbed by a colloidal complex which is usually protein-like. Loeb finds that the life of aseptic fruit flies doubles approximately for ten degrees drop in temperature, which suggests to him that life is a chemical reaction and that death occurs normally when the reaction is finished. If man could live at all with the temperature of his blood at 7.5° his average life would be about nineteen hundred years.

Henderson points out that life is often compared to a flame but that a candle is affected by the proportions of oxygen and nitrogen while man depends solely on the absolute amount of oxygen. Flexner shows that antitoxins are effective against diseases from toxalbumins, etc., but not against the more numerous diseases involving microbes which have penetrated deeply into the organs. Dr. Keen gives the almost incredible percentage of deaths after amputations owing to infection in the days before Lister. Going to a large hospital for an operation in those days was practically equivalent to a death sentence.

WILDER D. BANCROFT

Technical Records of Explosives Supply, 1915-1918. III. Sulfuric Acid Concentration. 91 pp., 30 illustrations. 12s. **IV. The Theory and Practice of Acid Mixing.** 93 pp., 25 illustrations. 12s. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1920. 19 x 28 cm. each.

Before the war the Kessler system was regarded in Europe as the most successful type of concentration plant for spent sulfuric acid, an unavoidable by-product in all nitration processes, though the Cascade system had long been used in this country. As, after entrance into the war, the English found it impossible to get delivery of Kessler plant, the Cascade system was adopted on a large scale because it admitted more readily of rapid improvization from accessible material than any other, but the higher temperatures required for the greater concentrations caused such volatilization of the sulfuric acid as to compel the covering in of the lower basins of the cascade and the aspiration of the fumes through coke scrubbers. As soon as possible, therefore, Gaillard and Gilchrist concentration plants were erected and Cottrell precipitation plants installed.

Volume III of this series is devoted to the description and consideration of these three types of plants. Under each section there are given, with detailed plans, a description of the plant and its method of operation, and the general principles governing its construction and operation, but one is most impressed by the extent of the data based on experience that are presented. Thus some 24 pages are given to illustrating in detail how the heat balance for the gas producers and Gaillard towers was ascertained, the object stated being "to estimate the thermal efficiency of the gas producers and to allocate all the thermal losses," and, in recording the method of solution of the problem, there is given a description of the means by which the experimental

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[1] See letter by S. R. Church, p. 240, of this issue.—EDITOR.

data were obtained. The truly practical character of this publication is emphasized by the paragraphs on "starting up a unit" and "shutting down a unit" of the Gaillard plant, for technical writers too often omit such essential information.

Volume IV deals, in Section I, with "acid cycles, acid balances, and control of plant output," the several classes of acid cycles dealt with being TNT, nitroglycerin, and guncotton and nitrocellulose, since each of these products requires for its manufacture a special "mix" and yields a characteristic "spent." Section II deals with "the position of the acid mixing plant in the acids cycle, and the procedure adopted in mixing," and seven pages are assigned to "the calculation of mixes" and thirteen to "the calculation of dopes," while graphs with which to facilitate the operations are given. Section III deals with "plant and process for acid mixing" in some 34 pages and, while necessarily descriptive, it contains many pages of illustrative calculations and several tables of data. Here as elsewhere, one is impressed by the careful accounting for energy as well as for matter.

What has been said of Volumes I and II of this series[1] holds true for the volumes now under consideration. Typographical errors are very uncommon and those observed are of little importance. These volumes should be especially valued by the teacher who seeks concrete examples for his pupils, for they are to be found here in great abundance, while the student will find in this record from practice convincing evidence of the importance of this method of accounting.

Charles E. Munroe

The Riddle of the Rhine. By Victor Lefebure. 279 pp. W. Collins Sons & Co. Ltd. Glasgow, Melbourne, Auckland; London, 48 Pall Mall, 1921. Price, 10s, 6d.

The importance of gas warfare, again emphasized by international consideration of reduced armaments, justifies the increasing literature of this field. The "Riddle of the Rhine" is a candid authoritative discussion of the subject from the standpoint of the English nation. Major Lefebure is a chemist, a veteran of two years at the front, and former liaison officer between England and France. He was a member of several interallied technical and supply organizations and after the Armistice played an important part in the official allied inspection of German chemical factories, and in bringing vital chemical data before his country. His broad qualifications for authorship in this field are evidenced in his scientific, military, and philosophical presentation, and in the fairness and justice with which he appraises the contributions of the several allied countries. France's quick success and courageous struggle for early production of yperite, her development of a bromine industry in Tunis under wartime handicap, America's overwhelming activities and great research organization, "second only to the I. G.," all are carefully accredited. The struggle for initiative, the strategic role of production in chemical warfare, the evolution of weapons through cloud attack, artillery shell, solid toxic substances, and finally mustard gas, which defied complete protective measures, are accurately analyzed and illumined by specific history. Germany's conceded lead in this mode of warfare was due to a flexibility in research and production, inherent in her varied chemical resources. These gave surprise possibilities, the essence of successful war. The allies lacked quick means of converting research ideas into casualties.

To Major Lefebure, the riddle of the Rhine is the ominous, impenetrable potentialities of the I. G. bristling the Rhine and its tributaries. "It has added economic cohesion to technical efficiency, and is to-day the largest technically efficient potential instrument of war in the world." The author avowedly believes in chemical disarmament of Germany, and points to the failures and difficulties in enforcing the Treaty of Versailles in chemical matters. The inherent difficulties in the inspection by a League under agreements to refrain in times of peace from chemical preparedness are searchingly presented. In fact, the logical end of the author's argument is a world balance of chemical power, either through competitive militarism, industrially disguised, or agreed ratios.

We had suspected that the war and the press had exhausted all the imaginary possibilities of future chemical weapons, but we are still able to react with interest to the author's suggestion of future armies staggering to their fate because of a change in the viscosity, through exposure to the desired chemical, of the liquid contents of the semicircular canals of the inner ear, thus destroying the sense of equilibrium!

The book is written by a man who knows and feels, and has the gift of utterance. It is peculiarly in line with American convictions on the subject and stirs the reader with the tremendous difficulties and weaknesses of current internationalism built along pre-1914 lines.

W. Lee Lewis

Coke-Oven and By-product Works Chemistry. By Thos. Biddulph-Smith. Cloth 6 x 9, x + 180 pp., 62 illustrations and 7 folding plates. Charles Griffin & Co., Ltd., London; J. B. Lippincott Co., Philadelphia, 1921. Price $7.00.

This book is essentially one of laboratory methods for use by chemists at by-product coke-oven plants and gas works; especially the former, for it does not cover the subject of photometry and gas purification. It gives methods for testing coal and coke, gas, flue gases, tar, pitch, ammonia, and benzene products. Several other tests which are frequently required in the above industries are given, and one chapter has been devoted to calorimetry and pyrometry.

The chapter on coal and coke includes methods for sampling and gives a method for testing the coking property of coal, but methods for ultimate analysis, porosity, and shatter tests are omitted.

The book is particularly useful at benzene recovery and refining plants. Thirteen graphs give boiling temperatures for any mixture of two oils, such as carbon bisulfide, benzene, toluene, and xylene. Other graphs show the relation of the specific gravity of benzene to carbon bisulfide and paraffin content and thus enable the benzene plant chemist to make a quick estimation of the carbon bisulfide or paraffin content.

The book comprises methods which are in general more familiar to the gas and coke-oven chemists of Europe than to those of America. The principles involved are essentially the same, except for modifications which American chemists have applied. It is not a serious objection that the work is based on English practice since it is almost imperative that our chemists should become familiar with the experience and practice of other chemists before they can judge the relative merits of various methods and their applications to individual problems.

A few examples of the differences between the methods given in this work and those of American practice are as follows: In the analysis of coal and coke the sample is ground to pass a 30-mesh sieve, not a 60-mesh sieve as in American practice. In the analysis of gas, oxygen is determined first, whereas in America oxygen is determined after the illuminants. In the distillation of benzenes a standard Engler flask is used, whereas in American practice a standard 200-cc. side-neck flask of slightly different dimensions has been adopted. In the refining of benzenes the acid wash test is judged by the color of the acid layer, apparently without comparison with standard colors, as is done in American practice.

The methods which are given are of a standard nature and generally those which have been accepted as reliable. The work is comprehensive, and the methods are stated as briefly as possible.

E. F. Blackie

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[1] This Journal, **13** (1921), 1176.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

January

The possibility of using the by-products of sugar making, especially the heavy molasses residue, for the production of **alcohol** as a **motor fuel** has only recently attracted general attention in Cuba. The current price for motor spirit as sold to the consumer is 27 to 30 cents, as compared with gasoline at about 45 cents, and while it does not appear probable that Cuban alcohol can give serious competition to gasoline outside the island, it is made from materials which, in many seasons, sell at very low prices, and its use appeals to local patriotism. (Pp. 24–5)

Statistics are given relative to the production of **mineral oil** in the Dutch East Indies during the calendar years 1917, 1918, 1919 and 1920. (P. 26)

A demonstration was recently given of the new type of **oil-fuel burner,** known as the "Reid-Erskine liquid fuel atomizer and burner." Among the advantages claimed for it are the high efficiency it possesses, due to the complete atomization of the liquid fuel, and the transformation of the atomized fuel into a light inflammable gas, thereby producing complete combustion. (P. 27)

Experiments have recently been conducted in Norway on the production of coal from **cellulose lye.** A factory has been erected which it is claimed will produce 8000 tons of coal from lye that was formerly dumped in the run as waste. (P. 31)

A decided decrease in British trade in **naval stores** during the first 10 months of 1921, as compared with the corresponding periods of 1913 and 1920, is reported. (P. 33)

The total French production of **naval stores** for 1921 is estimated at 31,000 tons of turpentine and 105,000 tons of rosin, pitch, etc., or 4000 tons less turpentine and 15,000 tons less rosin than in 1920. (P. 34)

Nysaland has revised its **import duties** on kerosene, petrol, motor spirits, and lubricating oils. (P. 47)

Western Samoa has established new import and export duties on **copra.** (P. 47)

The export restriction on **petroleum** products from Tunis has been removed. (P. 48)

The Italian government has announced a 30 per cent reduction in the fixed price for **lime citrate.** (P. 54)

German exports of **heavy chemicals** showed a decline, by volume, during November as compared with October of 12.0 per cent and of dyes of 3.0 per cent. (P. 57)

Statistics are given relative to the production of the **zinc** and lead mines of Algeria during 1920. (P. 65)

The oil industry in Russia under Bolshevik régime is described. (Pp. 87–9)

Recent developments in the Tampico oil fields show that the 25,000-bbl. well of heavy oil in the San Geronimo district contains oil of heavy gravity, testing around 14° Bé., or more like Panuco crude. It is the lowest gravity oil found between Panuco and the southern extremity of the south fields. (Pp. 89–90)

A change has been made in the Australian **import duty** on arsenate of lead, and import duties have been deferred until March 31, 1922, on carbonate and bicarbonate of soda and soda silicate; soda ash; caustic soda; and citric acid. (P. 99)

A market for **cement** is reported to exist in Guatemala. (P. 110)

Attention is called to the value as a **tanning material** of the plant *Acacia arabica,* which French experiments have shown can be used for tanning either alone or with sumac, quebracho, and oak bark. It would appear that it might replace Sicilian sumac, of which 7000 tons were imported into France in 1913. (P. 142)

Under the new Denmark Emergency Tariff Law increased duties are levied on **acetic acid.** (P. 156)

A Brazilian decree continues the American **preferential duties** for 1922 on paints and colors, cement, and varnish. (P. 157)

A French import duty of 2.50 francs per 100 kilos will be applied on **benzene** intended for motors and for fuels. (P. 157)

The Italian customs authorities have been instructed to permit the unrestricted exportation of **potassium salts.** (P. 157)

German production of **nitrogen** by **atmospheric fixation** is reviewed and the statement made that calcium cyanamide factories in Germany have an output now of approximately 500,000 tons, with a nitrogen content of about 100,000 tons. (Pp. 164–5)

The new statistical classification for **petroleum** and its products exported from the United States, which became effective January 1, 1922, is given. (P. 194)

The production of **crude oil** in Rumania is reviewed. (Pp. 194–5)

The **wolfram** mines at Hatch's Creek, Northern Territory, Australia, which, during the war, furnished 50 per cent of the wolfram marketed throughout the world, have been abandoned because of the fall of the market and the high costs of production. (Pp. 200–1)

The **import duty** imposed by Salvador upon chlorides of lime and calcium has been removed. (P. 212)

Beginning with the January number, the Monthly Summary of Foreign Commerce issued by the Statistical Division of the Bureau of Foreign and Domestic Commerce will present export figures for **chemical glassware.** Quantities as well as values will be given. (P. 255)

Exports of **crude petroleum** from the United States during December 1921 showed a decrease of approximately 40 per cent from the November figure. Comparative statistics are given of petroleum exports for the past three years, the 1921 exports showing a decrease over 1920 but an increase over 1919. The imports of petroleum for December showed an increase, as did also the total imports for 1921, the total 1921 imports increasing about 800,000 gal. over the 1920 imports and more than doubling the amount imported during 1919. (Pp. 267–8)

A translation is given, in part, of an address on the present status of the **petroleum** question in Argentina. (Pp. 268–9)

The production of **petroleum** in Argentine during 1921 showed a considerable increase over the 1920 production. (P. 270)

Peru has relaxed its control on the exportation of **cottonseed.** (P. 281)

An increase in the **import duty** on gasoline is proposed in Brazil and changes have been made in the duties on mineral oils and residues, paraffin candles, and calcium carbide. (P. 281)

France has increased her **import duties** on lubricating **oils,** heavy oils, and residues of petroleum and other mineral oils. (P. 281)

France has changed her **import duties** on **fixed oils** (cottonseed oil, sesame, and peanut oils) for the manufacture of alimentary fats. (P. 281)

A little-known source of **copra** is being developed in the former German possession in New Guinea. (P. 294)

The Japanese law and regulations relating to the **camphor oil** monopoly, with all amendments to 1910, is on file in the Far East Division of the Bureau of Foreign and Domestic Commerce. (P. 294)

The **mining laws** and regulations of China, which were last promulgated by the Chinese Government on March 11, 1914, are available in circular form upon application to the Bureau of Foreign and Domestic Commerce. (P. 294)

A copy of the translation of the June 21, 1915, Japanese law for the encouragement of the manufacture of **dyes** and **drugs** may be secured by addressing the Bureau of Foreign and Domestic Commerce. (P. 294)

STATISTICS OF EXPORTS TO THE UNITED STATES

Peru—(P. 18)	Bordeaux—(P. 34)	Brazil—(P. 128)
Vanadium	Rosin	Rubber

CURRENT PUBLICATIONS

NEW BOOKS

Aggregation and Flow of Solids. Sir G. Beilby. 256 pp. Price, 20s. net. Macmillan & Co., Ltd., London.

Colloids: The Formation of Colloids. The. Svedberg. 127 pp. Illustrated. Price, $3.00. D. Van Nostrand Co., New York.

Conductivity: Further Light on the Theory of the Conductivity of Solutions. Guy Clinton. 15 pp. Price, 50 cents. Chemical Publishing Co., Easton, Pa.

Construction Cost Keeping and Management. Halbert P. Gillette and Richard T. Dana. 572 pp. 264 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Dairy Chemistry: A Practical Handbook for Dairy Chemists and Others Having Control at Dairies. Henry Droop Richmond. 490 pp. Illustrated. Price, $6.00. J. B. Lippincott Co., Philadelphia.

Dietetics: A Laboratory Handbook for Dietetics. Mary Schwartz Rose. Revised edition. 156 pp. Price, $2.10. The Macmillan Co., New York.

Drug Industry: The Brown Book: Credit Guide and Reference Book, Published for the Drug, Chemical and Allied Lines throughout the United States. Drug and Chemical Credit Association. 1500 pp. Price, $50.00 net. Drug and Chemical Credit Association, New York.

Dyes: Matières Colorantes Artificielles: Leur Fabrication et leur Emploi. H. Vassart. Preface by J. Garçon. 233 pp. Price, paper, 30 fr. Albin Michel, Paris.

Edible Fats and Oils, Their Composition, Manufacture and Analysis. W. H. Simmons and C. Ainsworth Mitchell. 2nd revised and enlarged edition. 192 pp. Price 11s. Scott, Greenwood & Son, London.

Electrons and Ether Waves. Sir William Bragg. 23rd Robert Boyle Lecture. 14 pp. Price, 45 cents. Oxford University Press, New York.

Elements of Fractional Distillation. Clark Shove Robinson. International Chemical Series. 204 pp. Illustrated. Price, $2.50 net. McGraw-Hill Book Co., Inc., New York.

EMF Electrical Year Book: A Combined Dictionary, Encyclopedia and Trade Directory of the Electrical Industry. Frank H. Bernhard, Editor. 1000 pp. Price, $10.00. D. Van Nostrand Co., New York.

Equations: First Course in the Theory of Equations. Leonard Eugene Dickson. 168 pp. 26 figures. Price, $1.75 net. John Wiley & Sons, Inc., New York.

Fuel Research Board: Second Memorandum on Fuel for Motor Transport. Department of Scientific and Industrial Research. Price, 6d. H. M. Stationery Office, London.

Gas Cylinders: First Report of the Gas Cylinders Research Committee. Department of Scientific and Industrial Research. Price, 7s. 6d. H. M. Stationery Office, London.

Handbook of Laboratory Glass-Blowing. Bernard D. Bolas. 106 pp. Illustrated. Price, $1.50. E. P. Dutton & Co., New York.

Hydroelectrical Engineering: A Book for Hydraulic and Electrical Engineers, Students and Others Interested in the Development of Hydroelectric Power Systems. Richard Muller. 431 pp. Illustrated. Price, $6.00. G. E. Stechert & Co., New York.

Metallurgy of Zinc and Cadmium. H. O. Hofman. 340 pp. Illustrated. Price, $4.00. McGraw-Hill Book Co., Inc., New York.

The Microscope. Conrad Beck. 144 pp. Price, 2s. 6d. R. & J. Beck, Ltd., London.

Microscope, Its Design, Construction and Application. F. S. Spiers, Editor. 260 pp. Illustrated. Price, $5.50. J. B. Lippincott Co., Philadelphia.

Mineralogy: A Textbook of Mineralogy. Edward S. Dana and William E. Ford. 3rd edition, revised and enlarged. 720 pp. 1050 figures. Price, $5.00 net. John Wiley & Sons, Inc., New York.

Organic Chemistry: Fundamental Principles of Organic Chemistry. Chas. Moureu. Translated from 6th French edition by W. T. K. Braunholtz. 399 pp. Price, 12s. 6d. net. G. Bell & Sons, Ltd., London.

Perfumes, Essential Oils and Fruit Essences Used for Soap and Other Toilet Articles: A Concise and Practical Account, Including Their Chief Constants, Methods of Analysis, and Numerous Practical Recipes, for the Chief Perfuming Mixtures. Geoffrey Martin. 145 pp. Illustrated. Price, $3.50. D. Van Nostrand Co., New York.

Physics: Essentials of Physics. George Arthur Hoadley. Revised edition. 544 pp. Illustrated. Price, $1.60. American Book Co., New York.

Precious Metals: Les Métaux Précieux. Jean Voisin. 264 pp. Illustrated. Price, 35 fr. J.-B. Baillière et Fils, Paris.

Qualitative Chemical Analysis: A Systematic Qualitative Chemical Analysis: A Theoretical and Practical Study of Analytical Reactions of the More Common Ions of Inorganic Substances. George W. Sears. 199 pp. 4 figures. Price, $1.75 net. John Wiley & Sons, Inc., New York.

Rare Elements: An Introduction to the Analytical Chemistry of the Rarer Elements. 64 pp. Price, $1.25. Author and Publisher, Louis J. Curtman, College of the City of New York.

Sewerage and Sewage Disposal—A Textbook. Leonard Metcalf and Harrison P. Eddy. 598 pp. 220 illustrations. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Sewerage and Sewage Treatment. H. E. Babbitt. 531 pp. 186 figures. Price, $5.00 net. John Wiley & Sons, Inc., New York.

Soaps: A Practical Manual on the Manufacture of Domestic, Toilet, and Other Soaps. George H. Hurst. 3rd revised and enlarged edition. 432 pp. 92 illustrations. Price, 21s. net. Scott, Greenwood & Son, London.

Synthetic Tannins: Their Synthesis, Industrial Production and Application. Georg Grasser. Translated by F. G. A. Enna. 143 pp. Price, 12s. Crosby Lockwood & Son, London.

Thermodynamics, Abridged. William D. Ennis. 2nd edition, corrected. 244 pp. 73 illustrations. Price, $4.00. D. Van Nostrand Co., New York.

Works Chemistry: Der Betriebs-Chemiker: Ein Hilfsbuch für die Praxis des Chemischen Fabrikbetriebes. Richard Dierbach and Bruno Waeser. 3rd edition. 334 pp. Illustrated. Julius Springer, Berlin.

Vitamins. H. C. Sherman and S. L. Smith. American Chemical Society Monograph. 270 pp. Price, $4.25. Chemical Catalog Co., Inc., New York.

RECENT JOURNAL ARTICLES

Ammonia: La Saponificazione Ammoniacale e la Fabbricazione Industriale dell' Ammoniaca. Felice Garelli. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 11, pp. 487–89.

Artificial Musk: Le Musc Artificiel. E. Noelting. *Chimie et Industrie*, Vol. 6 (1921), No. 6, pp. 719–36.

Clay: The Microscopic Examination of the Mineral Constituents of Some American Clays. H. G. Schurecht. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 1, pp. 3–24.

Colloidal State in Metals and Alloys. I—Molten Metal. II—Crystallization. III—White Metal and Brass. IV—Iron and Steel. Jerome Alexander. *Chemical and Metallurgical Engineering*, Vol. 26 (1922), No. 2, pp. 54–58; No. 3, pp. 119–23; No. 4, pp. 170–72; No. 5, pp. 201–07.

Colloids: The Influence of the Concentration of Colloids on Their Precipitation by Electrolytes. Harry B. Weiser and Henry O. Nicholas. *Journal of Physical Chemistry*, Vol. 25 (1921), No. 9, pp. 742–57.

Copper Refining: Calculation of Anode-Furnace Charges in a Copper Refinery. C. M. Brister, Jr. *Engineering and Mining Journal*, Vol. 113 (1921), No. 4, pp. 167–69.

Dyeing of Acetyl Silk. J. F. Briggs. *Canadian Dyer and Color User*, Vol. 2 (1922), No. 1, pp. 5–8.

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Earthenware Bodies and Glazes. H. H. Sortwell. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 12, pp. 990–98.

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Explosives and Fertilizers. Alfred H. White. *Chemical and Metallurgical Engineering*, Vol. 26 (1922), No. 4, pp. 161–65.

Hydrogénation de quelques Huiles d'Animaux Marins. Henri Marcelet. *Chimie et Industrie*, Vol. 6 (1921), No. 6, pp. 765–68.

Isotopes: Notes on Some Recent Chemical Theories: Isotopes. Stephen Miall. *Chemical Age* (London), Vol. 6 (1922), No. 136, pp. 66–68.

Leather: Anthrax Prophylaxis in the Leather Industry. Alfred Seymour-Jones. *Journal of the American Leather Chemists Association*, Vol. 17 (1922) No. 2, pp. 55–65.

Lubrication and Lubricants. Leonard Archbutt. *Journal of the Society of Chemical Industry,* Vol. 40 (1921), No. 24, pp. 287*t*–93*t*.

Magnesium: Some Recent Applications of Magnesium in Synthetic Organic Chemistry. Harry Hepworth. *Journal of the Society of Chemical Industry,* Vol. 41 (1922), No. 1, pp. 7*t*–11*t*.

Microscope: Some Applications of the Microscope in Research. Henry Leffmann. *Journal of the Franklin Institute,* Vol. 193 (1922), No. 1, pp. 81–88.

Paint: Special Paint Vehicles and Varnishes. E. W. Storey. *Paint, Oil and Chemical Review,* Vol. 73 (1922), No. 4, pp. 10–12, 28.

Research: Finding the Better Way: How Scientific Research Aids Modern Industry. Charles E. Ruby. *Industrial Management,* Vol. 62 (1921), No. 5, pp. 303–08; No. 6, pp. 375–78; Vol. 63 (1922), No. 1, pp. 26–29.

Synthetic Tannins and Their Uses in Leather Manufacture. G. E. Knowles. *Journal of the Society of Leather Trades' Chemists,* Vol. 6 (1922), No. 1, pp. 19–23.

Textiles: The Utilization of X-Rays in the Examination of Textiles. Reginald Truesdale and C. Hayes. *Textile Colorist,* Vol. 44 (1922), No. 517, pp. 35–38; *The India-Rubber Journal,* Vol. 62 (1921), No. 27, pp. 1099–1102. Reprinted from *The Journal of the Textile Institute,* Vol. 12 (1921), No. 11.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Coal and Coke Mixtures as Water-Gas Generator Fuel. W. W. Odell. Illinois Coal Mining Investigations Coöperative Agreement. (This paper was prepared under a coöperative agreement with the Illinois State Geological Survey and the Engineering Experiment Station of the University of Illinois through its Department of Mining Engineering.) *Technical Paper* **284.** 32 pp. Paper, 10 cents.

Conditions in the Feldspar Industry. R. F. Ladoo. *Reports of Investigations* **2311.** 10 pp. Issued January 1922.

Growing Need for Preservation of Mine Timber. R. R. Hornor. *Reports of Investigations* **2310.** 8 pp. Issued January 1922.

Low-Temperature Distillation of Amalgams of Bituminous Noncoking Coal and Asphaltic Oils. J. D. Davis and C. E. Coleman. *Reports of Investigations* **2312.** 7 pp. Issued January 1922.

Milling Methods in the Tri-State Zinc District. Progress of Investigation by U. S. Bureau of Mines, in coöperation with Missouri School of Mines and Metallurgy and Miamai (Okla.) School of Mines. W. H. Coghill and C. O. Anderson. *Reports of Investigations* **2314.** 14 pp. Issued January 1922.

Momentary Heating of Inflammable Coal Dusts. G. B. Taylor, H. C. Porter, and E. C. White. Foreword. G. S. Rice. *Reports of Investigations* **2306.** 20 pp. Issued January 1922.

Silica. R. B. Ladoo. *Reports of Investigations* **2307.** 7 pp. Issued January 1922.

Solubility of Oil Shales in Solvents for Petroleum. M. J. Gavin and J. T. Aydelotte. *Reports of Investigations* **2313.** Issued January 1922.

Bureau of Standards

An Investigation of Oxyacetylene Welding and Cutting Blowpipes with Special Reference to Their Economy in Operation, Safety, and Design. R. S. Johnston. *Technologic Paper* **200.** Paper, 35 cents.

Characteristic Soft X-Rays from Arcs in Gases and Vapors. F. L. Mohler and P. D. Foote. *Scientific Paper* **425.** Paper, 10 cents.

Recommended Specifications for Limestone, Quicklime, and Hydrated Lime for Use in the Manufacture of Glass. *Circular* **118.** Paper, 5 cents.

Thermal Expansion of Nickel, Monel Metal, Metal, Stellite, Stainless Steel, and Aluminium. W. H. Souder and Peter Hidnert. *Scientific Paper* **426.** Paper, 10 cents.

Congress

An Act to Grant Extension of Time under Gas and Oil Permits. Approved, January 11, 1922. Public No. 127, 67th Congress. H. R. 8344.

Metric System. Metric System, extracts from hearings before subcommittee on S. 2667, to fix metric system of weights and measures for certain uses, October 24, 1921. Statement by David A. Molitor. 11 pp.

Metric System. Metric System, hearings before subcommittee on S. 2267, to fix metric system of weights and measures as single standard of weights and measures for certain uses, October 24–28, 1921. Part II. 119 pp.

Hearings before the Committee on Finance, United States Senate, of the Proposed Tariff Act of 1921 (H. R. 7456). Schedule I. Chemicals, Oils and Paints. Revised and Indexed. 1344 pp. 1922.

Department of Commerce

Ninth Annual Report of the Secretary of Commerce, 1921. 149 pp.

Federal Trade Commission

Summary of Report of the Federal Trade Commission on the Pacific Coast Petroleum Industry. Part II. Prices and Competitive Conditions. 21 pp. Paper, 5 cents.

Geological Survey

Alaskan Mining Industry in 1921. A. H. Brooks. Bulletin 722-A. Separate from Mineral Resources of Alaska, 1920-A.

Artificial Gas and By-products in 1917–18. R. S. McBride. Separate from Mineral Resources of the United States, 1919, Part II. 62 pp. Published November 16, 1921.

Barytes and Barium Products in 1920. G. W. Stone. Separate from Mineral Resources of the United States, 1920, Part II. 11 pp. Published December 6, 1921.

Candelaria Silver District, Nevada. Adolph Knopf. Separate from Contributions to Economic Geology, 1922, Part I. 22 pp. Published January 20, 1922.

Cobalt, Molybdenum, Nickel, Tantalum, Titanium, Tungsten, Radium, Uranium, and Vanadium in 1919. F. L. Hess. Separate from Mineral Resources of the United States, 1919, Part I. 19 pp. Published November 10, 1921.

Contributions to Economic Geology (Short Papers and Preliminary Reports), 1920. Part I—Metals and Nonmetals except Fuels. F. L. Ransome, H. S. Gale and E. F. Burchard. *Bulletin* **715.** 230 pp.

Contributions to Economic Geology (Short Papers and Preliminary Reports), 1920. Part II—Mineral Fuels. David White and M. R. Campbell. *Bulletin* **716.** 248 pp. 1921.

Forty-second Annual Report of the Director of the United States Geological Survey, Fiscal Year Ended June 30, 1921. 108 pp. December 1921.

Geologic Structure and Oil and Gas Prospects of a Part of Jefferson County, Oklahoma. H. M. Robinson. *Bulletin* **726-F.** Separate from Contributions to Economic Geology, 1921, Part II. 26 pp. Published December 20, 1921.

Gold and Silver in 1919. General Report. J. P. Dunlop. Separate from Mineral Resources of the United States, 1919, Part I. 45 pp.

Gold Lodes in the Upper Kuskokwim Region, Alaska. George C. Martin. *Bulletin* **722-E.** Separate from Mineral Resources of Alaska, 1920-E. 13 pp.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1920. Mines Report. C. G. Yale. Separate from Mineral Resources of the United States, 1920, Part I. 37 pp. Published November 25, 1921.

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Gold, Silver, Copper, Lead, and Zinc in Montana in 1920. Mines Report, C. N. Gerry. Separate from Mineral Resources of the United States. 1920, Part I. 25 pp. Published December 17, 1921.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1919. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1919, Part I. 15 pp. Published November 12, 1921.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1920. Mines Report. V. C. Heikes. Separate from Mineral Resources of the United States, 1920, Part I. 29 pp. Published January 13, 1922.

Iron Ore, Pig Iron and Steel in 1920. E. F. Burchard and H. W. Davis. Separate from Mineral Resources of the United States, 1920, Part I. 35 pp. Published January 23, 1922.

Tin in 1919. Adolph Knopf and B. L. Johnson. Separate from Mineral Resources of the United States, 1919, Part II. Published January 26, 1922.

Water-Power Investigations in Southeastern Alaska. G. H. Canfield. *Bulletin* **722-B.** Separate from Mineral Resources of Alaska, 1920-B. 41 pp. 1921.

Zinc in 1920. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1920, Part I. 17 pp. Published December 19, 1921.

Public Health Service

Carbon Monoxide Poisoning in Closed Garages. Reprint 694 from Public Health Reports. 6 pp. Paper, 5 cents.

Lead Poisoning in Pottery Trades. B. J. Newman, W. J. McConnell, O. M. Spencer, and F. M. Phillips. *Bulletin* **116.** 22 pp. Paper, 35 cents.

MARKET REPORT—FEBRUARY, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acid, Boric, cryst., bbls.	lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°	lb.	.01$^1/_4$	.01$^1/_4$
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.06$^1/_4$	.06$^3/_4$
Phosphoric, 50% tech	lb.	.12	.10
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66° tks. wks.	ton	16.00	16.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	.03$^1/_2$	.03$^1/_2$
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07$^1/_2$	.07$^1/_2$
Ammonia Water, drums, 26°	lb.	.07$^1/_2$	.07$^1/_2$
Arsenic, white	lb.	.07$^1/_4$	.07$^1/_2$
Barium Chloride	ton	50.00	55.00
Nitrate	lb.	*.06$^1/_2$	*.06$^1/_2$
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	2.00	2.00
Borax, cryst., bbls.	lb.	.05$^3/_4$	.05$^3/_4$
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.75	24.75
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.55	5.55
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.80	4.05
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.07$^1/_4$	.07$^1/_4$
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.50	1.50
Magnesium Carbonate, tech.	lb.	.06	.06
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*48.00	*49.00
Phosphorus, yellow	lb.	*.25	*.25
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.10	.10
Bromide, imported	lb.	*.14	*.14
Carbonate, calc., 80–85%	lb.	.04$^1/_2$	.04$^1/_2$
Chlorate, cryst.	lb.	*.05$^1/_2$	*.05$^1/_2$
Hydroxide, 88–92%	lb.	*.05$^3/_4$	*.05$^3/_4$
Iodide, bulk	lb.	2.90	3.15
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.14	*.14
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.44$^1/_2$	.44$^1/_2$
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.75	*1.65
Caustic, 76%	100 lbs.	*3.50	*3.30
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.30	2.30
Bichromate	lb.	.07$^3/_4$	.07$^3/_4$
Chlorate	lb.	.07	.07
Cyanide	lb.	.26	.26
Fluoride, technical	lb.	.09	.09
Hyposulfite, bbls.	100 lbs.	3.50	3.25
Nitrate, 95%	100 lbs.	2.37$^1/_2$	2.35
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04$^1/_4$	*.04$^1/_4$
Bisulfite, powdered	lb.	.04$^1/_2$	.04$^1/_2$
Strontium Nitrate	lb.	*.10	*.10
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride..50% sol'n	lb.	.10$^1/_4$	.10$^1/_4$
Oxide	lb.	.38	.38
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls.	lb.	.08	.08

ORGANIC CHEMICALS

		Feb. 1	Feb. 15
Acetanilide	lb.	*.29	*.32
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.09	.09
Acetylsalicylic	lb.	.80	.80
Benzoic, U. S. P., ex-toluene	lb.	.60	.60
Carbolic, cryst., U. S. P., drs.	lb.	.11	.12
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls.	lb.	*.43	*.44
Acid (*Concluded*)			
Oxalic, cryst., bbls.	lb.	.14	.14
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.24	.24
Tartaric, crystals, U. S. P.	lb.	*.25	*.24
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12$^1/_2$	.12$^1/_2$
Alcohol, denatured, complete	gal.	.40	.35
Ethyl, 190 proof	gal.	4.85	4.85
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.96	.93
Carbon Bisulfide	lb.	.06$^1/_2$	.06
Tetrachloride	lb.	.10$^1/_2$	.10$^1/_2$
Chloroform, U. S. P.	lb.	*.37	*.37
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.79	2.89
Imported Potato	lb.	.08$^1/_2$	.08$^1/_2$
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde	lb.	*.10	*.09$^1/_2$
Glycerol, dynamite, drums	lb.	.15	.15
Methanol, pure, bbls.	gal.	.75	.75
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	2.22	2.32
Potato, Jap	lb.	.06	.06
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Feb. 1	Feb. 15
Beeswax, pure, white	lb.	.33	.33
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$^1/_2$	.10$^1/_2$
Ceresin, yellow	lb.	.07$^1/_2$	.08
Corn Oil, crude, tanks, mills	lb.	.06$^3/_4$	.06$^3/_4$
Cottonseed Oil, crude, f. o. b. mill	lb.	.07$^3/_8$	.08
Linseed Oil, raw (car lots)	gal.	.77	.86
Menhaden Oil, crude (southern)	gal.	.38	.42
Neat's-foot Oil, 20°	gal.	1.32	1.32
Paraffin, 128–130 m. p., ref.	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.35	5.45
Rosin Oil, first run	gal.	.36	.36
Shellac, T. N.	lb.	.66	.67
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.77	.77
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.93	.91

METALS

		Feb. 1	Feb. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.45	4.45
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13$^3/_8$	.13$^1/_2$
Lake	lb.	.13$^1/_2$	.13$^1/_2$
Lead, N. Y.	lb.	.04$^3/_4$	.04$^3/_4$
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	93.00	93.00
Quicksilver, flask	75 lbs. ea.	48.00	49.00
Silver, foreign	oz.	.66$^1/_4$	.66$^1/_4$
Tin	lb.	.31$^1/_4$	.31$^1/_2$
Tungsten Wolframite	per unit	2.50	2.50
Zinc, N. Y.	100 lbs.	4.85	4.80

FERTILIZER MATERIALS

		Feb. 1	Feb. 15
Ammonium Sulfate, export	100 lbs.	2.60	2.60
Blood, dried, f. o. b. N. Y.	unit	3.50	3.50
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

Crudes

		Feb. 1	Feb. 15
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.29	.29
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07$^1/_2$	.07$^1/_2$
Phenol, drums	lb.	.11	.12
Toluene, pure	gal.	.30	.30
Xylene, 2 deg. dist. range	gal.	.45	.45

Intermediates

		Feb. 1	Feb. 15
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	2.00	2.00
H	lb.	.90	.90
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.30	2.30
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.30	1.30
Phthalic	lb.	.32	.32
Picric	lb.	.20	.20
Sulfanilic	lb.	.27	.24
Tobias'	lb.	1.60	1.60
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.17	.17
Aniline Salt	lb.	.22	.20
Anthraquinone	lb.	1.50	1.40
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.25	1.25
Benzidine (base)	lb.	.90	.90
Benzidine Sulfate	lb.	.70	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	.60	.60
Dimethylaniline	lb.	.38	.38
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.35	1.35
Metol (Rhodol)	lb.	3.50	3.50
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
a-Naphthylamine	lb.	.30	.30
b-Naphthylamine (Sublimed)	lb.	1.50	1.50
b-Naphthol, dist	lb.	.30	.30
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.11$^1/_2$	.11$^1/_2$
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb.	1.10	1.10
p-Phenylenediamine	lb.	1.60	1.60
Phthalic Anhydride	lb.	.35	.35
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb.	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.00	1.00
m-Toluylenediamine	lb.	1.10	1.10
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Feb. 1	Feb. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	7.50	7.50
Indigotin, conc.	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Feb. 1	Feb. 15
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc.	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00

Oil Colors

		Feb. 1	Feb. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb.	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

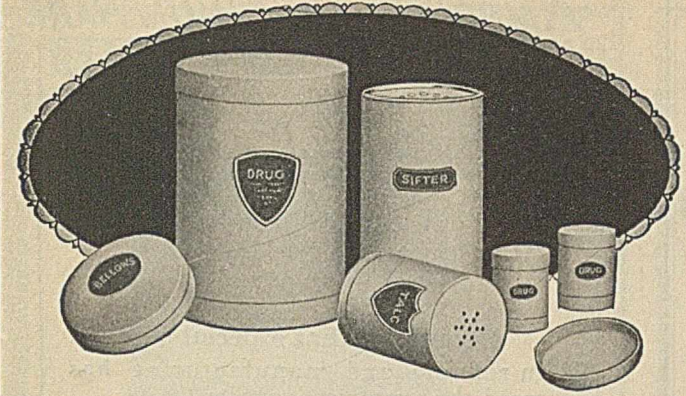
		Feb. 1	Feb. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

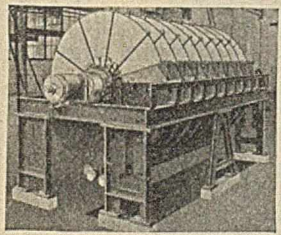
Chrome Colors

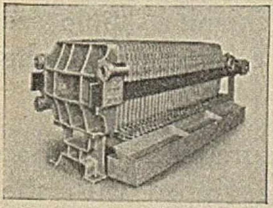
		Feb. 1	Feb. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.55	.55
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

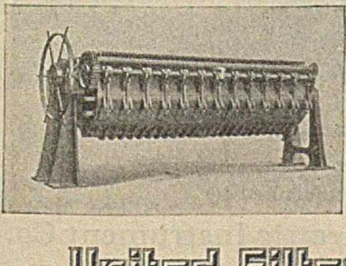
Basic Colors

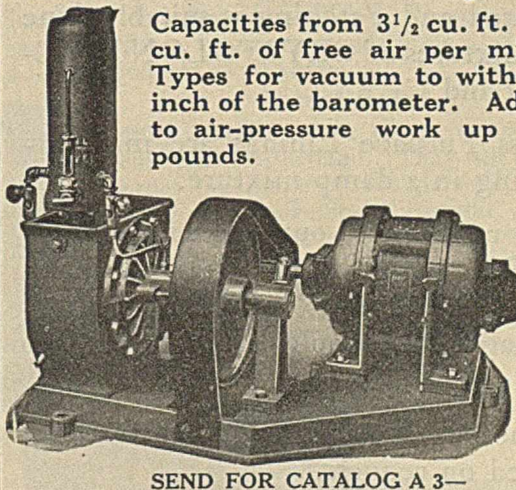
		Feb. 1	Feb. 15
Auramine, O, domestic	lb.	1.80	1.80
Auramine, OO	lb.	2.50	2.50
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2.25
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc.	lb.	8.50	8.50
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00


DRUG
SIFTER
BELLONS
TALC
DRUG
DRUG

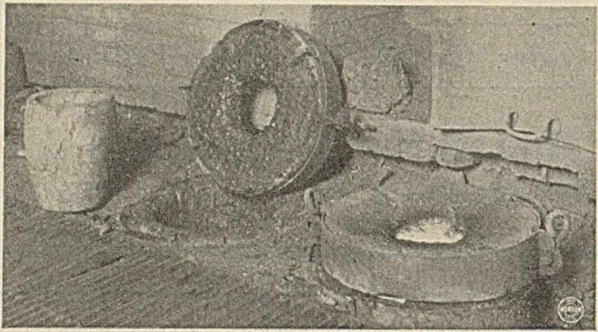








FIRESAND



The refractory properties of FIRESAND are due to the proportion of Silicon Carbide present.

CRYSTOLON FIRESAND is the trade name of the Norton product. It contains from 70-75% Silicon Carbide.

Our customers testify that CRYSTOLON FIRESAND gives most satisfactory results. The illustration shows a high temperature gas fired pit furnace which has been lined with a cement prepared with CRYSTOLON FIRESAND as a base. It is usual to add Fireclay in order to bond and hold the ingredients in place.

Troublesome Furnace Linings are renovated and Patching is suitably done with mixtures of CRYSTOLON FIRESAND and CLAY.

Brass Furnace Linings are made by ramming in a damp mixture.

Ask us to quote our prices for CRYSTOLON FIRESAND. Are you interested in "Graded" or "Run-of-pile" material? Our supply is ample to ship in carloads or less.

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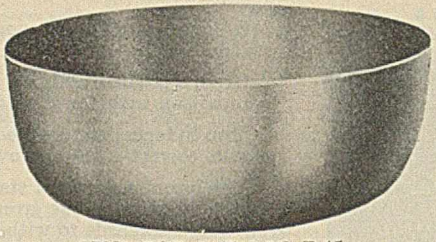

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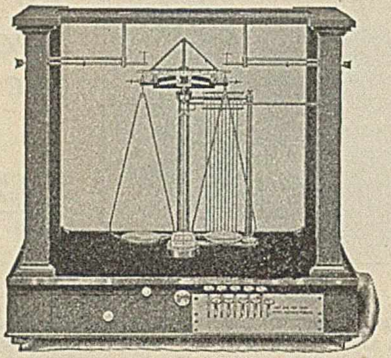

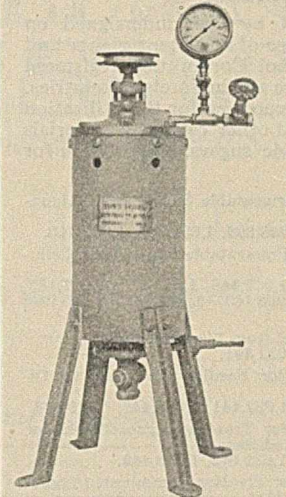

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Sugars, Alcohol, Turpentine, Etc.

from

Wood Waste and Cellulosic Materials

PATENT SALE

Proposals will be received by the undersigned on March 15, 1922, for the purchase of all patent rights and interests of International Alcohol Corporation registered in the United States Patent Office and in Foreign Countries, relative to the apparatus and processes for the utilization of wood waste, lignocellulose and other cellulosic materials in the production of fermentable sugars, composition for stock, alcohol, etc., as follows:

(a) Process of Producing Fermentable Sugars from Lignocellulose.
U. S. Patents Nos. 938,308, 1,032,392, 1,032,440.
(b) Processes of Producing Fermentable Sugars from Cellulosic Materials.
U. S. Patents Nos. 1,032,448, 1,032,450, 1,037,185, 1,056,161, 1,056,163, 1,091,327, 1,096,030, 1,056,162.
(c) Process of Producing Fuel from Lignocellulose.
U. S. Patent No. 1,032,391.
(d) Process and Apparatus for Feeding Materials to Digestors.
U. S. Patents Nos. 1,032,441, 1,032,442, 1,032,445.
(e) Process and Apparatus for Treating Lignocellulose for Recovering Turpentine and Sugar
U. S. Patents Nos. 1,032,443, 1,032,449.
(f) Process and Apparatus for Treating Comminuted Lignocellulose.
U. S. Patents Nos. 1,032,446, 1,032,447.
(g) Food Composition for Stock.
U. S. Patent No. 1,092,221.

Further details will be furnished upon request.

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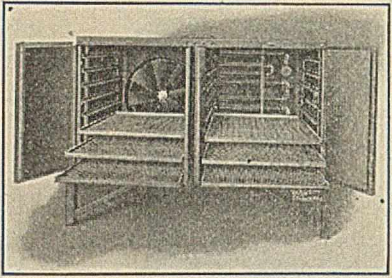

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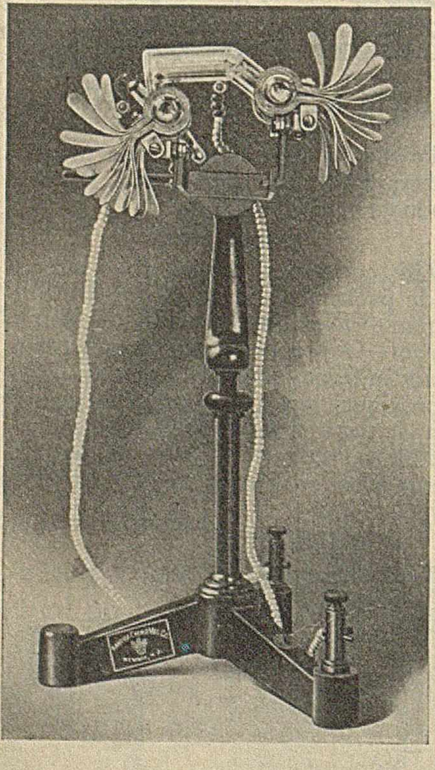

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