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EDITORIALS

Reclassification

FOR two years there has been a legislative struggle for a reclassification of federal employees which will make it possible for them to receive a more adequate wage. This action culminated in the passage, during the closing hours of Congress, of a law for the betterment of conditions for such employees. Unfortunately, however, the salary provisions do not become effective until July 1, 1924. The conferees struck out of the final bill descriptions of the duties of various positions and inserted in their place a paragraph directing the classifying board to follow the executive order of October 24, 1921. The skilled trades and common-labor services were eliminated. In fixing the compensation schedules, the law provides for the various services and the grades within those services. The first on the list is the professional and scientific service. The rates of compensation for Grade I in this service range from $1860 to $2400; for Grade II, $2400 to $3000; Grade III, $3000 to $3600; Grade IV, $3800 to $5000; Grade V, $5200 to $6000; Grade VI, $6000 to $7500; and for Grade VII, $7500 unless a higher rate is specifically authorized by law. The grades for subprofessional service are eight in number and provide salaries from $900 to $3000. There are fourteen grades for the clerical, administrative, and fiscal service, ranging from $1140 to Grade XIV, which is a special executive grade at $7500, unless a higher rate is provided by law.

The classifying agency will be composed of the director of the Bureau of the Budget or his alternate, a member of the United States Civil Service Commission, and the chief of the Bureau of Efficiency, with the chairmanship of the board resting with the Bureau of the Budget.

The essential features of the law are those for which the federal employees had been working, and its passage marks the beginning of a new era for scientific men in the government employ. The records of the service are filled with instances where scientific men have refused outside offers carrying very much higher salaries than those paid by the Government and have remained at their work out of a sense of loyalty and for the pleasure derived from work well done. The provisions of this law make it possible to pay more adequately for their services, particularly for positions of responsibility.

The type of work which should be done in government laboratories is of an importance requiring the best men that can be produced, and they should be paid accordingly.

Popular Books in Science

AS a part of our effort to have people generally more appreciative of the several natural sciences, it is important for us to be prepared to furnish lists of books suitable for collateral reading. We call attention, therefore, to a reading list of popular books in science issued by the American Library Association, Chicago. This list is suitably divided under several special subjects, and is supplied at twenty cents per copy or ten copies for a dollar, with reduced prices for larger quantities.

The *Journal of the Washington Academy of Sciences*, Vol. 12, No. 21, December 19, 1922, prints the revision of the Academy's list of one hundred popular books in science. Both of these lists should be in the hands of those interested in encouraging familiarity with our science.

Laboratory Purchases

SCHOOL laboratories are beginning to consider supplies for another year. Those who have had a little experience with laboratory apparatus and chemicals, as users, as purchasers, and as salesmen have observed that where laboratory men are particular they are careful to know as much as possible regarding the dealer and also the manufacturer from whom they purchase their supplies. They obtain satisfactory service when they definitely state what is desired and the sources from which it must come. In pre-war days, when nearly everything used in the laboratory was imported, there was wide familiarity with trade-marks. It was the habit of the men in the laboratory to specify definitely so that there could be no misunderstanding on the part of those filling the orders.

Fortunately, to-day the users of laboratory equipment have many new sources of supply. Unfortunately, these same users have a tendency to forget their long-established precaution and have failed to specify definitely American makers, when in fact they appear to have desired American-made wares. American manufacturers seldom serve the laboratory directly, and for many reasons it is better to market through dealers. Several former sources of supplies may be drawn upon and the ultimate consumer must specify apparatus and chemicals made in America if he wants to receive them.

Under the present tariff, with the duty-free privilege rescinded, the American manufacturer should be able to compete with the imported article. He is already maintaining a higher quality of product than the majority of foreign producers have made since the war. Reputable manufacturers who heretofore made no effort to obtain laboratory trade are now distinctly interested in laboratory requirements and in providing chemicals which will hold a permanent place on the laboratory shelf. Recently, a laboratory complained about a clamp, and when this was brought to the attention of the dealer he realized that in redesigning the laboratory-blown and volumetric glassware, as well as other important items in his catalog, full attention had not been given to chemical-laboratory hardware. He immediately undertook to redesign his entire line and has already invested more than $2500 in new patterns alone.

The buyer to-day, not only can, but should protect himself in several ways. He should know the manufacturer of fundamental apparatus and the items that are of greatest importance to him. These he should specify by trade-mark or name. He should deal with reputable, established dealers. It is then unnecessary for him to know the manufacturer of every one of the many thousands of items in the catalog. In other buying, the consumer has formed the habit of specifying nationally advertised wares and then depending upon the reputation of the merchant for satisfactory goods. Some laboratories have learned that nothing is gained by making a wide distribution of bidding lists when not more than a dozen dealers can give wholly satisfactory deliveries.

The buyer can also promote reasonable standardization of apparatus by which the dealer and the manufacturer can obtain quantity production and at the same time lower costs. We would particularly urge the consumer to remember that if he allows price alone to govern his purchases, he has little ground for complaint if he is disappointed in deliveries. Thus, anything may be a clamp at the time bids are secured, and it becomes an unsatisfactory piece of apparatus only when it is put in use.

The dealer finds that with the many new sources of supply he can buy to advantage and, if he will, coöperate with the American manufacturer. Stocks imported to advantage a year ago cannot be replaced so advantageously to-day from the same sources. A responsible dealer makes no effort to exploit the user. The dealer should sell no apparatus, no chemicals labeled "made in America," nor intimate that they were made here unless such is the case. Labels should be honest and should carefully state quality, including all substances which are important to the user. Apparatus must also bear an honest label.

Present conditions have continued the tri-party interests to which we have previously referred. The protected manufacturer can rest assured that quality is trumps. If he will remember this and at the same time be willing to meet the special needs of the ultimate consumer, his position is strong. The dealer can be helpful both to the manufacturer and the consumer. The chemist holds the whip hand. He was willing to forego advantages in order that the industry might become established, and he, in common with those whom he supports, must continue to be more interested in securing the permanence of the chemical and scientific apparatus industry in America than in a small temporary advantage in price.

Prices to-day are not out of proportion to other items entering into the cost of an education. There is sufficient competition to insure that. Let the chemist inform himself both as to manufacturers and dealers. When he really wants quality, let him specify the makers and be willing to pay a fair price. An equally liberal policy in merchandizing will soon produce mutually profitable conditions.

New Prizes

FROM the University of Wisconsin comes the announcement that the Palmolive Company has established a fellowship for the study of fundamental principles connected with the detergent action of soap. The fellowship is established for five years, carries an annual stipend of $2000 and an additional sum to provide special apparatus which may be required. The Fellow will be allowed to work in any university in the United States which has the necessary facilities for work of this character.

The Chicago Trust Company, in an effort to stimulate study and research in the field of business finance, will award $2500 triannually, beginning in 1925, for the best contribution on any subject relating to business development and the modern trust company. There will be annual prizes of $300 beginning this year for shorter studies on economy, business, finance, and law. Such researches are of immediate interest to the chemical industry. Suggested topics are: no par value stock; blue-sky legislation; relations of trust companies to the reorganization of jeopardized business concerns; and financing instalment sales.

The National Council of American Cotton Manufacturers has offered a prize of $1000 for the most valuable scientific contribution on the control of the cotton boll weevil, to be awarded at the close of the season.

At the American Institute of Baking a raisin fellowship has been established for the purpose of investigating the use of raisins in bread. A milk fellowship has also been created by the same organization for the study of the problems of the nutritive value of milk in the modern loaf of bread, as well as the storage, handling, and care of milk products in the bakery.

These are all encouraging indications that our business executives are looking more and more to scientific research as the most dependable insurance for the security of the future. If the work to be done by the fellows is successful, it is but a step to the further allocation of large sums for the general promotion of scientific research without respect to a specific field.

It is announced in *Chemistry and Industry* that the offer of Sir Albert Yarrow of £100,000 to the Royal Society, to be used at the discretion of the council of the society in promoting scientific research, has been gratefully accepted by the president and council. Sir Albert has made this gift "to mark his sense of the value of research to the community." He is wise in stating his preference that the income from this capital sum be used "to aid scientific workers by adequate payment and by the supply of apparatus and other facilities, rather than to erect costly buildings."

For years the AMERICAN CHEMICAL SOCIETY has had an Endowment Committee, which has sought funds that will enable research to be undertaken under the auspices of the SOCIETY, but financial support has not been secured on as large a scale as could be wished. Perhaps this example of our friend across the water may lead some American to make a substantial contribution for the advancement of American science.

Congressional Procedure

IS there another country where the closing days of a lawmaking body are crowded with such procedures as characterize many sessions of our Congress? Where else can one man by the simple method of the "pocket veto" absolutely prevent an important measure from being discussed and brought to a vote? It may not be generally known that the Rules Committee of the House has managed to obtain such power that bills when presented must go to it, and if it does not see fit to report them out, there is no way of bringing them before the House for consideration. The bill to increase adequately the salaries of school teachers of the District of Columbia is said to have been given this "pocket veto" by the chairman of the Rules Committee. This same chairman and the floor leader, neither of whom was reëlected for the next Congress, refused to allow the reclassification bill to come to a vote until the Senate agreed to postpone from July 1, 1923, to July 1, 1924, the date on which its provisions become effective. In effect these two men dictated the procedure.

Where else than in our Senate are speakers permitted to discuss anything with the avowed purpose of preventing a decision upon pending legislation? We were taught that when a motion is before the house all speeches must be upon that motion, but in practice "senatorial courtesy" makes it impossible to hold discussion within such limitations. The lack of attention given a speaker makes us wonder whether after all there is such a thing as "senatorial courtesy." It is such procedure that makes a filibuster possible, and a filibuster enables a very small group to override the majority, leaving the majority the choice between sacrificing its legislative program or yielding to a filibuster. It was a filibuster conducted essentially by two men that defeated the dye-embargo bill in 1920.

Some of these abuses which disturb us would be ineffective but for the way Congress must watch the clock. By law all legislation not passed dies with the Congress. Time can be wasted at will through many months, but there comes a day when everybody is in a hurry. It is then that filibusters are effective, ill-considered measures have their opportunity, bills are killed to ease the legislative pressure and, in the end, a great deal that is pressing is left undone. The plan to retire those defeated for reëlection at an earlier date and to have their successors assume their duties more promptly was one of the constructive measures lost in the shuffle. Is there not a way to make Congress in fact what it often has been called—"the greatest deliberative body in the world?"

The Reward of Genius

IN an address before the British Science Guild, Sir Ronald Ross made the plain statement that Britain is throwing her genius on the dustheap. To prove his statement he cited the treatment accorded the man "who saved countless lives in India by discovering methods of inoculation against cholera and plague," and extends his indictment to America by recalling that Walter Reed, who wrote his name high in the records of science by his work in yellow fever, was rewarded by assignment to a position with an inadequate salary.

There are various ways of rewarding genius. Many a man has been satisfied with the special recognition accorded by those governments which dispense titles and other extraordinary honors. Membership in certain learned societies is a mark of appreciation. Some men have been called to high positions as a reward for their work.

Medals, cash prizes, and similar rewards have a very important place, but it seems to us that nothing could be more satisfactory to the average man of science than to have as his reward the establishment of conditions under which he could do that which he is best qualified to do, and which he enjoys doing. We believe that in many educational institutions the man who has made a brilliant record in research or who has proved himself to be a teacher of rare inspiration has too often been promoted to an executive position with a high-sounding title. It should be possible to develop men for these executive positions, men who can neither engage upon research nor a career of teaching with the same success as their fellows. Probably finance has been the chief obstacle in carrying out such a plan. If so, it offers another reason for constantly increasing the endowment for the support of the faculties in our educational institutions.

International Critical Tables

FOR some time the compilation of the International Critical Tables, sponsored by the National Research Council and the International Union of Pure and Applied Chemistry, has been under way. It is an undertaking with which chemists should be in close touch, especially now that an editorial staff is rapidly developing the work and beginning its coöperative activities. Announcement was recently made of some topics for research which were suggested as a result of preliminary work, and a tentative list of nearly three hundred topics is now available. In addition, there will be detailed computation tables and other material yet to be selected.

Physical and chemical constants are a necessity in research and applied science. We have an opportunity through these International Critical Tables to obtain a comprehensive work international in scope, yet compiled primarily from the viewpoint of American needs. It is very important that chemists establish contact with the editors, make suggestions and contributions, and thus take some part in the completion of the task.

Monthly Dye Statistics

WE wish to congratulate the Department of Commerce on the publication of its new monthly bulletin in coöperation with the United States Tariff Commission. This is the first step that has been taken to furnish detailed information about chemical imports. The new bulletin gives statistics of dyes imported for consumption through the Port of New York, and shows the Schultz number, the name of the dye, the manufacturer, the quantity in pounds, the percentage by country of origin, and, where publishable, an invoice value. This information will reach our own manufacturers promptly, will be of immediate benefit to any who contemplate developing a new line of products, and will assist our dye-makers in meeting the demands of American consumers. It is a service which will be greatly appreciated and which can be made still more beneficial when it is extended to include all synthetic organic chemicals. We need to know as much as possible concerning fine organic chemicals, medicinals, synthetic flavoring compounds, photographic chemicals, synthetic aromatics, synthetic tanning materials, and all the host that owe their origin to the chemical laboratory and plant. The bulletin is an innovation in government statistical service, not only in the information conveyed, but in the unusual promptness with which it is made available. We hope the Department of Commerce in coöperation with the Tariff Commission may speedily find a way to enlarge the scope of this bulletin to include at least all lines of synthetic organic chemicals.

American Degrees for Sale

ON numerous occasions attention has been called to the efforts made in foreign countries to interest those unfamiliar with the status of American universities in the purchase of degrees. We again refer to this matter in the hope that we may protect some one who might otherwise be misled. We regret that on this occasion we must refer to the following advertisement carried by the *Chemical News* on advertising page 3 of the issue of January 26, 1923:

> AMERICAN UNIVERSITY DEGREES (Statutory)—B.A., B.Sc., D.Sc., and B.Comm., obtained by Thesis written at Home. Send self-addressed, stamped envelope to Lawrence (Ch.), 16, Derwent Street, Leigh, Lancs.

We are greatly surprised that a publication of the standing which the *Chemical News* has enjoyed should accept an advertisement of this character.

It should go without saying that no reputable educational institution in America or elsewhere offers its degrees for sale. It is this fact, among others, which makes it difficult to stop the activities of organizations which endeavor to prosper by this disreputable brokerage business. It is necessary to prove that a fraud has been perpetrated. Those who realize that they have been duped hesitate to give evidence and, since it is well known that degrees are not for sale, it is hard to show that the purchaser at the time of purchase really believed that he was getting a bona fide degree. We do not know who is responsible for this advertisement, but there is a group operating which so far has not been reached because of several technicalities, although the case has been before several government departments. We call upon the *Chemical News* and other scientific and technical publications to assist us in placing this matter properly before all classes of scientific readers.

Coal Carbonization and the World's Fuel[1]

By Horace C. Porter

1833 Chestnut St., Philadelphia, Pa.

After stressing the ever-increasing need for greater fuel economy which is brought about by the growth of industry and the slowly diminishing natural resources, the author has discussed the possibilities of coal carbonization as a solution of the problem. The difficulties involved, principally the excessive costs of the process, due to high expenditure of energy, heavy plant expense, and insufficient "form values" of its products, are pointed out; and the progress of the industry in eliminating these difficulties, particularly the possibilities of the low-temperature carbonization processes in increasing the "form value" of the products, is described.

The world's fuel is basic in our civilization. Not only does it give heat for homes, offices, and factories, but, more important, as the main source of industrial power—it provides 90 per cent of all mechanical energy for railways, streetcars, steamships, manufacturing. Each household in this country—averaging the many small with the few large ones—uses directly and indirectly 20 tons of coal per year and spends for it $150 to $200. The industrial fabric would go to pieces without fuel—without coal.

The savage in primitive times used no coal—in fact, but little fuel of any kind—and yet for his own ends he got along very well. He was more healthy, as a rule, than the present generation, highly ornamented and educated and pampered by civilization. Our fuel goes to meet the needs of our complex civilization, elaborately organized and developed as it is, to give us clothing, food, and shelter of a high order, communication, education, luxuries, and pleasure—much of it, indeed, to the latter two ends.

But, notwithstanding all this, we are not a generation utterly abandoned to waste and extravagance. The figures in respect to fuels will confirm this fact. We devote, in increasing measure and with favorable results, a great deal of attention to research looking toward improvement in the utilization of fuel and the securing of economies.

We do waste, to be sure, a great deal of coal. Under industrial and locomotive boilers, for example, where nearly 70 per cent of our coal consumption is applied, we waste on the basis of efficiencies now possible by best engineering practice, one-third or more of what is being used. But the encouraging feature is that in large centralized stations now in actual operation, we obtain by condensing steam turbine equipment and entirely practical furnace and boiler operation, twice as much power from a pound of coal as was obtained in average practice a few years ago. As it becomes practicable gradually to scrap the old equipment and to concentrate more and more the production of power into large central units, our expenditure of coal for a given output in this field will steadily decrease.

As to the railroads which consume nearly one-third of our bituminous coal, and are admittedly extravagant in its use, we are able to answer the pessimist by pointing to the increasing favor which is accorded to electrification. A western division of the Chicago, Milwaukee & St. Paul Railway has been converted from steam to electric operation and by actual records has secured a gain in train locomotive power cost of 53 per cent. The Pennsylvania Railroad, according to announcement in the daily press, will electrify its Mountain Division in Pennsylvania in the near future. This step by the railroads is a real advance in fuel economy. We are to consider here, of course, the large indirect savings in addition to that of the fuel on the locomotives. For example, the haulage of coal by the railroads has been estimated to amount to one-third of the total ton-miles of freight which they handle. By electrification this is very greatly reduced.

The use of coal for heating houses and for making into gas for cooking and lighting is comparatively among the minor forms of application. From 15 to 20 per cent would easily cover these needs. The large accomplishments in fuel economy, therefore, are to be looked for in the industrial field. By a reasonable amount of centralization of industrial power production and by improvement of efficiency therein, coupled with electrification of a reasonable part of the railway system, the country's coal consumption on the basis of present power requirements may readily be cut by 30 per cent. Still greater reductions are to be expected from future improvements as yet undeveloped in the application and distribution of energy. The mercury-vapor engine, and the powdered-coal, explosion-driven turbine are in the minds and on the work-benches of inventors—destined possibly at some time in the future to turn into useful channels a large part of the 90 per cent loss commonly occurring to-day in the realization of the energy of coal through steam-power application.

With increase of population and continued development of industry in this country, now sparsely settled and relatively undeveloped, the need for increased fuel economy will be felt more and more strongly. Efficiency and technical skill must ease the burden of expanding requirements and slowly diminishing natural resources.

Now comes the question, how far can coal carbonization enter into this fuel-economy program? Is it true that for highest efficiency, as some have said, bituminous coal should not be, and eventually will not be, burned raw? We frequently have our attention drawn, through appeals from economists and conservationists, to the immense possibilities in the saving of by-products from coal now burned raw under boilers. It has been said that large, central power stations located at coal-mine mouth could utilize carbonization methods, produce power thereby, and save vast quantities of coal by-products now going to waste.

The needs of agriculture for the fixed nitrogen, of motor transportation and the Diesel engine for the oils, of industry and the household for a larger and cheaper public fuel-gas supply—all these seem to cry out against the waste of by-products from the furnace stacks.

DIFFICULTIES TO BE OVERCOME

But we must be reasonable in this boosting for carbonization—we must analyze the difficulties involved. There is the cost of carbonization, excessive under the present methods, and therefore standing as an obstacle to wide development for the purpose of general fuel application.

If power is to continue to be obtained through steam, the carbonization products coke and gas, applied thereto, have not, under present conditions, a "form value" sufficiently great to pay the costs of their manufacture. Furthermore the supplementary value of ammonia and oils fails to even the balance.

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[1] Presented before the Syracuse Section of the American Chemical Society, Syracuse, N. Y., December 8, 1922.

The cost of carbonization is made up of two factors, the energy expenditure, and the plant operation and maintenance. First, in energy expenditure we have a loss of 18 per cent of the original heat value of the coal. (Figures of average, high-temperature industrial carbonization, not the "optimum" figures.) In other words, there result from carbonization available fuels having a heating value of 82 per cent of that of the original coal. The loss is not only in the gas burned in the oven flues but in leakage, carbon, and soot, and the unavoidable mechanical losses of operation. This energy is lost, it is not stored or converted so as to be available in the products. S. W. Parr's researches on carbonization at the University of Illinois look to the reduction of this item of loss by utilization in greater measure of the exothermic reaction occurring in carbonization, the inducing of a coking process in part from the inside of the charge by its own heat of reaction.

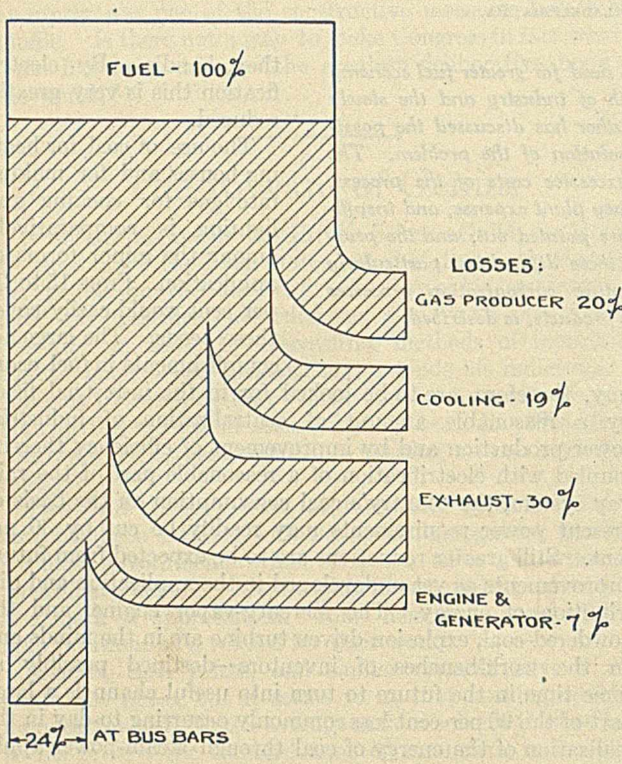

Fig. 1—Energy Conversion in Gas-Engine Electric Plant*

* Illustration from pamphlet of W. S. Rockwell Company.

Other advances in reducing this energy expenditure are constantly being made through practical improvements in plant-operating methods and design of apparatus. It may be noted that the newer types of by-product coke ovens are now expending in the form of fuel gas only about 1000 to 1100 B. t. u. per lb. of coal carbonized, as compared to 1500 to 1600 B. t. u. common in the practice of ten years ago.

The other factor in carbonization costs—plant expense—is larger even than the energy cost. It is difficult, however, to put it into figures of dollars and cents or in percentage of the coal value, owing to fluctuation in labor and materials costs. The latter, however, parallel ordinarily the fluctuation in coal cost, so that we may say, with some approximation of a general rule, that the plant and conversion cost of carbonizing coal in a modern plant of medium size will amount to a figure between 25 and 35 per cent of the cost of the coal.

These plant costs, both investment and operating cost, are of course lowered as the rate of output is increased. Late developments in coke-oven design make possible a decided advance in rate of operation without undue increase in the temperatures used or deterioration of products. The Semet-Solvay regenerative six-flue-high, silica oven, with its large charges, its high degree of heat economy, and successful application of the principle of efficient and uniform heat transfer by high velocity of heating gases, attains remarkable coking velocities, and is able to coke, at some of the later plants, 26 to 27 tons of coal per oven per day. The new-type Koppers oven, recently developed in this country under patents of J. Becker, secures an advantage through the use of cross-over flues from the row of vertical-heating flues on one side, *over the top* of the oven to the row on the other side, enabling the oven to be built higher than has formerly been possible with vertical-flued ovens, and securing much more uniform heating. This oven is built narrower than the older type, but higher and longer, and attains a great increase in coking capacity. A small battery of these ovens built at Chicago a year ago for experimental purposes has been successful in securing very uniform heats and high capacities. It cokes, if required, 28 tons or more of coal per oven per day.

These capacities, compared to those of 8 to 12 tons per oven per day prevailing fifteen years ago in this country, or even now in Europe, illustrate how investment and operating costs can be cut in two by careful attention to engineering design and operating methods.

Yet, with the best of design and of operating method so far attained, coal carbonization must carry a burden of costs amounting to 25 to 30 per cent for plant and operation and 17 per cent for heat expenditure, a total of, say, 45 per cent of the cost of the coal. In average practice to-day it exceeds 50 per cent.

Following a graphic method used by W. S. Rockwell Company, in showing the losses in various energy conversion

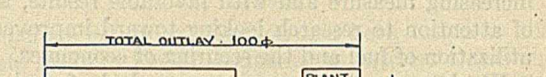

Fig. 2—Coal Carbonization. Input and Outgo of By-product Coke Plant, Applied as Steam Auxiliary. (Without Disposal of By-products)*

* This chart is based strictly on fuel value relationships, assuming equal values per unit for B. t. u. in whatever form occurring; for example, the item "heat used," 13.5 cents (equal to 17.5 per cent of the value of the coal), is the proportionate value of the loss of B. t. u. in carbonizing obtained by difference

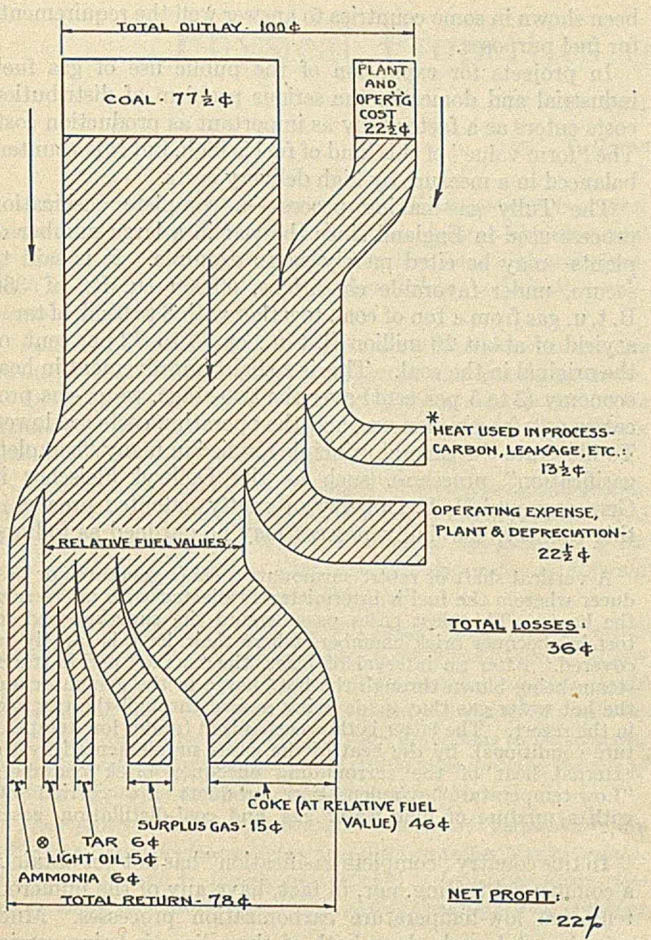

FIG. 3—COAL CARBONIZATION. INPUT AND OUTGO OF BY-PRODUCT COKE PLANT, APPLIED AS STEAM POWER AUXILIARY. (ASSUMING ENHANCED FORM VALUES FOR BY-PRODUCTS AND FUEL VALUE FOR COKE)

* Possible improvements, if and when developed, would utilize some portion of this loss—e. g., the sensible heat of the coke if fired hot directly under boilers.

⊕ These by-products are assumed at favorable disposal values, light oil for motor fuel, tar for chemical conversion or special fuel, and gas for city distribution.

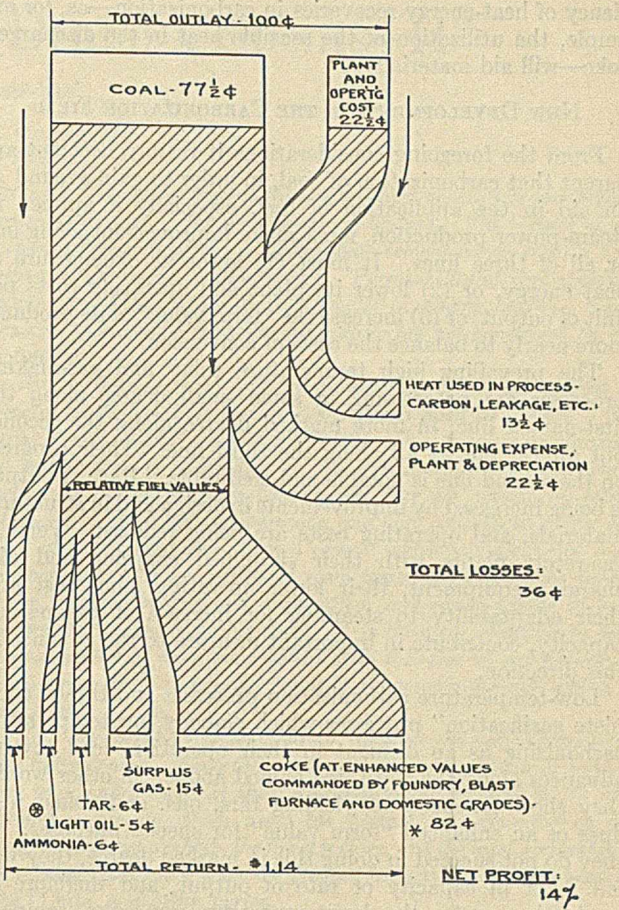

FIG. 4—COAL CARBONIZATION. INPUT AND OUTGO OF BY-PRODUCT COKE PLANT, APPLIED TO FAVORABLE OUTLETS FOR COKE AND BY-PRODUCTS. (FIELD LIMITED BY DEMAND FOR COKE AND GAS AT ENHANCED VALUES SHOWN)

⊕ These are the relative values referred to the outlay of $1.00 in coal and plant; with coal, for instance, at $7.75 per ton, assumption is made of coke at $11.00 per ton, coke breeze at $2.00, ammonium sulfate at 3 cents per lb., light oil (suited to motor fuel) at 17 cents per gal., tar at 5 cents per gal., and gas at 25 cents per M. cu. ft.

processes, there may be depicted the energy distribution and losses in coke-oven carbonization. Fig. 1 merely illustrates the diagrammatic method used, and shows the energy distribution in the gas-engine electric plant. Fig. 2 shows the losses and the recoveries based on use of the products strictly as fuels in steam production—in other words, making the coke-oven plant a fuel feeder to the steam-power plant, with no attempt to find better markets outside. Figs. 3 and 4 illustrate in the same manner how the dollar investment (77$^1/_2$ cents in coal and 22$^1/_2$ cents in plant and operating cost) yields returns by the aid of carbonization—Fig. 3 on the basis of fuel values, with ammonia added as a by-product, and Fig. 4 on the basis of enhanced form values which the products command in a limited market.

On the basis, therefore, of relative heat units contained, ready for application to steam raising (Figs. 2 and 3), it is evident that the products of carbonization leave a large margin between their value and that of the investment in plant, labor, and coal. Obviously, on this basis alone the carbonization plant as a steam-power producer is a failure. But now there come the by-products, chiefly ammonia and the "form values" of the fuel products—coke, gas, and light oils—to even up the balance.

In Fig. 4 we add, without question, 6 cents for ammonia and a 4-cent "bonus" to the light oil for enhanced "form value" used as motor fuel, for both of which no immediate danger of an over-supplied market and thereby reduced valuation appears to threaten. Tar and gas also are given an enhanced "form value," assuming special uses wherein their adaptability and convenience make the demand, but it is problematical to what extent the market would absorb them and sustain the higher valuation in case of great expansion of the carbonization industries. Dyestuffs and coal-tar chemicals and the increasing industrial demand for gas at something more than its fuel value (compared to coal) do now justify some degree of boosting of the "form value" for the tar and surplus gas from carbonization. But until the public acceptance of these products (and coke as well) can be obtained at an average valuation 60 to 70 per cent higher than their mere heat unit value, carbonization can hardly be expected to overstep greatly the metallurgical coke and domestic gas fields.

Certainly, for power production through steam, concluding from the charts and analysis above shown, carbonization processes leave now, on the wrong side of the balance sheet, too great a margin to justify hope of conservation through their wide application therein. The gas-engine power plant is a possible aid in this connection for future development, but, under the present status of relative costs, it offers only uncertain advantages. Further improvements in the efficiency of heat-energy recoveries in carbonization—as, for example, the utilization of the sensible heat in the discharged coke—will aid materially.

New Developments in the Carbonization Field

From the foregoing considerations it readily becomes apparent that carbonization of coal, in order to gain ground as an aid in the application of fuel, especially if applied in steam-power production, must make improvement along one or all of three lines. It must (1) lower its expenditure of heat energy, or (2) lower its plant and operating costs per unit of output, or (3) increase the "form value" of its products more nearly to balance the costs of conversion.

The prevailing high temperature coke- and gas-making processes are progressing in some small degree along the first-named line, in more marked degree along the second, but almost not at all along the third line. Their progress on the second line is notable and creditable. Rate of output is being increased by improvements in design and in structural materials, and operating costs are being reduced. Vertical gas-retort plants with their simplified charging and discharging equipment, their lower operating labor cost and their adaptability to steaming for increase of gas-making capacity, contribute in important measure to the advance in this direction.

Low-temperature carbonization processes and those "complete gasification" processes which embody low-temperature carbonizing as an element in their operation, lead toward advances along the third line named above; in other words, they show prospects of yielding tars, oils, and coked residues of an enhanced "form value" for special purposes. If they do not succeed in doing this in marked degree, they will fail. For in capacity or rate of output, and therefore in production costs, the low-temperature processes compare very unfavorably with the established high-temperature processes.

The great virtue of low-temperature carbonizing is the saving of the oils from the coal—the preserving of these presumably "high form-value" materials from cracking and degradation into soot and gas carbon. The oil yield is doubled; and, if all or nearly all is found applicable to motor fuel use, both in light-fuel motors and the Diesel heavy-oil motor—as is claimed to be possible—the form value in this product should compensate for much of the increased plant and operating costs. The coked residue, however, must also create for itself, perhaps in the domestic field, a high form value and win its way in public favor before these processes can satisfactorily overcome their handicap of high costs.

" Complete Gasification " Processes

"Complete gasification" processes are those effecting complete conversion of the coal into gas, except for the ash residue and a certain amount of tar. Ordinarily, the term is now applied to those processes involving destructive distillation in one zone, and the making of producer gas or water gas in an adjoining zone of the same apparatus. The distillation is usually effected, in part at least, by the sensible heat of the producer gas or water gas passing directly through the raw coal in the upper or distilling zone.

This is an application where low-temperature carbonization finds great promise. It is an adjunct here to a gas-making process of a high degree of heat economy and low operating cost. Its special virtue of yielding rich, uncracked vapors and oils may be utilized, and its solid residue converted to the higher "form-value" gas. Such gas, however, being lower in heat value per cubic foot than the now-used public gas supply—say, 350 B. t. u. as against 570—will have to await public acceptance as of suitable quality. It has been shown in some countries to answer well the requirements for fuel purposes.

In projects for expansion of the public use of gas fuel, industrial and domestic, the serious problem of distribution costs enters as a factor fully as important as production cost. The "form value" of this kind of fuel is high, but it is counterbalanced in a measure by high delivery costs.

The Tully gas-making process—a complete gasification process used in England since the war in a large number of plants—may be cited merely as an example. It is said to secure, under favorable conditions, 50,000 cu. ft., of 360 B. t. u. gas from a ton of coal, together with 8 to 9 gal. of tar—a yield of about 20 million B. t. u., or 70 to 72 per cent of the original in the coal. This is a slight improvement in heat economy (3 to 5 per cent) over the two-stage, water-gas processes now in common use, and the operating costs are lower. To illustrate the general principle applied in many "complete gasification" processes, such as the Dellwyk-Fleischer in Germany, and H. L. Doherty's recently patented process in this country, the Tully process may be outlined as follows:

> A vertical shaft or retort surmounts a shaft generator or producer wherein the fuel is intermittently blasted with air to raise the heats. The blast gases pass around the superimposed retort in checquer brick chambers where their heat is largely recovered. After an interval of blast, the "make" period starts, steam being blown through the hot charge in the generator and the hot water gas thus made being passed through the raw coal in the retort. The latter is thus carbonized (under low-temperature conditions) by the heat of the gases supplemented by the external heat of the surrounding checquer brick chambers. "Low-temperature" condensation products are carried off, with a mixture of blue water gas and coal-distillation gases.

In this country "complete gasification" has not yet obtained a commercial footing, nor, in fact, have any of the numerous tentative low-temperature carbonization processes. Much experimental work along both of these lines is being carried on, however, some of which has been brought to an industrial scale of operation. In this work there is great promise of an improved efficiency in coal carbonization and gasification, and an increase in the aggregate "form value" of the products.

Abroad, Bergius has made recent researches worthy of note on distilling coal mixed with oil under high pressures whereby a hydrogenation is accomplished and remarkable yields of the lighter hydrocarbon oils are obtained.

An Efficient Reflux Air Condenser

By George T. Dougherty

American Steel Foundries, Chicago, Ill.

In the saponification of oils and fats in an alcoholic solution of potassium hydroxide it has been found convenient to use an air condenser made from a condenser tube, with adapter sealed to it, such as is furnished by all apparatus dealers for Liebig condensers. The condenser tube is inserted through the cork stopper of the flask with the adapter in the top. A test tube nearly filled with cold water is placed in the adapter and kept from fitting tightly by extending a wire between the adapter and test tube, nearly to the bottom of the latter. This prevents blocking of the outlet by any alcohol fumes.

In making these extractions the flask is placed in a sand bath heated by a Bunsen burner. In case the flask breaks, the alcohol is absorbed in the sand and not ignited.

This apparatus is also available for the determination of crude fiber in flour and core compounds, and for other purposes where it is desired to maintain a fairly constant volume of liquid during boiling.

Physical Properties of Dental Cements—II[1,2]

By Paul Poetschke

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

A knowledge of the physical properties of dental cements is of great importance to the dentist and the public because dental cement occupies a prominent place in many restorative dental operations, such as cementation of crowns, bridges, inlays, orthodontic appliances, and fillings.

Failures in operations involving the use of dental cement are due to inferiorities in the cement or to its incorrect mixing and application. A knowledge of the physical properties of dental cements enables the dentist to avoid the use of inferior products and to intelligently mix and apply cements of suitable quality.

Apparatus and methods are described for determining heat generation, texture, permeability, and setting time of dental cements. The results of tests of the more prominent brands of dental cement of the zinc oxyphosphate type are given, and the relationship of different properties discussed from a dental viewpoint.

Heat generated in the setting of zinc oxyphosphate cements varies considerably in the six prominent brands which were tested. Under proper conditions of mixing none of the existing products would cause damage to a vital tooth. Unpleasant thermal effect would result more from hurried mixing than from differences in the cements. The heat generated may be controlled within wide limits by the rate of addition of powder to liquid and the time of mixing.

Heat generation, crushing strength, texture, and permeability are all properties of dental cements which show an intimate relationship. Crushing strength is directly proportional to heat generation. Cements which generate the most heat in setting show the highest crushing strength. Cements showing the greatest heat generation and highest crushing strength, also show the finest texture. The texture of six prominent brands of zinc oxyphosphate cement varies from a fine, vitreous to a coarse, chalky texture. Permeability of zinc oxyphosphate cements to aqueous fluids is greater in cements having a coarse texture. Cements of fine vitreous texture are not penetrated by dye solutions.

Setting time at room and body temperature was determined by several methods. Commercial designations such as "slow," "medium," and "rapid" setting are of little value, because no standard of setting time is adhered to by manufacturers. A cement which sets more rapidly at room temperature does not necessarily follow the same order at body temperature, and may actually be slower setting at body temperature than a cement which sets slower at room temperature. Slower setting at room temperature gives the dentist more time for mixing and application, and rapid setting at body temperature economizes his time. It is therefore desirable to have slower setting at room temperature with a degree of acceleration at body temperature which will result in reasonably prompt setting in the mouth.

Zinc oxyphosphate cements do not all show the same characteristics in hardening. Some that show a fair or even good rate of hardening in 15 min. may not show a proportionate increase in the next 24 hrs. Cements which show the highest heat elevation on setting, the greatest strength, the finest texture, and the least permeability to aqueous fluids also show the greatest increase in strength between the 15-min. and 24-hr. period.

HEAT GENERATION

It is well known that dental cements and even such industrial cements as magnesium oxychloride and portland cement generate heat in the process of setting. In dental cements the heat generation is much more pronounced and the setting time is correspondingly more rapid.

Heat generation of dental cements is of importance in connection with dental practice, especially in crown and bridge work, because the bulk of cement used is in many cases large enough to give a decided thermal effect. This is especially true when the cement is hurriedly mixed by rapid and large additions of powder and limited spatulation on the slab, for under these conditions more heat is generated than when the cement is properly mixed.

The degree of heat that may be applied to the healthy tooth varies somewhat with individuals. Some will tolerate 135° F., whereas others are unpleasantly affected by a temperature of 120° F. The tooth is more susceptible to irritation by cold than by heat, and it will tolerate a temperature of 130° F. better than one of 40° F.

Apparatus—Fig. 1 shows the apparatus designed and used in this laboratory for studies on the heat generation of dental cements. The most important part of the apparatus is the special thermometer A. Instead of the usual mercury bulb, the thermometer has a depressed mercury bulb with a cavity 7.5 mm. deep and 7.5 mm. in diameter. It is graduated from 40° to 200° F. in single degrees. The total length of the instrument is 12 in. B is a small thermometer of special form used to control the temperature of the apparatus. C is a Kolle culture flask. F is a battery jar. E is a heating element, and G a stirrer. The apparatus as described is virtually an artificial mouth.

Standard Procedure for Zinc Oxyphosphate Cements—Fill the jar F with water to the neck of the flask C. Turn on the current and heat up the water until the control thermometer B reaches 100° F., and maintain at this temperature during the test. Weigh 1.5 g. of powder and transfer to a mixing slab previously regulated to a temperature of 68° F. Then transfer 0.5 cc. of the liquid to the slab and add the powder to the liquid in eight portions, completing the mix in 2 min.

Collect the cement mix on the end of the mixing spatula, quickly remove the cover D and control thermometer B; raise the thermometer A and fill the cavity flush with the cement by running the spatula sidewise over the edge of the cavity. Immediately replace A, D, and B, and begin readings. This part of the process must be carried out quickly, and with a little experience the first reading may be taken $^3/_4$ min. after completing the mix. A stopwatch is used for timing the readings. Readings are taken every $^1/_4$ min. for the first 4 min., then every $^1/_2$ min. for the next 4 min., and finally every minute until the temperature on thermometer A has dropped to 101° F.

(The set cement is removed from the thermometer by immersing the bulb in dilute hydrochloric acid. A single test requires approximately $^1/_2$ hr. Results may be duplicated with an accuracy of 0.5° F.)

Results—Fig. 2 shows graphically the results obtained on six of the most prominent brands of zinc oxyphosphate

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[1] Received September 1, 1922. Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This paper is a continuation of studies on dental cements published in the previous papers: "Germicidal Efficiency of Dental Cements," This Journal, 1 (1915), 195; "Physical Properties of Dental Cements," *Ibid.*, 8 (1916), 303.

cements. It will be observed that the maximum temperature is reached in all cases in approximately 3 min. and that the temperature reached varies from 115° to 133.5° F.

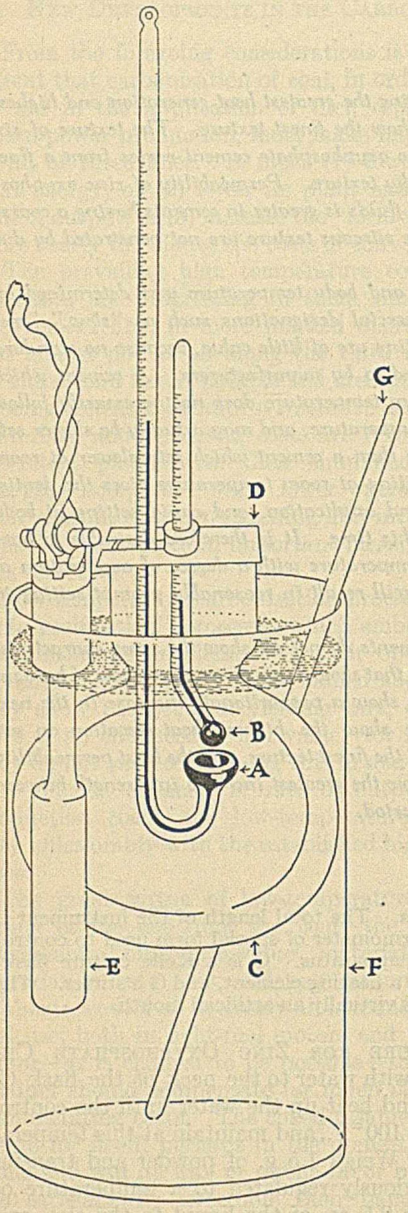

Fig. 1

Fig. 3 shows graphically some results obtained on Cement M of Fig. 2 by varying the initial temperature and mixing conditions. If we start with the thermometer at room temperature (75° F.) instead of 100° F. then the maximum temperature reached is only 98.75° F., but if the initial temperature is 100° F. then the maximum temperature reached is 133.5° F. This shows the importance of a definite initial temperature such as 100° F.

When the powder is added to the liquid in fewer and therefore larger portions and the time of spatulation is reduced, the heat elevation is greater. Test B of Fig. 3 was made under average correct mixing conditions, and the temperature reached was 133° F. By adding the powder twice as fast, as in A, a temperature of 143° F. is reached. By retarding the mixing time as in C, a temperature of only 128° F. is reached, which can be still further reduced by spatulating the mass for a minute after all powder has been added, as in D where the maximum temperature rose to only 122° F.

Significance of Results—The bulk of cement used in the test is considerably greater than would be employed in cementing a single crown or a bridge on a single tooth or abutment. The cement only fills the space between the crown or cap and the tooth structure. The thickness of cement will vary with the size and form of the tooth and the extent to which the enamel and dentin may have been removed by decay or design. Therefore, the intensity of the heat transmitted by the setting cement to the tooth structure is dependent upon bulk of cement, kind of cement, and conditions of mixing. However, the maximum temperature recorded for any of the properly mixed cements is a little less than 135° F., which is tolerated by the healthy tooth, and under no circumstances could we conceive of such a large bulk of cement being used on a single tooth. If the cement is not mixed too hurriedly, no unpleasant sensation of pain or irritation to a vital pulp can occur to the patient under practical working conditions. Furthermore, it is an everyday practice among dentists to have the patient flow cold water over the cemented region should any undue heating take place.

Relation of Heat Generation to Crushing Strength of Oxyphosphate Cements

Fig. 2 also shows the crushing strength of the various cements in relation to the heat elevation. The rather interesting and important discovery was made that higher heat generation was accompanied by increased strength and resistance to saliva.

Reference to Fig. 4 will show that, notwithstanding the fact that six different brands of cement were tested, the crushing strength of all is directly proportional to the heat generated on setting. Therefore, the higher the degree of chemical reactivity, the higher the strength of the cement. This observation may be worth investigation in connection with other industrial cements.

Relation of Heat Generation to Texture

Method—Cylinders 5 mm. high and 5 mm. wide are allowed to set under paraffin oil at body temperature for 15 min., then rinsed in ether and dropped into an aqueous dye solution (as used for permeability tests) at body temperature. After 24 hrs. storage at body temperature, they are broken through the middle by placing a sharp knife blade against the cylinder and striking quickly with a hammer. This breaks the cylinder open with a clean cross cut. The surface is then examined under a magnifying glass.

Fig. 6 shows the texture of six commercial brands of dental cement at a magnification of approximately six diameters. The texture varies from a fine vitreous, as in A, to a coarse chalky, as in F. Cement A is the same as M in Fig. 2, B the same as O, C the same as P, D the same as Q, and E the same as R. These comparisons show that the higher the heat generation the finer and more vitreous the texture. Cements showing the lowest heat generation have a coarse, chalky texture.

Permeability

For a long time tests of dental cements have been made by placing the set cement in a solution of dye or red ink. These tests have been largely valueless and misleading, because no attention was given to consistency, conditions of mixing, time of initial setting at body temperature, or time of storage.

Method—In this laboratory test cylinders 5 x 5 mm. are prepared in the same manner as in tests for texture. In fact, the same cylinder serves for both tests. The cylinders are hardened under paraffin oil at body temperature for 15 min., rinsed in ether, and placed in an aqueous solution of dyestuff and stored at body temperature for 24 hrs. Various vegetable and coal-tar dyes may be employed. A very satisfactory solution for the purpose is made by dissolving 2 g. of cotton scarlet extra (Badische) in 500 cc. of distilled water and adding thereto 0.1 cc. of 40 per cent formaldehyde solution. After 24 hrs. storage the

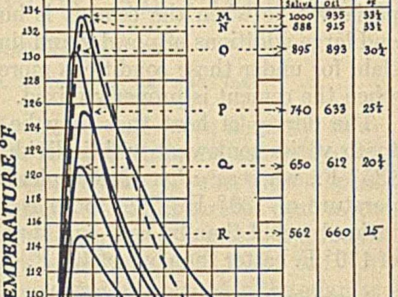

Fig. 2

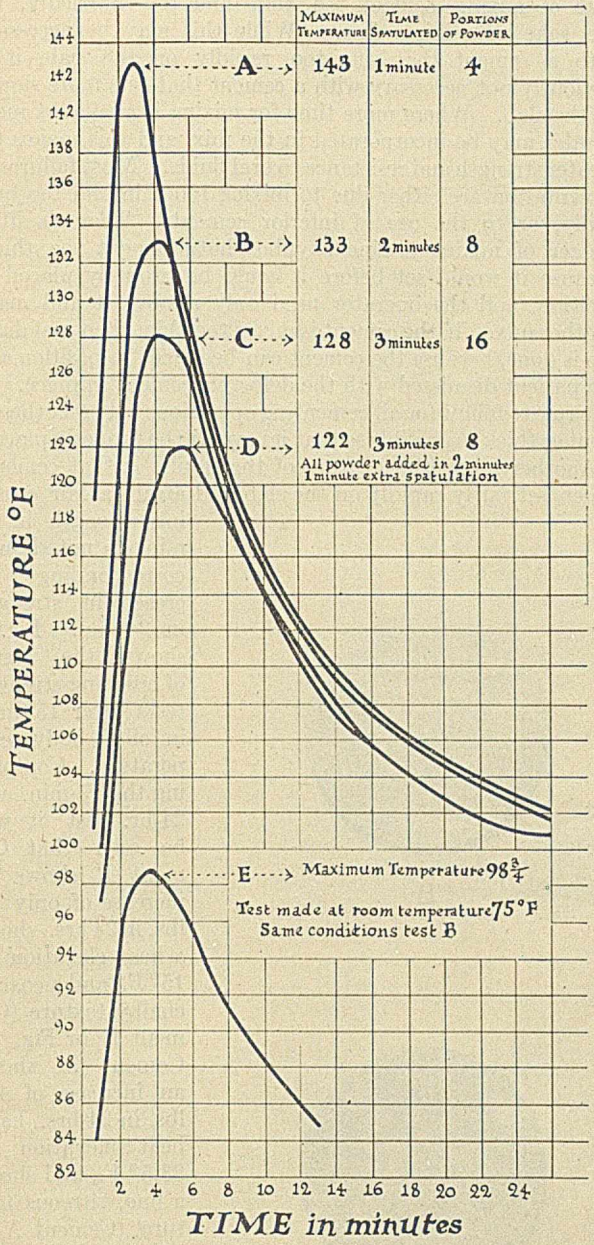

Fig. 3

cylinders are rinsed in distilled water, dried with filter paper, split open in the same way as outlined for the texture tests, and the depth of penetration of the dye measured at four approximately equidistant points along the edge of the cylinder.

The following results were obtained on six cements, the textures of which are shown in Fig. 6.

A = None
B = None
C = 1/4 to 1/2 mm.
D = 1/8 to 1/4 mm.
E = 1/8 mm.
F = 1 mm.

The significant thing about these results is that the cements having a fine vitreous texture are not penetrated by the dye, whereas those having a coarse, chalky texture are penetrated. Cement F, which has a very coarse texture, shows the greatest penetration. The presence of soluble constituents in the set cement mass probably accounts for the slight differences in permeability of Cements C, D, and E, but the general results indicate that texture plays an important part—the finer the texture the less the penetration.

Time of Setting

In a previous paper[2] a method was given for determining the relative setting time of dental cements at 68° F. This is the average room temperature, and the results obtained are of value in grading cements as to their relative working time—that is, the time which may be taken by the dentist to make the mix and apply the cement. However, when the cement is placed in position in the mouth, the setting is accelerated by the heat of the mouth. It is, therefore, important to know to what extent the setting time of zinc oxyphosphate cements is accelerated by increased mass of cement and by the body temperature. Two methods were employed to determine the relation between setting time at room temperature and body temperature.

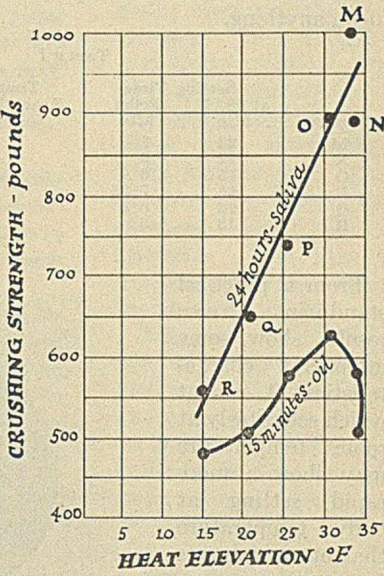

Fig. 4

Method 1—The cement mix, using 0.25 cc. of liquid, was collected on the end of the spatula and allowed to remain there undisturbed for 1 min., and then quickly rolled into a pellet in the palm of the hand and deposited upon a clean sheet of paper. The time required for the pellet to set so that it is no longer indented by a pointed instrument, applied with moderate pressure while being held in the fingers as one would hold a pen, is taken as the pellet-setting time. This method shows the accelerating effect due to increased mass of cement at room temperature.

Method 2—Cylinders are prepared in the same manner as for crushing-strength tests,[2] and the time required for a cylinder to reach 325 to 350 lbs. crushing strength at body temperature is determined. At this point a cylinder of zinc oxyphosphate cement breaks sharp and does not squash under the load. This method gives results which agree very closely with practical tests made by cementing facings and crowns at body temperature.

Fig. 5 shows the results obtained by the two methods as compared to the setting time at 68° F. The figures in the circles show the time required for the cylinders to reach 325 to 350 lbs. crushing strength.

Discussion of Results—The setting range of six commercial brands of zinc oxyphosphate cement at 68° F. is from 12 to 22 min. The pellet-setting range (Method 1) is 3 min. at 70° to 80° F. This shows the accelerating effect of increased mass of cement on the setting time due to the heat generated within

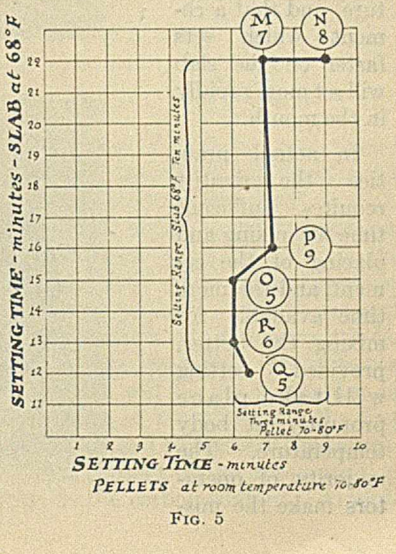

Fig. 5

the pellet, the setting range being narrowed down from 12 to 3 min.

The figures in the circles show a range of from 5 to 9 min. for the different cements.

Table I gives a comparison of the three methods. Five of the cements are designated commercially as "medium setting." It is evident that there is a wide difference in the setting time of the five "medium-setting" cements, indicating that manufacturers have no definite standard and that the commercial designation "medium," "rapid," and "slow setting" may mean anything.

TABLE I

CEMENT	Setting Time at 68° F. Min.	Pellet Min.	Time Required to Reach 325 to 350 Lbs. Min.	Commercial Designation
M	22	7	7	Rapid
N	22	9	8	Medium
O	15	6	5	
P	16	7.25	9	
Q	12	6.5	5	
R	13	6	6	

From a practical standpoint these results show some important characteristics. A cement which sets slowly at room temperature may show a more rapid setting at body temperature than one which sets faster at room temperature. Cement M requires 22 min. at 68° F. and only 7 min. at body temperature, whereas Cement P, which sets in 16 min. at 68° F. requires 9 min. at body temperature. A dentist using zinc oxyphosphate cements is apt to assume that a cement which sets slowly on the slab will also set slowly at body temperature, and that a cement which sets faster on the slab will set more rapidly in the mouth.

In actual practice the dentist requires sufficient time for mixing and placing of the cement, and the more time available for mixing the better, provided setting will take place promptly at body temperature. The majority of operators make the mistake of mixing cement too thin and too hurriedly, for the sake of gaining time. While this may be necessary with a cement that sets too rapidly on the slab, it is obviously not necessary with a cement that sets more slowly on the slab. Where more time for mixing is available, more powder may be incorporated in the mix, and this makes for greater strength and resistance to oral fluids. Most failures in cementation are either due to mixing too thin and too hurriedly, or to the use of inferior cements. There is little danger of mixing a zinc oxyphosphate cement too thick, because it would set before it could be properly placed in position, and the operator need only remove it and make another mix. If the cement is mixed too thin, then real damage is done, because the cement can be placed in position and the patient dismissed with the defective cement in place. A safe rule to follow for all cementing operations is to mix the cement as thick as possible so that it may still be properly placed.

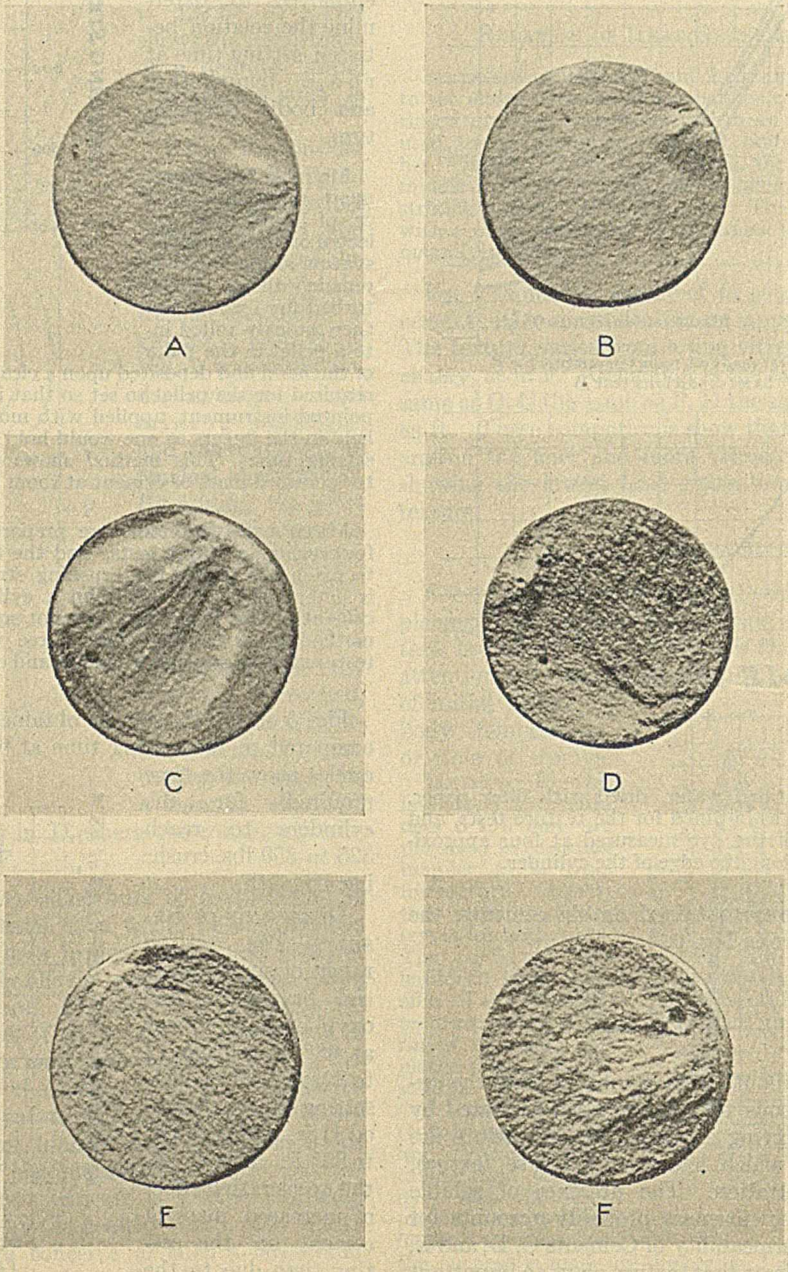

FIG. 6

Another interesting feature of the results is that cements which set fairly rapidly on the slab and attain a fair crushing strength in 15 min. do not show a corresponding increase in strength in 24 hrs. Fig. 4 shows the result of crushing-strength tests after 15 min. in oil at body temperature. Comparing the 15-min. and 24-hr. test it will be seen that Cement R shows an increase of only 82 lbs. in 24 hrs., shows a heat elevation of 15° F., and a coarse, chalky texture (Cement E in Fig. 3). Cement M shows an increase of 418 lbs. in 24 hrs., has a heat elevation of 33.5° F., and shows a fine, vitreous texture (Cement A in Fig. 3). Cement M has a higher strength than R in 15 min. (102 lbs. greater), and while M requires 22 min. to set at 68° F., R requires only 13 min. Cement O, which shows a high 15-min. strength due to under-calcination of the powder, increases only 268 lbs. in 24 hrs. and sets in 15 min. at 68° F. This cement shows a heat elevation of 30.5° F. and a fine, vitreous texture.

The Organic Matter in Oil Shales[1]

By Ralph H. McKee and Ralph T. Goodwin

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The motor-fuel and lubricating oils of the near future will largely come from oil shale, and therefore we should determine accurately and without delay the nature of American oil shales and the methods available for the production of oil from this material. In this paper a careful study of the organic material present in oil shales has been made by the use of the action of solvents, chemical reagents, heat, and ultimate analysis.

The pyrolysis curves show unexpected exothermic and endothermic differences between shales from different localities.

The action of solvents and chemical reagents confirms previous views on kerogen, but shows that it is highly unsaturated in character.

Ultimate analyses show a variation in carbon-hydrogen ratio in shales from different formations. A rough relation exists between this ratio and the oil yield from a shale.

An intermediate, highly unsaturated, high melting product between the kerogen of the shale and the shale oil has been isolated and studied. This intermediate product on cracking gives a shale oil much more "saturated" than the material before cracking, a phenomenon without parallel in the cracking of well petroleum.

THE fundamental problem of the shale-oil industry is to produce from shale an oil that will compete favorably in a physical, chemical, and economic sense with petroleum from wells. The solution of this problem must be based on exact information attained by systematic research. This fundamental information involves the values of all the physical constants, a knowledge of the manner in which oil-forming material decomposes, and information concerning the chemical composition of the organic material that undergoes decomposition to form the oil and other products.

CHEMICAL COMPOSITION

Oil shale varies considerably in character, both physical and chemical, in different parts of the world and in different geological formations. There has been more experimental work on Scottish oil shales than on shales from other parts of the world, but owing to the different nature of the shale in other areas, this work will not generally apply. However, there are a few essential characteristics that are common to all oil shales.

In order to determine whether the organic matter varies in composition, and, if so, what the nature and extent of the variation is, proximate and ultimate analyses were made on several different types of oil shales—that is, shales that yield products differing in character upon destructive distillation. A shale from Elko, Nevada, will yield an oil containing a high percentage of paraffin wax. A shale from Colorado gives an oil of the mixed base type, whereas certain Utah shales yield asphaltic oil.

Oil shales cannot be graded as to oil content by the method of proximate analysis. There seems to be no fixed ratio between the volatile matter in shale and the amount of oil that can be recovered by a laboratory assay. It has been demonstrated that many variable factors in retorting have a definite effect on the quantity and quality of the oil produced. Some of these factors are—rate of heating, time of heating, pressure in retort, use of steam or other atmosphere such as hydrogen, and the final temperature reached.[1,*]

In ultimate analyses the organic or combustible part of the shale was analyzed for its elemental constituents—carbon, hydrogen, nitrogen, sulfur, and oxygen—by the methods outlined by Fisher.[2] The Kjeldahl-Gunning-Arnold method[3] was employed for the nitrogen estimations. The sulfur was estimated by heating about a 1-g. sample of the dried shale with about 10 g. of Eschke's mixture, using the double crucible methods as described by Sadtler.[4]

The nitrogen of shale appears to be present in several forms. A few shales carry practically no nitrogen. In retorting, a part of the nitrogen comes off at a low temperature in the form of ammonia, pyridines, and isoquinolines, while another part comes off only at a higher temperature, principally as ammonia. The use of superheated steam increases the yield of ammonia.

The carbon-hydrogen ratio of oil shales has been used by Robertson[5] to indicate the possible yield of oil from a shale. The rule, as stated, is that the yield of oil varies directly as the percentage of organic matter and inversely as the carbon-hydrogen ratio. In other words, if the organic percentage is high and the carbon-hydrogen ratio is low, then the shale will give a good yield of oil. The greater the proportion of hydrogen the larger will be the yield of oil.

GENERAL RESULTS OF ULTIMATE ANALYSES OF OIL SHALES

SHALE	C	H	N	S	O (by Diff.)	Ash	C:H Ratio	Oil Gal./Ton
Scotch[5] (Broxburn)	19.51	2.48	0.69	1.36	3.31	72.65	7.9	23.3
Scotch[5] (Pumpherston)	24.88	3.67	0.68	0.80	8.07	61.90	6.8	31.0
Australian[5] (Commonwealth)	63.58	7.81	0.81	0.43	4.41	22.96	8.11	10.8
Utah[6] (Soldiers' Summit)	13.51	1.70	0.39	0.28	18.00	66.12	7.9	16.8
Nevada[6] (Elko)	37.65	5.43	0.39	1.08	10.04	46.21	7.21	86.8
Colorado (Grand Valley)	23.67	3.50	0.66	1.78	3.79	66.60	6.8	63.5
California (Ione)	50.95	5.77	0.42	2.12	18.06	22.68	8.8	51.8
Lignite[7] (Black, U. S.)	54.91	6.39	1.02	....	32.54	5.14	8.6	....
Crude Shale Oil[8] (Autun, France)	79.70	11.80	....	....	8.50	....	....	....
Crude Petroleum (P. Heavy)	84.9	13.7	....	....	1.40	....	....	....
Crude Petroleum (Calif.)	84.00	12.70	1.70	0.75	1.20	....	....	....
Asphalt[9] (Trinidad)	82.60	10.50	0.50	6.50	nil	....	....	....
Cannel[10] (English)	79.23	6.08	1.18	....	7.24	4.84	....	....

The low hydrogen content in an oil shale has been stated as a reason for the unusually high percentages of unsaturates (part of oil dissolved by 95 per cent sulfuric acid) in shale oils.[11] Analysis of Colorado shale shows a carbon-hydrogen ratio of 6.7 in the undistilled shale, while the ratio in the product obtained from this same shale under reduced pressure is 5.5. The original shale has an excess of about 18 per cent of carbon over that necessary to form an oil having a ratio as determined. It is inferred that the higher the hydrogen content of the shale, the greater will be the percentage of saturates in the oil, and cracking of the oil during the first or subsequent distillations would tend to increase the saturation of the oil if the hydrogen content of the decomposition products had a higher ratio to the carbon content. Accord-

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[1] Received September 20, 1922. For a complete report of this investigation see No. 1, Supplement A, of *Quarterly of the Colorado School of Mines*, January, 1923.

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

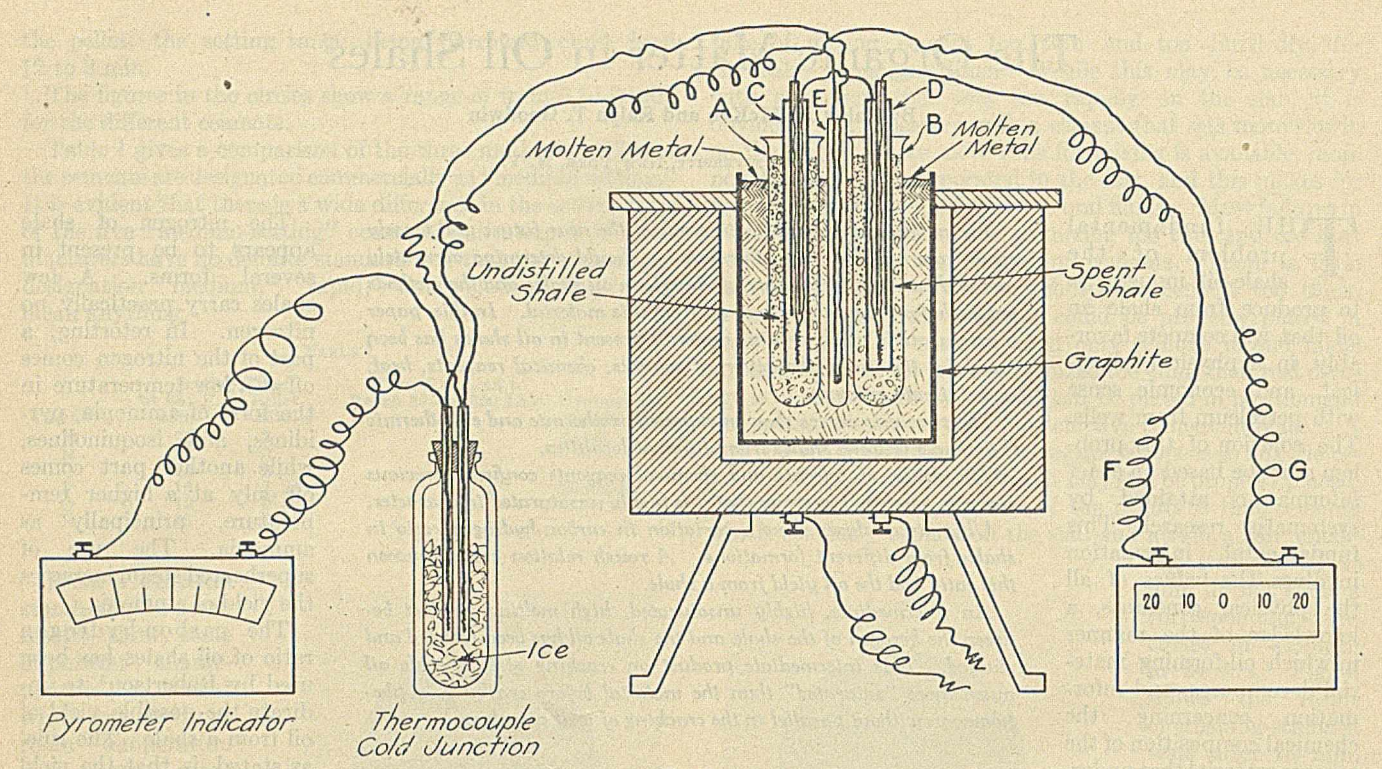


Fig. 1

ingly, if the shale is heated slowly, the yield of oil is less, but its content of saturated compounds is increased. The results obtained in this investigation agree only in part with this view.

Thermal Decomposition of the Organic Content of Oil Shales

This work on pyrolysis was carried out because of the inconclusive nature of the evidence supporting the current conceptions of oil-shale distillation. McKee and Lyder[12] report quantitative results in the decomposition of shales. They determined the amount of heat involved in the conversion of the organic matter in shale to oil and other products. The reaction is endothermic and the values for three different types of shales range from 421 to 484 cal. per g. of oil and gas produced.

In this work no attempt was made to calculate the thermal balance of distillation, but simply to show that there are at different temperatures definitely exothermic and endothermic reactions, which in the complete distillation balance more or less as to quantity so that the actual heat consumed is small.

The experimental method employed consisted in heating side by side, under the same conditions, a shale that had not undergone pyrolysis and a shale that had undergone complete pyrolysis. The extent to which the temperature of the undistilled shale became higher or lower than that of the "spent" shale in the various stages of the pyrolysis was determined by means of a differential arrangement of thermocouples. The essential parts of the apparatus used are shown in Fig. 1.

The method of plotting the differential heating curve is the same as that commonly employed in metallurgical work. The galvanometer deflections are noted each 5 min. and then the differences in temperature between the new and spent shale are plotted as abscissas against the actual temperature of the metal bath as ordinates. The curves as given represent for each shale the average of four closely agreeing determinations.

Fig. 2 shows the thermal-decomposition curve for an oil shale from Green River, Wyoming. Fig. 3 shows the thermal-decomposition phenomena of an oil shale from Grand Valley, Colorado. A sample of Ione, California, shale material under thermal examinations indicates several exothermal and endothermal points. (Fig. 4, Curve II)

Hollings and Cobb[13] made a thermal study of the carbonization of coal and the evidence obtained showed that coal went through several stages of decomposition, some being accompanied by exothermic and others by endothermic heat changes. Curve I of Fig. 4 shows the thermal decomposition phenomena of such lignitic coal.

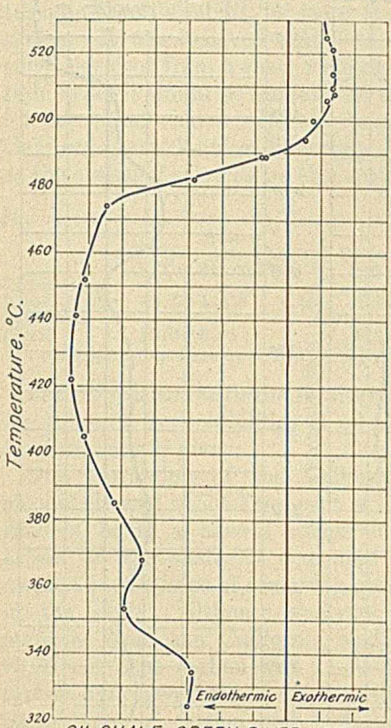
Primary Reactions in the Decomposition of Oil Shale

When oil shale is heated with exclusion of oxygen, chemical reactions occur that are highly complex and a variety of new substances appear in place of the original kerogen. The yield and character of these products may be varied widely by changing the factors in the process of retorting, such as temperature, pressure, time, and contact surface.[14] An examination of a large number of suggested "processes" for the treatment of oil shales, and the conflicting ideas on which they are designed, indicates the importance of a knowledge of the primary reactions in the decomposition of oil shale.

The object of this part of the present investigation was to study the primary volatile products liberated from the kerogen by heat. In order to avoid secondary reactions as far as practicable, distillation at reduced pressure was used in obtaining these primary products. It is believed that secondary reactions have been largely prevented by reducing to a minimum the temperature and the time of contact of the volatile matter with heated surfaces.

It is a generally known fact that the overheating or cracking of well petroleum will give products of lower boiling point and an increase in the percentage of unsaturated compounds. Knowing this fact regarding the action of well petroleum on overheating, it has been assumed that shale oil acts likewise under the same conditions. Many have advocated retorting in a current of steam or under reduced pressure.[15, 16]

The oil-yielding materials of different shales, and even of a single shale, differ in constitution, in their manner of breaking down when undergoing destructive distillation, in their reactions with chemical reagents, and in their decomposition temperatures. Because of these variations each shale presents a distinct problem. It is thus obvious that the refining of shale oil really begins with the retorting, and that the production of a satisfactory finished product from any one type of shale will not represent a universal solution of the retorting problems of the American shale-oil industry.



OIL SHALE, GREEN RIVER, WYO.

FIG. 2

DISTILLATION OF SHALE UNDER REDUCED PRESSURE—A sample of Ione, California, shale was dried and distilled under reduced pressure (8 mm.) from a metal retort (500 cc.). Up to 225° C. only a few drops of light yellowish oil collected in the receiver. From 225° to 450° C., at which temperature the distillation was complete, a straw-colored, wax-like solid collected in the condenser. This solid material constituted 90 per cent of the total distillate collected.

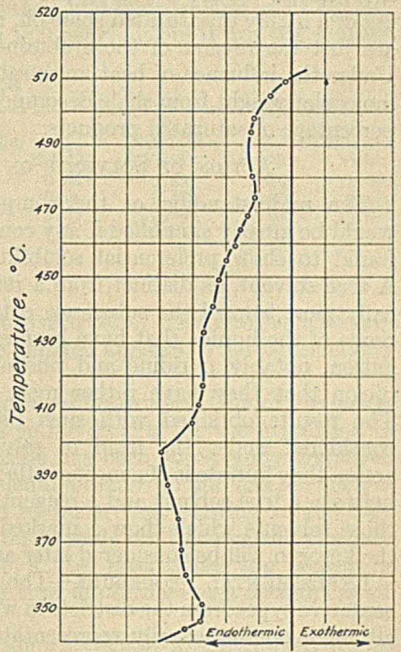
On account of the importance of this product, several of its physical properties were determined. It dissolves very readily in acetone and alcohol, and precipitates as a finely divided, light yellow material when the alcohol solution is diluted with water. The solid melts rather sharply at 46° C. It is completely soluble in sulfuryl chloride with the evolution of heat. When this sulfuryl chloride solution is hydrolyzed with an excess of water, a light yellow solid separates. If the material is dissolved in 95 per cent alcohol and the solution boiled with an absorbent carbon and filtered hot, a straw-colored solid separates from the alcohol on evaporation in an atmosphere of nitrogen. This material darkens readily on exposure to air, apparently because it is highly unsaturated and readily oxidized. This unsaturation is also demonstrated by its decolorization of a potassium permanganate solution and by its complete and rapid solubility in selenium oxychloride. Lehner[17] states that selenium oxychloride unites with the unsaturated hydrocarbons of the aliphatic series. On hydrolysis of the selenium oxychloride solution with an excess of water, a solid separates, but it is contaminated by the presence of red selenium.

Determination of the "saturation percentage" of this material was made in the customary way by the use of 66° Bé. sulfuric acid and Babcock cream-test bottles. After mixing with the sulfuric acid and centrifuging for several minutes there was no separation of saturated oil from the acid. The material is completely soluble in concentrated acid and therefore is composed entirely of unsaturates, as determined by this method.

An ultimate analysis of this material shows it to contain 82.83 per cent carbon and 16.79 per cent hydrogen, or a total of 99.62 per cent. This confirms the absence of nitrogen, sulfur, and oxygen, as was also indicated by qualitative tests for nitrogen and sulfur. The material contains a lower carbon-hydrogen ratio (C:H=4.9) than either that of the original shale or oil distilled from the shale at atmospheric pressure.

A weighed amount of this solid was distilled at atmospheric pressure. Up to 135° C. a few drops of water and water-oil emulsion were distilled from a compound. The distillation proper began at about 290° C. and from this temperature up to 365° C. a straw-colored oil distilled over. From 365° to 380° C. there appeared to be a decomposition of the material, a light yellow semisolid collecting in the condenser. The distillation was complete at 380° C. The specific gravity of the material used for distillation was 0.913 at 15.5° C., while that of the distillate was 0.902 at 15.5° C. In the distillation 7.5 per cent of coke was formed, with a loss of 6.6 per cent by uncondensed gas. The oil obtained from this distillation was light yellow and solidified at room temperature. It contained 48 per cent by volume of unsaturates, while the product obtained by vacuum distillation was 100 per cent unsaturated compounds. This increase from 0 to 52 per cent of saturated compounds by one distillation is phenomenal.

Samples of Colorado shale (Grand Valley) were distilled under reduced pressure, using the same method as outlined above for the distillation of California shale. These distillations gave a dark-colored product, which was semisolid at room temperature. The material had a specific gravity of 0.952 at 15.5° C. and contained but 11.0 per cent by volume of saturates. By ultimate analysis the material gave a carbon-hydrogen ratio 5.5, contained 2.6 per cent nitrogen and 1.1 per cent sulfur. The saturates obtained by treating the oil with 66° Bé. sulfuric acid solidified at room temperature and were almost colorless. The material from the vacuum distillation was redistilled under the same conditions as outlined for the California shale. The distillation was slow, 5 per cent by volume distilling up to 280° C., after which the distillation was quite constant and was complete at 360° C. In the distillations 5.7 per cent by weight was lost as uncondensable gases and a residue of 10.6 per cent remained in the distilling flask. The distillate had a gravity of 0.894 at 15.5° C. and contained 38.0 per cent by volume of saturates. The saturates were liquid at room temperature. The distillation at atmospheric pressure of the vacuum product from California shale increased its saturates 52 per cent, while a similar distillation of the Colorado vacuum product increased the saturates 27 per cent. These distillations were carried on with other types of shales from Elko, Nevada, and Canada, and always with the formation of the heavy, semisolid vacuum product that gave a greater saturation per cent by redistillation at atmospheric pressure.



OIL SHALE. GRAND VALLEY. COL.

FIG. 3

Franks[18] has advanced the view that crude shale oils are not produced from the organic material in the shale by a single operation. He outlines the decomposition as occurring in two stages. The crude oils are mixtures of primary and secondary products formed during these two steps of the decomposition. This work of Franks confirms the theories of McKee and Lyder[12] on the decomposition of oil shale. The theories of these authors are now further confirmed by different methods than those used by Franks.

The results outlined above indicate several very important facts in the distillation of oil shales. In the pyrolysis of shale it is doubtful whether any of the final products are liberated as such from the shale kerogen. The authors believe that this solid, waxy material obtained by vacuum distillation of the crude oil shale represents the intermediate product between kerogen as such in the shale and the oil as obtained by pyrolysis. The decomposition of kerogen to form the oil products tends to occur in two stages. A primary decomposition takes place in which the insoluble kerogen is changed into a soluble solid, or semisolid. This intermediate product is not of the same composition as the kerogen, as indicated by analyses and by the ready solubility of the product. It is unstable toward heat, and a second decomposition by heat changes it into oils of the petroleum type of greater stability and higher saturation. It has been established that the less the decomposition of this "intermediate" product during the distillation of the shale the more unsaturated, unstable, and heavy is the oil. The saturates of the shale oil are increased in amount by distillation at atmospheric pressure.

The decomposition or "cracking" of well petroleum under the influence of temperature and pressure, to produce a more volatile product, is accompanied by a change in the products of higher molecular weight to form those of lower molecular weight. This cracking causes a decrease in the amount of saturates in the lower boiling product formed. In the heating of a highly unsaturated shale oil, results are obtained that are just the reverse of those obtained from well petroleum. Under the influence of heat an unsaturated material of high molecular weight from shale decomposes to form an increased percentage of saturated products.

ACTION OF SOLVENTS ON OIL SHALES

The understanding of the composition of the kerogen would be greatly simplified if any considerable part of it were found to show preferential solubility in any given liquid. A true solvent, as distinct from a reagent, should be chemically inert toward the substance extracted and the residue. Some of the liquids that have been employed in this investigation, notably pyridine and phenol, are open to the suspicion that they have rather more than a solvent action. The results obtained with such liquids can, however, be considered under the head of solvents, for any chemical action they initiate is of a most gentle nature.[19] The difference between a true solvent and a reagent is difficult to state, but those solvents which show a marked chemical reaction with the kerogen will be considered later as reagents.

EXPERIMENTAL PROCEDURE—The shales used were representative types from the districts in which they were collected, although not necessarily representative as regards oil yield. The oil yield from the different shales was determined by use of the standard laboratory assay method of the Bureau of Mines.[20]

About 25 g. of the moisture-free shale were placed in a paper thimble and extracted in a Soxhlet extraction apparatus. Results reported are based on two or more closely agreeing determinations. For convenience in comparing the different types of shales the solubilities are given in tabulated form. The nature of the extract is described under the discussion of the particular solvent used for obtaining it.

EXTRACTION WITH ANILINE—Aniline removed 15.60 per cent of the weight of a California shale. The high percentage of this shale soluble in aniline may be due to a partial decomposition of the organic content at the boiling point (184° C.) of the solvent. A dried sample of this same shale heated 6 hrs. at 200° to 250° C. in an atmosphere of nitrogen lost 4.40 per cent by weight. If this temperature was increased to 300° C., the physical appearance of the shale changed slightly and a few oily drops collected on the cooler part of the tube and absorption bottle. This shows that the shale at this temperature undergoes a change other than just the loss of water from the hydrated mineral content, if such were present. A Colorado shale heated under the same conditions (200° to 250° C.) gave an average loss of weight of 1.82 per cent. The loss of weight of the shale does not necessarily show the total change that has taken place in the organic content, for a part of the changed material may not be volatile at this temperature. Engler[21] found that certain bitumens when heated to 250° to 300° C. became soluble in organic solvents such as benzene. Vignon[22] found that the amount extracted from the same sample of a rich coal with pyridine (b. p., 114.5° C.), aniline (b. p., 184° C.), and quinoline (b. p., 238° C.) increased in the same order as the increase in the boiling points of the solvents. Bone[23] believes that the action of these solvents on coal is primarily a

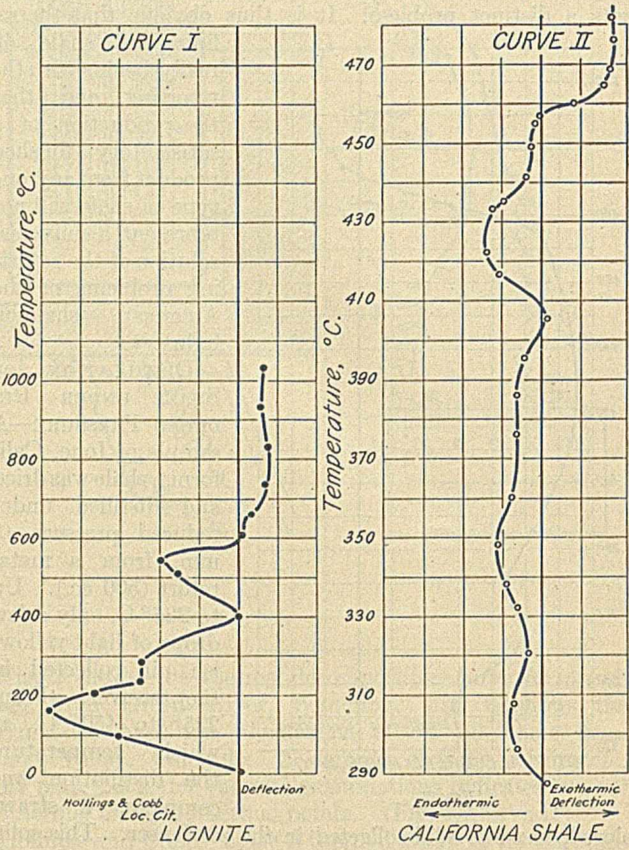


FIG. 4

ANILINE EXTRACT

	Oil Yield by Distillation Gal./Ton	%	Aniline % Soluble	Extract % of Distillation Yield	Absolute Alcohol Extract (Same Sample) % Soluble
Colorado (Grand Valley)	63.5	23.8	1.8	7.6	0.5
Wyoming (Green River)	58.8	22.0	1.6	7.3	...
California (Ione)	52.0	19.0	15.6	82.1	5.2
Nevada (Elko)	7.3	2.7	1.2	44.4	2.6
Scotch	18.2	6.8	0.7	10.3	1.0
Kentucky	18.2	6.8	1.3	17.6	...

question of temperature. In view of this evidence, the action of aniline on shale should not be considered as merely that of a solvent.

A sample of Colorado shale (Grand Valley) yielding 63.5 gal. of oil per ton was extracted with several solvents to determine the advisability of using the same solvents for other shales. It was believed that if the solvent extracted but a small per cent from a shale yielding as much oil as the Colorado type, it would be inadvisable to consider such a solvent for the other shales. It was found that shale from Ione, California, acted quite differently from the Colorado shale, so the action of solvents on this shale is given for comparison.

SOLUBILITY OF COLORADO AND CALIFORNIA SHALE IN VARIOUS SOLVENTS

	Oil Yield Gal./Ton	Absolute Alcohol	Acetone U. S. P.	Petrolic Ether	*m*-Cresol	Pyridine	Phenol	CS_2
Colorado (Grand Valley)	63.5	1.43[a]	1.48	1.39	0.87	2.04	0.87	1.00
California (Ione)	52.0	6.98		2.25				

[a] All percentages are by weight on dry weight of shale.

For comparison with the results obtained above the following table of the solubilities of oil shales in various solvents for petroleum is given.

The extraction of the California shale with absolute alcohol showed about 7 per cent of the material to be soluble. Alcohol being a *neutral solvent*—i. e., having no chemical action on the shale—it was used to dissolve the organic content in the hope of removing one constituent as it occurs in the shale. Ultimate analyses on this alcohol-soluble material from the California shale show that it contains 73.50 per cent carbon and 11.40 per cent hydrogen, or a carbon-hydrogen ratio of 6.4:1. Nitrogen was absent. The percentages of carbon and hydrogen in the original shale on an ash-free basis are 65.90 per cent carbon and 7.46 per cent hydrogen. The carbon and hydrogen percentages in the intermediate product, obtained by distilling this same type of shale under reduced pressure, are 82.83 and 16.79 per cent.

SOLUBILITY OF OIL SHALES IN VARIOUS SOLVENTS FOR PETROLEUM[30]

		Carbon Tetrachloride		Carbon Bisulfide		Acetone		Benzene		Chloroform	
SOURCE	Yield Gal. Oil per Ton	% Soluble	%[a] Distillation Yield	% Soluble	%[a] Distillation Yield	% Soluble	%[a] Distillation Yield	% Soluble	% Distillation Yield	% Soluble	% Distillation Yield
Kentucky	18.22	0.037	0.51	0.015	1.44	....	....	0.06	0.82	0.14	1.99
Utah (Soldiers Summit)	44.60	0.74	4.45	0.76	4.57	0.53	3.16	0.91	5.47	1.05	6.32
Colorado (DeBeque)	37.75	2.04	15.42	1.85	13.97	1.33	10.04	2.23	16.84	2.41	18.22
Wyoming (Green River)	58.65	1.195	5.27	1.27	5.58	1.22	5.35	1.37	6.02	1.75	7.72
California (Ione)	52.00	7.555	33.46	5.83	29.68	10.98	55.80	....	....	10.16	51.73

[a] Represents the per cent of the distillation yield soluble in the solvent.

After drying this alcohol-soluble material at 70° C., it was distilled at atmospheric pressure. The temperatures were not uniform for the distillation on account of the cracking of the material under the influence of heat. The distillate was a dark brown, wax-like solid, melting at about 80° C. This same material was returned to the distilling flask and redistilled. On second distillation the material decomposed still more, as evidenced by the vapors set free and variation in boiling points. The distillate was a straw-colored liquid having a petroleum odor. The oil was very much unsaturated, as indicated by its darkening on exposure to air and its rapid decolorization of potassium permanganate solution.

Ultimate analyses of the dried material from the alcohol extract of Colorado shale give carbon 74.25 per cent and hydrogen 11.52 per cent, or a carbon-hydrogen ratio 6.4:1, a figure identical with that of the California shale. The percentages of these elements in the original shale on an ash-free basis are—carbon 71.01 per cent, and hydrogen 10.50 per cent, or a ratio of 6.8:1. It will be noted that the percentages of carbon and hydrogen in the original shale and the extracted material are about the same, indicating that the alcohol extracts a part of the kerogen from the shale about as it exists *in situ*. A distillation of this resinous material gives a viscous liquid having a characteristic petroleum odor.

From this investigation of the action of solvents on oil shale, it is evident that only a part of the kerogen of the shale can be extracted by solvents, and that the material extracted is not an oil and only resembles an oil when subjected to destructive distillation. Accordingly, we have one more proof that the shale contains no oil as such, but that it contains an organic material from which oil may be produced by destructive distillation.

Obviously, it is not commercially possible to produce oil from shale by extraction with organic solvents, because the amount of material extracted is very small, and because the material extracted is not an oil and can only be changed into a petroleum-like product by heat. Apparently, the only possible commercial method for the recovery of oil from shales is by pyrolysis—i. e., thermal decomposition.

ACTION OF REAGENTS ON OIL SHALE

Use has been made of reagents to aid in determining the constitution of coal and oil shale, chiefly by geologists and paleobotanists, who have found in the partial breakdown of the mass by concentrated acids and oxidants suitable means of isolating organized structures for examination under the microscope. Chemists have been dismayed by the complexity of such reactions, and as a rule have confined their investigations to other lines of attack. By this method of chemical attack by means of various reagents which oxidize, saturate, decompose, or otherwise alter the kerogenous substance, it was our hope to convert this organic content of the shale into recognizable derivatives—a hope not fulfilled. An attempt was made to isolate the kerogen by the action of solvents on the inorganic, ash-forming constituents. Many attempts were made to reduce the ash content by means of acids. By alternate treatments of a Colorado shale with hydrofluoric and hydrochloric acids the ash content was reduced to 13.0 per cent, but it was not possible to reduce the ash content to near zero. This is rather a strenuous treatment, and the kerogen appears to be considerably altered by it.

LIQUID SULFUR DIOXIDE—Fischer and Gludd[24] have reported the use of liquid sulfur dioxide for the extraction of coal. Liquid sulfur dioxide has been successfully employed in the refining of petroleum because of its specific solvent reaction on unsaturated hydrocarbons. Owing to the high percentages of unsaturates in shale oil, this reagent was used on shales to determine if the unsaturates are present as such in the kerogen or if they are formed as a decomposition product.

A dried sample of California shale was extracted for 24 hrs. with liquid sulfur dioxide. The extraction apparatus was of a Soxhlet type and was constructed of iron pipe. The average loss in weight of the shale by these extractions was 4.5 per cent. The extracted material was a heavy, mobile, tar-like residue, having a disagreeable odor resembling burnt rubber.

Colorado shale gave an average extraction of 0.30 per cent after 24 hrs. extraction. The extracted matter was a dark brown to black, resin-like semisolid. These extractions indicate that if the organic content of oil shale is unsaturated it is not the type that is dissolved by liquid sulfur dioxide.

The organic content of the shale is so slightly soluble in ordinary solvents that an attempt was made to transform it by known chemical treatment into simpler and more easily definable products, capable of separation, purification, and recognition by ordinary analytical methods. The two reagents used for this chemical and solvent reaction on the shales were selenium oxychloride and sulfuryl chloride. Lehner[17] reports that selenium oxychloride reacts slowly with the saturated paraffin hydrocarbons and that the unsaturated hydrocarbons of the aliphatic series unite with it directly.

SELENIUM OXYCHLORIDE—A California shale was treated with an excess of selenium oxychloride, allowed to stand for 3 hrs. and filtered through an alundum crucible. The shale showed an increase in weight of 13.5 per cent by this treatment. The excess selenium oxychloride containing the extracted matter was evaporated to dryness under reduced pressure. A semisolid material was formed which was badly contaminated with the red form of selenium. This form of selenium was also present in the extracted shale, thus increasing the weight of the extracted material. If water is added to the extracted shale before drying, or to the selenium oxychloride filtrate, a large amount of red selenium is formed. This contamination with red selenium makes impossible the identification of the extracted materials.

Samples of Colorado shales gave an average increase in weight of 20.9 per cent when treated with selenium oxychloride as outlined above. Both the extracted shale and the extract contained red selenium. An attempt was made to remove this red selenium by dissolving it in carbon disulfide, but after extracting for several hours the selenium was not all dissolved. On account of the difficulties encountered in eliminating this red selenium from the extract, further experiments were not tried with this reagent.

SULFURYL CHLORIDE—This reagent reacts with the higher olefins, amylenes, and hexylenes to yield dichlorides. If sulfuryl chloride is run rapidly into a boiling mixture of benzene and aluminium chloride, chlorination occurs almost to the exclusion of all other reactions.[25] If lignite is treated with sulfuryl chloride, it yields a dark brown resin in small quantities.[26] On account of the action of sulfuryl chloride both as a chlorinating agent and a solvent for hydrocarbons it was used on oil shales in an attempt to separate recognizable substances.

Samples of California shales were refluxed for 48 hrs. with sulfuryl chloride. The filtrate was hydrolyzed by adding it to water, and a light yellow solid separated out. This separated solid was partially soluble in alcohol, leaving a residue of inorganic chlorides formed from the ash content of the shale. The shale lost by this treatment 8.9 per cent of its weight.

California shale was refluxed for 24 hrs. with an excess of sulfuryl chloride. The shale was found to have increased in weight 37.2 per cent by this treatment. This dried shale was extracted to completion with absolute alcohol, using a Soxhlet extraction apparatus. The loss of weight by this alcohol extraction was 47.74 per cent, calculated on the original weight of the shale used.

An Elko, Nevada, shale, after refluxing 12 hrs. with sulfuryl chloride, increased in weight 6.75 per cent. A Colorado shale under the same treatment increased in weight 9.32 per cent. There appears to be no definite relation between the percentage of volatile matter in the shale and the increase in weight by the action of sulfuryl chloride. The Nevada shale contains 20.2 per cent volatile matter and increases in weight 6.75 per cent, while the Colorado shale contains 53.9 per cent volatile matter and increases in weight only 9.52 per cent.

ACTION OF CHLORINE ON SHALES—Chlorine, bromine, and iodine were found to be absorbed by different coals, showing the presence in them of different proportions of compounds containing unsaturated groupings.[27] When lignite is treated with chlorine or bromine without external heating, the temperature increases to 90° to 100° C.[28] If this reaction product is extracted with carbon disulfide, a halogen-containing resinous substance is obtained. Cross and Bevan[29] have shown that coal is attacked by chlorine with the production of a chlorinated derivative similar to that previously obtained by them from lignified tissue. A shale oil obtained by distillation often contains 50 to 75 per cent of "unsaturates;" so these chlorination experiments were performed to see if the unsaturation is present in the organic content of the shale, or if it is produced by decomposition, and to see if it is possible to obtain less complicated chlorine products than those obtained with sulfuryl chloride.

Colorado shale was suspended in carbon tetrachloride and chlorine gas was passed through the solution for 36 hrs. The solution was filtered through an alundum crucible, and the residue dried and weighed. The increase in weight after this chlorine treatment was 0.59 per cent. This same sample of shale was then extracted with absolute alcohol in a Soxhlet extraction apparatus until the siphoning liquid was colorless. The absolute alcohol extracted from the chlorinated shale 6.23 per cent, calculated on the weight of the original shale. Absolute alcohol extracts 1.43 per cent from this shale before chlorination.

California shale, treated with chlorine in a carbon tetrachloride suspension for 24 hrs., filtered, and dried, increased in weight 6.5 per cent. This sample was also extracted with absolute alcohol. The loss in weight by this extraction was 26.8 per cent. This shale after extraction with absolute alcohol and drying was again suspended in carbon tetrachloride and rechlorinated. It was found that the shale increased in weight 8.28 per cent by this second chlorination. The shale was dried and again extracted with absolute alcohol until the extraction was complete. The alcohol dissolved 14.5 per cent of soluble matter from the rechlorinated shale. The solubility of this California shale in absolute alcohol before chlorination was 6.9 per cent, while its solubility in this solvent after two chlorine treatments was 41.5 per cent.

The organic constituent of shale, kerogen, is highly unsaturated, as evidenced by the increase in weight on chlorination and by the high chlorine content of the product resulting from its treatment with sulfuryl chloride. This unsaturation is present in the shale before it has undergone any heat treatment other than drying at 104° C. In the distilled oil itself unsaturation is not caused by the heating during distillation, as it has been shown that heating and cracking of the oil result in *higher* rather than *lower* saturation.

CONCLUSIONS

Different oil shales give different products under similar treatment. The commercial extraction of such shales by solvents is not feasible. The organic content of the shales studied is highly unsaturated. Pyrolytic decomposition at atmospheric pressure is accompanied by a marked decrease in the unsaturates. The retorting of each shale is a separate problem. The problem of refining of the oils begins with the retorting of the shales.

BIBLIOGRAPHY

1—Gavin and Sharp, "Some Physical and Chemical Data on Colorado Oil Shale," *Bur. Mines, Report* **2152** (1920).

2—Fisher, "Laboratory Manual of Organic Chemistry," J. Wiley & Sons, Inc., New York, **1920**, p. 217.

3—Sherman, "Organic Analysis," Macmillan Co., New York, **1919**, p. 291.
4—Sadtler, *J. Am. Chem. Soc.*, **27** (1904), 1188.
5—Robertson, *Proc. Royal Soc. Edinburgh*, **34** (1914), 190.
6—Winchester, "Oil Shales of Northwestern Colorado," *U. S. Geol. Survey, Bull.* **641F**, 161.
7—*U. S. Geol. Survey, Professional Paper* **48.**
8—Sainte-Claire-Deville, *Compt. rend.*, **66** (1868), 442.
9—Peckham, *J. Soc. Chem. Ind.*, **16** (1897), 727.
10—Groves and Thorp, *Chem. Tech.*, **1** (1917), 55.
11—Botkin, *Chem. Met. Eng.*, **26** (1922), 398.
12—McKee and E. E. Lyder, THIS JOURNAL, **13** (1921), 613.
13—Hollings and Cobb, *J. Chem. Soc. (London)*, **107** (1915), 1106.
14—Gavin, "Analytical Distillations of Typical Shale Oils," *Bur. Mines, Report* **2332** (1922).
15—George, "Oil Shales of Colorado," *Colorado Geol. Survey, Bull.* **25** (1921).
16—Redwood, "Treatise on Mineral Oils and Their By-products," p. 52.
17—Lenher, *J. Am. Chem. Soc.*, **43** (1921), 33.
18—Franks, "Studies of Colorado Shale Oils," *Colorado School of Mines Quarterly*, **16** (1921), 73.
19—Lewes, *Progressive Age*, **29** (1911), 1030.
20—*U. S. Geol. Survey, Bull.* **641,** 148.
21—Engler, "Das Erdol," **1** (1917), 35.
22—Vignon, *Compt. rend.*, **158** (1914), 1421.
23—Bone, "Coal and Its Scientific Uses," London, **1918**, p. 82.
24—Fischer and Gludd, *Ber.*, **49** (1916), 1469.
25—Dunans, *J. Chem. Soc. (London)*, **121** (1922), 44.
26—Badische Co., *J. Soc. Chem. Ind.*, **31** (1912), 151.
27—Hart, *Chem.-Ztg.*, **30** (1906), 1204.
28—German Patent 313,875 (1918).
29—Cross and Bevan, *Phil. Mag.*, **5**, Sect. 13, 328.
30—Gavin and Aydelotte, "Solubility of Oil Shales in Solvents for Petroleum," *Bur. Mines, Report* **2313** (1922).

A Laboratory Fractionating Column[1,2]

By H. T. Clarke and E. J. Rahrs

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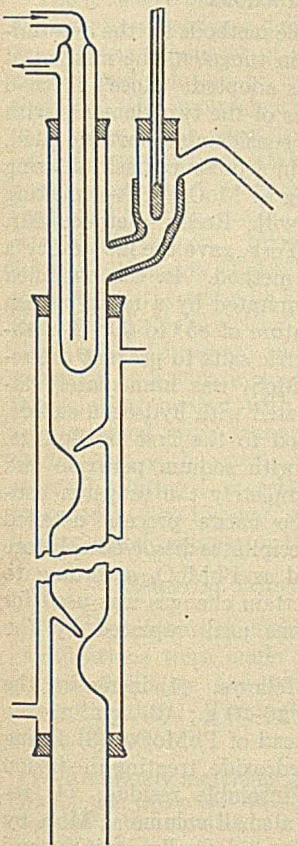
THE PRINCIPAL desiderata for a laboratory fractionating column are, after efficiency, simplicity of construction, strength, and absence of movable parts. The column here described, while undoubtedly less efficient than one constructed with wire-gauze plates, has been found satisfactory in the remaining respects; and since metals are entirely absent, it is suitable for the fractionation of corrosive liquids.



The column consists of a Pyrex tube 90 cm. in length and 20 mm. in internal diameter. Beginning 15 cm. from the upper end a series of semi-bulbs (25 mm. longitudinal diameter, 10 mm. transverse diameter, and 12 mm. depth) are sucked in, and points sloping downward from the opposite side of the tube are poked in (by means of the butt end of a small file or the "lead" of a pencil) to within about 1 mm. of the upper part of the convex surface of each bulb. Below every set of bulb and point, and as near as possible to it, is placed a similar set arranged at an angle 90 degrees on the periphery of the tube; in this way every fourth set occupies a corresponding position. This series is continued until finally 10 cm. of the unaltered tube remain at the lower end. At 8 cm. from the upper end a side arm is placed, similar to that of a Claisen distilling flask; the delivery tube, situated at the mid-point of its vertical portion, is so bent as first to ascend for a short distance before descending to the condenser. This side arm, in which is fitted the thermometer, is 15 mm. in internal diameter, and may profitably be lagged with asbestos over its lower portion, in order to minimize errors in temperature readings due to radiation from the bulb of the thermometer. At the top of the tube forming the column is stoppered a Pyrex tube 16 cm. in length and 15 mm. in external diameter, through which cold water can be passed. The entire length of the column below the side arm to within 8 cm. of the lower end is jacketed with a stout glass tube 30 mm. in internal diameter, tubulated at top and bottom, and secured with India-rubber stoppers.

In fractionating, distillation is carried out at the usual rate of one drop of condensate for every 3 to 5 sec., the size of the flame and the distance to which the water-cooled tube projects with the column below the side arm being so regulated that condensed liquid returns to the distillation flask 10 to 15 times as rapidly as it collects in the receiver.[3] For liquids of high boiling point the cooling tube may have to be withdrawn until only its lower end is level with the side arm, while for those of low boiling point, not only will it be necessary to expose its maximum length to the vapor but to pass a downward current of cold air at a regulated rate through the jacket. In fact, for very low-boiling liquids, such as acetaldehyde, it is advantageous to jacket the column with water at a suitable temperature. For liquids boiling above 70° C. the tubulations should be closed, so that the jacket acts as a heat insulator.

The column has been found to act satisfactorily in fractional distillation under reduced pressure without material modification. In such an operation it is well to dispense with a capillary tube, if possible, in order to avoid the entrainment of vapors by the gas thereby admitted.

As an example of the operation of the column the following table shows the results obtained on distilling a mixture of 1000 cc. each of commercial benzene and toluene from a 3-liter flask:

RANGE ° C.	VOLUME Cc.	TIME
72–81	15	5 min.
81–83	455	6 hrs. 30 min.
83–85	180	2 hrs. 45 min.
85–88	240	3 hrs. 40 min.
88–91	90	55 min.
91–95	185	3 hrs. 15 min.
95–100	95	1 hr. 45 min.
100–105	95	1 hr.
105–109	185	2 hrs. 55 min.
109–110	400	25 min.
Residue	40	

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[1] Received January 10, 1923.

[2] Communication No. 167 from the Research Laboratory, Eastman Kodak Company.

[3] The authors are greatly indebted to Prof. W. K. Lewis for drawing their attention to the principle of refluxing from the top of the column.

Determination of Small Quantities of Molybdenum in Tungsten[1]

By Walker J. King

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In this article the discoloring effect of molybdenum in tungsten filament wire is discussed. The limitations of gravimetric methods for small quantities of molybdenum are explained. A new method for the separation and colorimetric estimation of small quantities of molybdenum in tungsten is described. The present method utilizes the property of reduced molybdenum to form a blood-red compound of molybdenum sulfocyanate with a sulfocyanate salt. Ether is used as a medium for extracting the molybdenum sulfocyanate and colorimetrically estimating the quantity present. A special colorimeter, a modification of the Campbell and Hurley colorimeter, has been developed for use with the more volatile ether solution. The method has the following advantages: (a) None of the elements usually associated with tungsten ores interfere with the method. (b) The method is adaptable to the detection and accurate determination of very small amounts of molybdenum. (c) The time required for a single determination is less than two hours, or less than one-fourth the time of the usual gravimetric processes.

A special procedure for analyzing tungsten which is very low in molybdenum is described. Limitations of the colorimetric method are presented.

THE presence of small quantities of molybdenum in tungsten is important when the latter is used in filament wire for incandescent lamps. Tungsten filament wire made from carefully purified oxide usually contains about 0.01 to 0.05 per cent molybdenum. With increasing contamination of tungsten by molybdenum above 0.05 per cent there is a greater tendency of the latter to evaporate from the hot filament and deposit as a dark discoloration upon the walls of the bulb, thereby lowering the operating efficiency of the lamp. Most metals or compounds having higher vapor pressures than tungsten evaporate when present in the hot filament, but only the metals are likely to cause objectionable discoloration. When the quantities of impurities are below definite limits, undesirable deposition may be largely prevented. In the vacuum type of lamp chemicals are introduced in such a form that they combine with the metallic vapors to form colorless compounds or in some manner prevent discoloration, while in the gas-filled lamp the shape of the bulb is designed to localize the deposit in the neck.

The metals reducible by hydrogen contaminating crude tungstic acid, such as iron, copper, and tin, along with the oxides or salts of manganese, calcium, silicon, aluminium, tantalum, columbium, and the alkali metals, may be separated from tungsten by rather simple chemical purification processes or reduced to such small limits that no harm will be done. In addition to chemical purification, tungsten is purified after reduction by heat treatment at high temperatures, about 150° to 200° C. below the melting point of pure tungsten. Most impurities left in tungsten at this point, metals and nonmetals alike, are volatilized in the order of their vapor pressures, those possessing the lowest vapor pressures, such as molybdenum[1,*] and thorium dioxide, volatilize so slowly that the quantities removed by the process are negligible.

Experience has shown that crude tungstic acid made from ores and concentrates containing 0.01 per cent molybdenum or over when purified will contain a considerable portion of the molybdenum originally present. This fact coupled with our present knowledge that all tungsten ores contain molybdenum would furnish strong evidence that no filament wire is entirely free from it. From the results of over three hundred analyses of tungsten concentrates, powders, and wire, made by the writer, it was found that no material except special, purified oxide contained less than 0.01 per cent molybdenum. Smith and his co-workers[2] in their numerous works on tungsten and molybdenum recognized the distribution of molybdenum in tungsten ores, and have developed methods for separating traces of molybdenum from tungsten with the object of obtaining a suitable material for atomic-weight determinations. The purpose of the analytical work in this paper was to fix the allowable limits of molybdenum contamination of tungsten filament wire by the accurate analysis of small quantities of molybdenum in the presence of large amounts of tungsten.

Gravimetric Methods

After an examination of available methods for the determination of traces of molybdenum in tungsten, the method of Rose as described by Mellor[3] was adopted. Rose's method consists in treating the alkali salts of the two elements with an excess of sulfuric acid and considerable tartaric acid, saturating with hydrogen sulfide in a pressure flask, filtering the MoS_3, igniting, and weighing as MoO_3. After making some preliminary experiments with Rose's method, Mr. Smoot, of Ledoux and Co., New York, gave the laboratory a procedure for improving Rose's method. In the modified procedure molybdenum was precipitated by a rapid stream of hydrogen sulfide at a temperature of 85° to 90° C. without pressure in the presence of ferric salts to prevent the reduction of molybdenum. The MoS_3 was immediately filtered on asbestos, the filtrate treated with hydrogen sulfide, the precipitate filtered and united to the first precipitate, and the two dissolved directly with sodium peroxide and water. In order to separate completely the tungsten contaminating the molybdenum the entire process detailed above was repeated, the sulfide precipitates dissolved as before and the molybdenum determined as $PbMoO_4$ according to Ibbotson.[4] This method with certain changes was used for a large number of determinations until replaced by the colorimetric method.

The changes referred to are as follows: (1) increasing the size of the sample from 3-5 g. to 10-20 g.; (2) igniting the MoS_3 and weighing as MoO_3 instead of $PbMoO_4$; (3) fusing the weighed MoO_3 with sodium hydroxide, treating the fusion with water and filtering off the insoluble residue; (4) reprecipitating the molybdenum in a small volume as MoS_3 by the same procedure given above, and finally igniting and weighing as MoO_3. The two weighings were regarded as separate determinations and are designated in this article as Methods A and B, respectively. The caustic fusion eliminated many impurities contaminating the first MoO_3 residue and gave the most concordant results among the gravimetric methods mentioned. The method was accurate within 0.01 per cent when the quantity of molybdenum was

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[1] Received September 8, 1922.

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

within the limits 0.03 and 0.1 per cent, but wholly unreliable with amounts less than 0.02 per cent. This is shown by referring to the gravimetric analyses (Table I) of tungstic oxide, Samples C and D given under Method B. Sample C prepared by the method of Smith and Exner was exceptionally pure. Sample D was low in molybdenum since it was obtained from the recovered tungstic acid of the molybdenum sulfide precipitate, from which the original starting material analyzed less than 0.03 per cent. Both samples analyzed a higher per cent of molybdenum than their method of preparation warranted or their behavior during analysis indicated. All previous samples of tungsten gave rather bulky sulfide precipitates and a characteristic blue color of reduced molybdenum during the hydrogen sulfide treatment readily destroyed by ferric salts. Samples C and D gave small sulfide precipitates and no blue color. Further experiments were made upon the weighed MoO_3 residues of both samples by treating with hydrochloric acid gas at 250° C. according to Pechard.[5] Sample D gave no appreciable loss while C gave a loss less than one-half the original weight. The volatilization tests showed conclusively that the MoO_3 contained impurities other than molybdenum and that the correct amount of molybdenum was far less than the weighed residue indicated. With the limitations of the gravimetric methods fixed it was evident that a colorimetric method might be used advantageously to give the required sensitivity.

MOLYBDENUM SULFOCYANATE COLOR TEST

The sensitive blood-red color of molybdenum sulfocyanate has long been used as a delicate test for molybdenum. A. D. Braun,[6] the originator of the test, employed zinc in hydrochloric acid solution to reduce the molybdenum, and concentrated the molybdenum sulfocyanate by shaking out with ether. The exact composition of molybdenum sulfocyanate has not been established with certainty. Mass and Sand[7] and their contemporary workers, Roenheim and Garfunkel,[8] have made extensive studies of this related class of compounds. The value of the sulfocyanate color test for the estimation of small quantities of molybdenum was suggested to the writer by L. Leley of the Philips' Lamp Works, Holland. Leley's method required that a solution of the alkali salts of tungsten and molybdenum be treated with an excess of hydrochloric acid in the presence of tartaric acid, the solution treated with sulfocyanate salt, the molybdic acid reduced with stannous chloride, and the red color shaken out with ether. Without transferring, the colored ethereal solution is matched against molybdenum standards prepared in like manner, due attention being paid to maintaining equal volumes of the solutions.

ESSENTIAL POINTS OF THE NEW METHOD

With the essential principles of Leley's method in mind, modifications were made in the new method which allow greater flexibility and refinement than is possible in the original method. The important features of the new method are as follows:

1—Accurately matching the color of the ethereal solution containing the extracted molybdenum, against a similar solution containing the standard by means of a special colorimeter.

2—Regulating the size of the sample to obtain the proper quantity of color.

3—Employing a shaking flask with siphon for shaking out with ether and transferring the ethereal solution to the colorimeter.

4—Standardizing the source of light for the colorimeter with a 500-watt "Trutint" daylight unit.

5—Fixing the concentrations of the constituents in the solution containing the sample within the limits obtainable through the accurate and systematic addition of the reagents and the maintenance of uniform conditions.

Other details necessary for trustworthy results are covered elsewhere in this article. The colorimetric apparatus and shaking flask, with accompanying sketches, are described below and are followed by a description of the present method of analysis.

APPARATUS

COLORIMETER—The special colorimeter which was used in all colorimetric analysis is shown in Fig. 1. It is essentially the type described by Campbell and Hurley,[9] in which one-half of a circular field of light from a standard solution is observed in juxtaposition with the opposite half of the image of the field of light from an unknown solution, whose color is to be matched. The present apparatus is larger than the Campbell and Hurley apparatus and has certain additions which permit easier manipulation and greater flexibility.

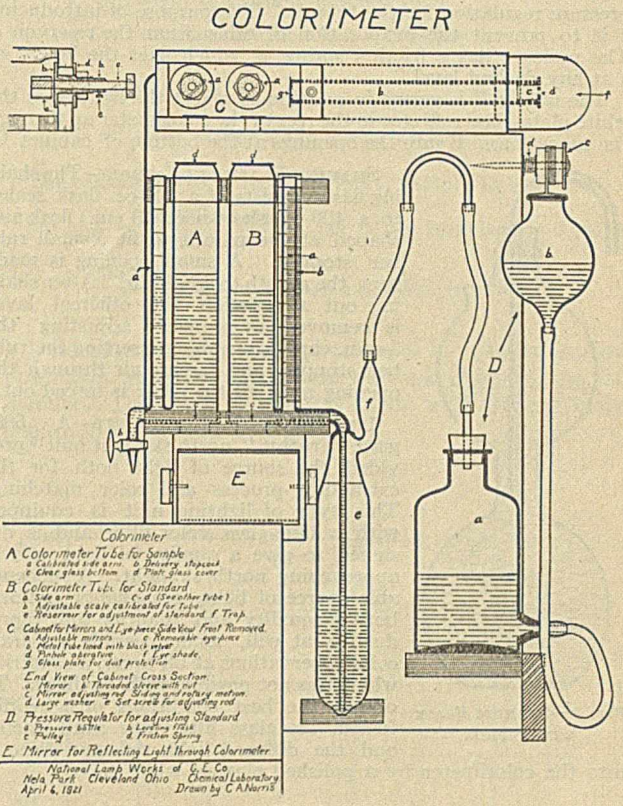

FIG. 1

The colorimeter tubes A and B with attached reservoir, *e*, are made of Pyrex glass. They have an approximate capacity of 250 cc., an inside diameter of 4 cm., and an approximate height of 23 cm. The bottoms of the tubes are clear glass made by sealing pieces of large flasks on the bottoms, which have been previously ground to a plane. The tops of the tubes are ground level so that the plate-glass covers fit snugly over the tops. Tube B is calibrated to contain 250 cc. and marked on side-arm *a*. A separate scale equal to the length of side-arm *a* to mark, and graduated in 100 equal divisions, is fastened behind *a*. The use of a separate scale with a white background and black markings facilitates rapid and accurate readings. The length of the side-arm of the tube A is equal to the length of side-arm of tube B. Side-arm *a* is divided into 10 equal divisions and etched on the glass. Fractional readings of the large divisions are made with a movable glass sleeve fitted with a paper scale equal to the length of a large division and subdivided into 10 equal divisions. This device saves extra calibrating and provides accurate readings from 1 to 100. No correction for the taper of the tube is necessary if the diameters of the tubes are reasonably uniform and the inside diameters of their opposite ends do not vary more than 0.4 mm. The correction for the difference in the volumes of the tubes is equal to volume of tube A (to mark) divided by volume of tube B (to mark). The volume of reservoir *e* (to mark) is equal to the volume of tube B and side-arm to calibrated mark. Trap *f* prevents the loss of ether solution while mixing the standard.

The cabinet C is a dustproof box inclosing two mirrors and telescope. The mirrors are supported with a mechanical device to give three adjustments: (1) rotary movement, (2) sliding movement parallel to axis, (3) displacement movement relative to the position of the telescope and the direction of the light from the tubes. Glass plates covering the openings in the bottom of the box transmit light from tubes A and B to the mirrors. The tube B is 20 cm. long, 1.2 cm. in diameter, and is lined with black velvet to prevent disturbing reflections. The pinhole aperture *d* in the removable eyepiece *c* is 1 mm. in diameter while the opening *g* in the opposite end of the telescope is 4 mm. An eyeshade, *f*, is attached to the end of the telescope, which cuts off light from the outside and permits the observer to keep the left eye open while making observations.

The height of the standard solution in B is controlled by a pressure regulator, D. The pressure bottle *a* has a capacity of 500 cc. and is half filled with water saturated with ether. By turning the pulley *c* the height of the leveling flask *b* regulates the amount of water and air in *a*, which automatically provides pressure regulation for the tube B. The purpose of introducing *a* is to prevent the evaporation of ether from the reservoir *e*. The pulley *c* has a friction spring, *d*, which fixes the height of *b* at any desired level.

The mirror E is swung in position to reflect the light from the white plate-glass reflector in the rear of the colorimeter up through the tubes A and B into the openings at the bottom of cabinet C.

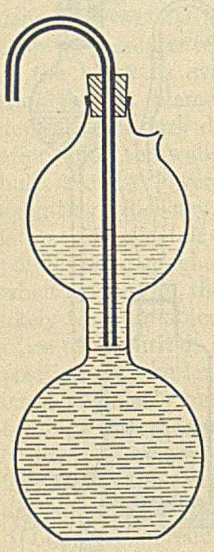

FIG. 2—SHAKING FLASK WITH SIPHON

Shaking Flask and Siphon—The shaking flask consists of a 300-cc. flask sealed to a 400-cc. short-neck (3 cm.) flask and shaped at the mouth to fit a small rubber stopper. A small opening is made near the mouth to admit air. After shaking out a solution the ethereal layer is removed by properly adjusting the 3-mm. capillary siphon, inserting the rubber stopper, and forcing air through the opening until all the ether is forced out.

Illuminating Equipment—A 500-watt "Trutint," north skylight unit[10] provided the source of light both for the extraction process and color matching. This type of lighting unit is equipped with a blue-glass color filter and is designed to give a quality of light closely approaching north skylight. A dependable source of light, reasonably uniform both in quality and quantity and reproducible at will, made possible accurate color observations at all times, a condition which was not possible with daylight. To obtain the best conditions of light diffusion, the glass filter was sand-blasted and the diffused light reflected directly into the colorimeter by a polished plate of white glass.

REAGENTS

Sodium Hydroxide Solution—A solution of NaOH is prepared by dissolving 20 g. C. P. NaOH (electrolytic) in 600 cc. of distilled water, diluting to 1 liter, and allowing to stand until the iron precipitate settles.

Tartaric Acid Solution—This solution is made by dissolving 600 g. C. P. tartaric acid in 700 cc. of boiling water, cooling, and diluting to 1 liter.

Stannous Chloride Solution—Freshly prepared C. P. $SnCl_2$ is used. It is prepared by dissolving 150 g. $SnCl_2.2H_2O$ in 100 cc. concentrated HCl and 250 cc. distilled water. Solution should be clear when prepared, and protected from oxidation.

Ether—The ether used for the extraction should be tested with potassium iodide and starch. If a blue color develops, the ether should be shaken with a 10 per cent solution of sodium thiosulfate and redistilled. A blank test should give no color after several hours' standing. The precaution of redistilling has never been found necessary.

Standard Sodium Molybdate Solution—Pure molybdic trioxide is prepared by igniting C. P. $(NH_4)_2MoO_4$ to MoO_3 and resubliming in silica or platinum dishes. The sublimed oxide is dissolved in a small excess of a 10 per cent NaOH solution, neutralized with dilute HCl_3 and then made alkaline to litmus. The solution above is diluted to approximately 0.1 *N*, after which the molybdenum is accurately determined by precipitating and weighing as $PbMoO_4$. A portion of this solution is diluted so that 1 cc. will contain 0.05 mg. molybdenum.

METHOD OF ANALYSIS

The colorimetric method of analysis has given satisfactory results on a variety of samples, and it is believed that with reasonable care the method as outlined will give reproducible results.

Solution of Sample—Tungsten and molybdenum must be in the form of their alkali salts. Tungsten metal is oxidized in the wet way. Weigh 4 g. of metal into a 200-cc. platinum dish, cover with 30 to 40 cc. of hydrofluoric acid, and add drop by drop concentrated or dilute nitric acid, as the violence of the reaction indicates, until the tungsten is dissolved. Evaporate the solution nearly to dryness, add concentrated nitric acid, and evaporate to dryness. Repeat acid treatment three times, evaporating to dryness each time. Ignite at a low temperature not to exceed 550° C. Ignition of all tungsten samples is necessary to eliminate organic matter and to break up the tungstic acid hydrates and complexes.

Tungstic acid is treated three times with concentrated nitric acid, evaporated to dryness, and ignited. Tungstates soluble in caustic are treated directly. Boil a 5-g. sample, after treatment as directed above, with 25 cc. sodium hydroxide solution (35 cc. for sample over 12 g.) until solution is complete. To the solution add 75 cc. hot water and boil. No appreciable residue of tungsten should remain. Fusion of sample of tungstic oxide with sodium and potassium carbonates is apt to cause a slight loss of molybdenum. This will be shown by referring to the analyses of Samples A and B (Table I). Filter the solution in a Gooch crucible on an asbestos mat, wash with 5 per cent sodium chloride solution, and transfer to a 250-cc. calibrated flask and dilute to mark.

Preliminary Treatment—Transfer a 75-cc. aliquot to a 500-cc. Erlenmeyer flask, and neutralize with dilute hydrochloric acid (1:10) using neutral litmus paper. At no time should a precipitate of tungstic acid be allowed to form. When the solution is slightly acid immediately add tartaric acid solution proportionate to the amount of tungsten present, using 20 cc. of solution for every 6 g. of WO_3 or fraction. Transfer to a 400-cc. shaking flask, add 25 cc. dilute hydrochloric acid (1:5) and 5 cc. of a 30 per cent potassium sulfocyanate solution, and dilute to approximately 350 cc. Cool to 5° or 10° C.

Extraction with Ether—To the cooled solution add 20 cc. of stannous chloride solution. Thorough mixing is best done by blowing forcibly into the pipet and directing the emerging stream into the solution. Immediately add 90 cc. ether and sufficient water to bring the water meniscus up to the bottom of the constriction when the two layers are saturated with each other. Insert a cork in the flask, hold the finger over the small opening at the top, and shake the flask vigorously one-half minute. Cool the flask in ice water until the ether layer separates. Adjust the siphon and transfer the ether to color tube A. Add a 50-cc. portion of ether to the shaking flask, and repeat the extraction as long as any color is removed. When aqueous solutions turn slightly blue after the addition of stannous chloride some of the molybdenum stays in a form which cannot be shaken out. In some cases over 20 per cent of the molybdenum remains undetected. This is probably due to the formation of hydrated or complex compounds of tungsten when precipitated metatungstic acid or insoluble residues are redissolved. The resolution of the fine precipitate by the addition of tartaric acid is not sufficient to prevent the formation of the blue color. In several cases a poor quality of tartaric acid has been known to cause a blue color, but this can be detected by a blank test. When an appreciable quantity of blue color has formed it has been considered a safer plan to discard the determination and start a new one.

Standard Ether Solution—Standard ether solution is prepared by adding molybdenum to specially purified tungsten and shaking out in the regular way. A suitable quality of purified tungsten very low in molybdenum may be obtained by recovering and purifying the tungstic acid from the aqueous solutions of the ether extraction. Purification is best made by ammonium paratungstate precipitation followed by nitric acid digestion. Sample E (Table I) was prepared in this manner. Weigh 3 g. of ignited oxide into a 500-cc. flask, add 10 cc. of a standard molybdenum solution, equivalent to 0.5 mg. molybdenum and follow the procedure to the extraction with ether. After shaking the solution out with ether, transfer the ether solution to tube B and continue extracting with 50-cc. portions until the reservoir *e* is filled to mark. Mix the standard by blowing air through the reservoir replacing the evaporated ether if necessary, using only the ether which has been shaken out. The volume of the reservoir *e* filled to mark is equal to 100 scale divisions. Loss of ether is largely prevented by covering the tops of the color tubes.

Matching of Colors—The standard solution in tube B is matched against the unknown solution in tube A. To accomplish this, disconnect the rubber tubing from the trap *f*, fill the reservoir *e* to the mark, and lower the leveling reservoir *b* until the pressure bottle *a* is empty. Connect the rubber tubing again to the trap *f*. With the light properly adjusted behind the colorimeter, the mirror E is turned so that uniform illumination is provided in both tubes. Manipulate pulley so that the height of the solution in B is regulated to give equal color densities in both tubes, and note reading on the scale. With a little practice readings can be duplicated within one or two scale divisions. If the color reading is over 90 divisions, fill A to a convenient mark, mix and drain off sufficient ether to permit the readings to fall between 70 and 90 scale divisions. The volume of the ether aliquot may be accurately measured by using the calibrated sleeve described under "Colorimeter." When it is necessary to remove more than half of the ether aliquot, a second but smaller sample is taken and sufficient purified tungstic acid, from which the standard was prepared, added to make a total of 1.5 to 3 g. of WO_3. If the color reading is less than 50 divisions a proportionally larger sample is taken so that an approximate reading of 75 divisions is obtained. However, the quantity of tungstic acid used in making the standard need not be increased except where great refinement is desired. It will be seen by reference to Table II that the first determination containing no tungsten showed the largest error of the entire set of analyses. The next largest error is on the determination containing 4 g. of tungstic oxide. The per cent error on the total molybdenum added is less than 5, which can be classed within the limits of experimental errors. The results indicate that quantities of tungstic oxide between 1 and 12 g. would have little or no effect upon the quantity of molybdenum extracted.

Calculation of Molybdenum—The quantity of molybdenum in parts per million is as follows:

$$\frac{\text{Mg. of Mo} \times \text{factor A} \times \text{factor B} \times \text{color reading} \times 10}{\text{G. sample} \times \text{aliquot taken}} = \text{P.p.m. Mo}$$

Mg. Mo in standard = Mg. Mo added plus Mo in sample

$$\text{Factor A} = \frac{\text{Area of cross section of tube A}}{\text{Area of cross section of tube B}}$$

$$\text{Factor B} = \frac{\text{Divisions read in tube A before taking aliquot}}{\text{Divisions read in tube A after taking aliquot}}$$

Analysis of Tungsten with 5 P. P. M. Molybdenum—In an attempt to make an accurate analysis of Sample E (Table I), which was believed to contain a very small quantity of molybdenum, the following scheme was adopted: A 16.5-g. sample of E was carried through the regular procedure and the ether extractions transferred to tube A. Another 16.5-g. sample of E was treated in like manner, except that 0.25 mg. of molybdenum was added to the sample at the beginning of the procedure and the ethereal solution used as a standard. The amount of molybdenum in milligrams is determined as follows:

Let X = Mo in A
a = Mo added to B (standard)
$X + a$ = Total Mo in B filled to mark
b = Total height of B filled to mark
c = Height of B when matched to A
$\frac{c}{b}$ = Fractional height when B matches A

$$X = (X + a) \times \frac{c}{b}$$

$$X = \frac{ac}{b - c} = \text{mg. Mo in A when } a \text{ is in mg.}$$

The calculation for Determination 1, Sample E, is:

$$\text{Mo in A} = \frac{26 \times 0.25 \text{ mg.}}{100 - 26} = \text{mg. Mo in Sample E} = 0.087 \text{ mg.}$$

$$\frac{0.087}{16.5} \times 1000 = 5.3 \text{ p. p. m. molybdenum}$$

Determination 2 was a duplication of 1. Determination 3 was made with a new standard and was made in the same manner. Determination 4 was made with 0.5 mg. molybdenum in the standard.

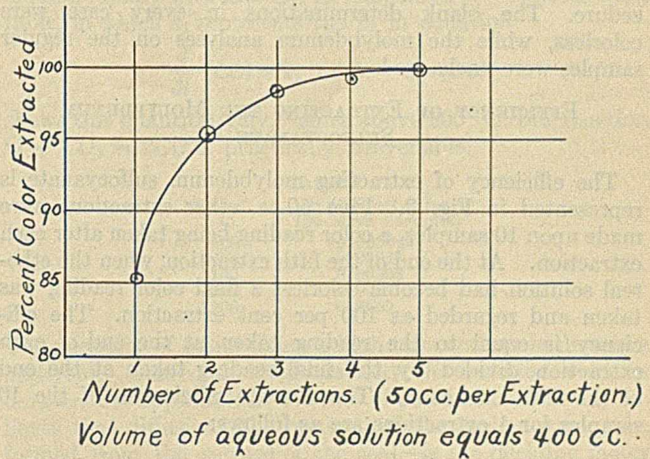

Fig. 3—Efficiency of Extraction of Molybdenum Color

In preparing a reliable procedure for colorimetric analysis of molybdenum, the importance of adopting uniform conditions cannot be too strongly emphasized. This applies especially to the quality of reagents and the conditions effecting their concentration. New reagents should be tested by running blank determinations. After the addition of the sulfocyanate an analysis should be carried through promptly. Turbidity or precipitation occurring in either solution prevents the complete extraction of molybdenum, or makes accurate color matching impossible. Although standard solutions have stood over a week without measurable deterioration, it is probably better to prepare a fresh solution each day and check against a standard sample of tungstic acid. The stability of the solutions is probably due to the reducing action of stannous chloride held in solution by ether.[11]

Table I—Comparative Analyses of Mo in Samples of WO_3

Sample	Detn. No.	Colorimetric				Gravimetric				
		G. WO_3	Color Reading	Mo Found		G. WO_3	Method A		Method B	
				Mg.	P. p. m.		Mg.	P. p. m.	Mg.	P. p. m.
A.........	1	1.2	74	0.375	310	9.2	5.00	540	2.80	305
	2	1.5	87	0.440^a	295	9.2	6.10	660	2.70	295
	3	1.4	91	0.460	330	9.2	4.35	475	2.80	305
	4	1.4	95	0.480	340	9.2	3.70	400	3.70	400
	5	1.4	90	0.460	330	9.2	4.35	475	2.30	250
	6	1.3	82	0.420	320	9.2	4.15	450	2.70	295
	Average				321	9.2	4.61	500	2.84	308
B.........	1	1.5	43	0.220	147	9.2	3.25	355	1.80	195
	2	2.5	79	0.400	160	9.2	3.00	325	1.50	165
	3	3.0	83	0.425^a	142	18.4	7.40	400	3.80	205
	4	2.6	76	0.390	150	18.4	8.70	475	4.60	250
	5	2.8	85	0.435	155	18.4	5.25	285	3.00	165
	Average				151			368		195
C.........	1	1.2	12	0.061	51	8	2.60	325	1.00	125
	2	9.0	79	0.400	44	8	4.50	560	1.40	175
	3	7.2	68	0.345	48					
	Average				48		3.55	443	1.20	150
D.........	1	1.4	8	0.041	29.3	9.2	3.30	360	1.30	140
	2	8.3	48	0.244	29.6	18.4	4.70	255	1.85	100
	Average				29.5			308		120
E^b.........	1	16.5	26	0.088	5.3	Gravimetric separation with hydrogen sulfide made. No indication of the presence of Mo				
	2	16.5	24	0.079	4.8					
	3	17.0	30	0.107	6.3					
	4	17.0	16.5	0.097	5.7					
	Average				5.5					

[a] Slight loss from Na_2CO_3-K_2CO_3 fusion.
[b] Formula used to calculate per cent Mo.

Interfering Elements

None of the elements commonly associated with tungsten ores interfere with the molybdenum determination. The following elements were found not to interfere: iron, copper, manganese, nickel, cobalt, titanium, columbium, tantalum, uranium, chromium, vanadium, thorium, aluminium, phosphorus, calcium, arsenic, and silicon. Separate tests were made by adding a solution containing the element to a blank determination and to a regular tungsten determination, and completing the analysis according to the standard procedure. The blank determinations in every case were colorless, while the molybdenum analyses on the regular samples were unchanged.

Efficiency of Extracting the Molybdenum Sulfocyanate

The efficiency of extracting molybdenum sulfocyanate is represented in Fig. 3. Five 50-cc. ether extractions were made upon 10 samples, a color reading being taken after each extraction. At the end of the fifth extraction, when the ethereal solution had become colorless a final color reading was taken and regarded as 100 per cent extraction. The efficiency is equal to the reading taken at the end of each extraction divided by the final reading taken at the end of the fifth extraction. The average efficiencies of the 10 samples for 4 extractions are as follows:

Extraction	1	2	3	4	5
Average per cent efficiency	85.7	95.4	98.4	99.7	100.0
Color	Very strong	Light	Very light	Doubtful	None

Limitations of Method

An examination of the colorimetric analyses of Samples A, B, C, and D (Table I), containing 321, 151, 48, and 29 p. p. m. molybdenum, respectively, shows that the variation between the maximum and minimum value for each sample is less than 10 per cent of the total molybdenum present.

Table II—Determination of Mo with Variable Quantities of WO_3[a]

G. WO_3 Taken	Color Reading	Mo Found		Mo Added		Error-Mo Present	
		Mg.	P. p. m.	Mg.	P. p. m.	Mg.	P. p. m.
None	64	0.325	...	0.375	...	−0.050	...
1	74	0.376	374	0.380	380	−0.004	−6
2	75	0.381	190	0.385	193	−0.004	−3
3	77	0.391	130	0.390	130	+0.001	0
4	80	0.406	101	0.395	99	+0.011	+2
5	75	0.382	76	0.400	80	−0.018	−4
7	80	0.406	58	0.410	59	−0.004	−1
9	80	0.406	45	0.420	47	−0.014	−2
12	85	0.431	36	0.435	36	−0.004	0

[a] WO_3 Sample E (5 p. p. m. Mo). 100 divisions of scale = 0.508 mg. Mo.

An analysis containing no tungsten (Table II) analyzed approximately 85 per cent of the total molybdenum added, while the samples in the remainder of the series of analyses containing varying amounts of tungstic oxide from 1 to 12 g. analyze in every case over 95 per cent of the total molybdenum added.

A comparison of the gravimetric and colorimetric analyses (Table I) shows that the gravimetric method is unreliable for quantities of molybdenum in tungsten less than 300 p. p. m., while the colorimetric method is trustworthy for quantities of molybdenum as low as 10 p. p. m.

Table III—Determination of Variable Quantities of Mo in Equal Amounts of WO_3[a]

Analysis No.	Color Reading	Mo Found		Mo Added		Error-Mo Present	
		Mg.	P. p. m.	Mg.	P. p. m.	Mg.	P. p. m.
1	2±1	0.010±5	10±5	0.008	6	....	....
2	14.2	0.072	51	0.058	41	+0.014	+10
3	26.5	0.134	96	0.108	77	+0.026	+19
4	37.5	0.190	136	0.158	113	+0.032	+23
5	46.5	0.236	168	0.208	148	+0.028	+20
6	53.1	0.270	193	0.258	184	+0.012	+9
7	62.7	0.322	230	0.308	220	+0.014	+10
8	70.8	0.360	257	0.358	256	+0.002	+1
9	77.1	0.392	280	0.408	291	−0.016	−11
10	86.3	0.439	314	0.458	327	−0.019	−13

[a] WO_3 Sample E (5 p. p. m.). Sample taken equals 1.4 g. WO_3. 100 divisions of scale = 0.508 mg. Mo.

Note: Readings corrected for volume change of standard.

Errors of color matching are reduced to a minimum by adjusting the size of the sample so that a scale reading of 60 to 90 divisions is obtained. By referring to the analyses in Table III, it will be seen that the effect of low readings on the scale is to give high results.

Acknowledgment

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Bibliography

1—Langmuir and Makay, *Phys. Rev.*, **4** (1914), 377.
2—Smith and Exner, *Proc. Am. Phil. Soc.*, **43** (1904), 123; Marbaker, *J. Am. Chem. Soc.*, **37** (1915), 86.
3—Mellor, "Quantitative Inorganic Analysis," **1913**, p. 417.
4—Ibbotson, "The Chemical Analysis of Steel Works Materials," **1920**, p. 140.
5—Pechard, *Compt. rend.*, **114** (1891), 173.
6—Braun, *Z. anal. Chem.*, **6** (1867), 86.
7—Mass and Sand, *Ber.*, **41** (1908), 3367.
8—Roenheim and Garfunkel, *Ber.*, **41** (1908), 2386.
9—Campbell and Hurley, *J. Am. Chem. Soc.*, **33** (1911), 1112.
10—Supplied by Nela Specialties Division, Nela Park, Cleveland.
11—Seidell, "Solubilities of Inorganic and Organic Substances," **1911**, p. 140.

Producer Gas from Powdered Coal[1,2]

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The literature describes several attempts to make a satisfactory producer gas from powdered coal, but the process has not been extensively developed. The following article is a report of some experiments which were carried out to find the reason for this lack of development, and, if possible, to devise means for overcoming any difficulties which stood in the way.

IN generating electrical or mechanical power from coal through the use of steam, an over-all efficiency of about 18.5 per cent is the maximum obtained to date. This efficiency has been reached only by the extraordinary efforts exerted during the last two decades in the development of efficient steam-boiler and turbine practice. Compared with efforts in the development of efficient power through steam, relatively little attention has been paid to the production of power through the gas engine, although the theoretical operating efficiency of the gas engine at reasonable compression ratios is considerably higher than the theoretical efficiency of a condensing steam turbine, even at such pressures as 300 lbs. per sq. in. The lack of development in the production of power through producer gas may be attributed to the difficulty of generating a satisfactory gas, the chief disadvantages in the production of producer gas from bituminous coal, the only commercial coal to-day, being (1) dirty gas due to tar, (2) nonuniform composition of gas, and (3) lack of flexibility. The last two disadvantages are caused by the thick fuel bed required by the gas producer.

POWDERED COAL FOR GAS PRODUCERS

A scheme mentioned a number of times in the literature, which seems capable of eliminating these three disadvantages, is the burning of powdered coal with an insufficiency of air for complete combustion to carbon dioxide. Any tar formed would be decomposed by the high temperature, leaving a dry dust (ash) the only material to be removed. The ease of regulation in the feeding of coal and air would insure a constant gas composition, while the small amount of fuel in the "producer" hearth at any one time would insure flexibility in the handling of varying loads.

Several attempts to carry out such a process have been made. Latta[3] mentions a producer in operation which yielded a gas containing 23 to 27.5 per cent carbon monoxide. In Germany,[4] a producer using powdered anthracite-coal refuse was used to generate a gas having a composition of 17.6 to 24.2 per cent carbon monoxide. In the Marconnet[5] producer, a vertical-shaft type, a mixture of powdered coal and air is fed in at the bottom. Satisfactory results were obtained with powdered coals having an ash content from 5 to 10 per cent. Bourcoud[6] mentions several other types of powdered-coal-gas producers. He proposed a vertical type of producer in which the presence of powdered coal in the resulting gas would be minimized, and a long time of contact of powdered coal with gas effected by causing the flow of powdered-coal-gas stream to be alternately up and down through three vertical compartments in the producer.

In view of the remarks made in the literature, it is surprising that such an apparently promising field has not been developed more extensively. In order to obtain some idea as to the cause for the lack of development in this field, preliminary experiments[7,8] were made with the results noted below. Efforts were made to determine the most favorable conditions for the partial combustion (to carbon monoxide) of powdered coal.

PARTIAL COMBUSTION OF COAL

The combustion of coal with an amount of air insufficient for complete combustion to CO_2 may be divided into three stages—namely, (1) distillation of volatile matter, (2) combination of residual carbon with oxygen to form CO_2, and (3) reduction of the CO_2 to CO by the interaction of the CO_2 with the excess carbon.

The rate at which the first two reactions take place above 1000° C. is so rapid, compared to the third reaction, that the rate at which coal and air unite to form CO depends entirely on how fast the carbon reacts with the CO_2.

EFFECT OF TEMPERATURE

Rhead and Wheeler[9] found that the *equilibrium* ratio of $CO : CO_2$ in the equation $CO_2 + C = 2CO$ increased rapidly with temperature, so that at 800° C. the ratio of $CO : CO_2$ was 6.3 : 1, while at 1100° C. the ratio was about 500 : 1. The *rate* at which the reaction came to equilibrium also increased rapidly with increase in temperature. The following table, in which k_1 represents the k_1 in equation

$$\frac{d}{dt}(\mathrm{CO}) = k_1(\mathrm{CO_2}) - k_2\ (\mathrm{CO})^2,$$

shows this quantitatively,[10] since above 900° C. the reaction $C + CO_2 = 2CO$ is practically irreversible.

TABLE I

Temp. ° C.	k_1 (Corrected for 100-Mesh Particles)
900	0.000046
1000	0.00046
1100	0.00268
1200	0.0032
1300	0.0269

The necessity of maintaining a high temperature is therefore apparent. Bourcoud[6] considers that the reaction velocity data are not applicable in the case of powdered coal. He believes that diffusion—the removal of the carbon monoxide, formed from the surface of the coal—is the deciding factor which determines the rate of reaction. However, that this reaction is not controlled by diffusion may be deduced from the work of Kreisinger, Ovitz, and Augustine.[11]

EFFECT OF PREHEATING AIR

Under ordinary circumstances carbon and oxygen burn to CO_2 directly, and any CO formed comes from the subsequent reduction of CO_2 by carbon. Above 1000° C. there can be no appreciable amount of CO_2 present in contact with carbon after equilibrium has been attained. Carbon monoxide may be formed by burning the powdered coal with cold air and then reducing the CO_2 to CO by excess carbon; but conditions for the *immediate* formation of CO are more favorable

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[1] Presented before the Section of Gas and Fuel Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 34 from the Department of Chemical Engineering, M. I. T.

[3] "American Producer Gas Practice."

[4] Glaser, *Annalen für Gewerbe und Bauwesen*, **1909**, 111.

[5] *Génie civil*, **51** (1907), 22.

[6] *Chem. Met. Eng.*, **24** (1921), 600.

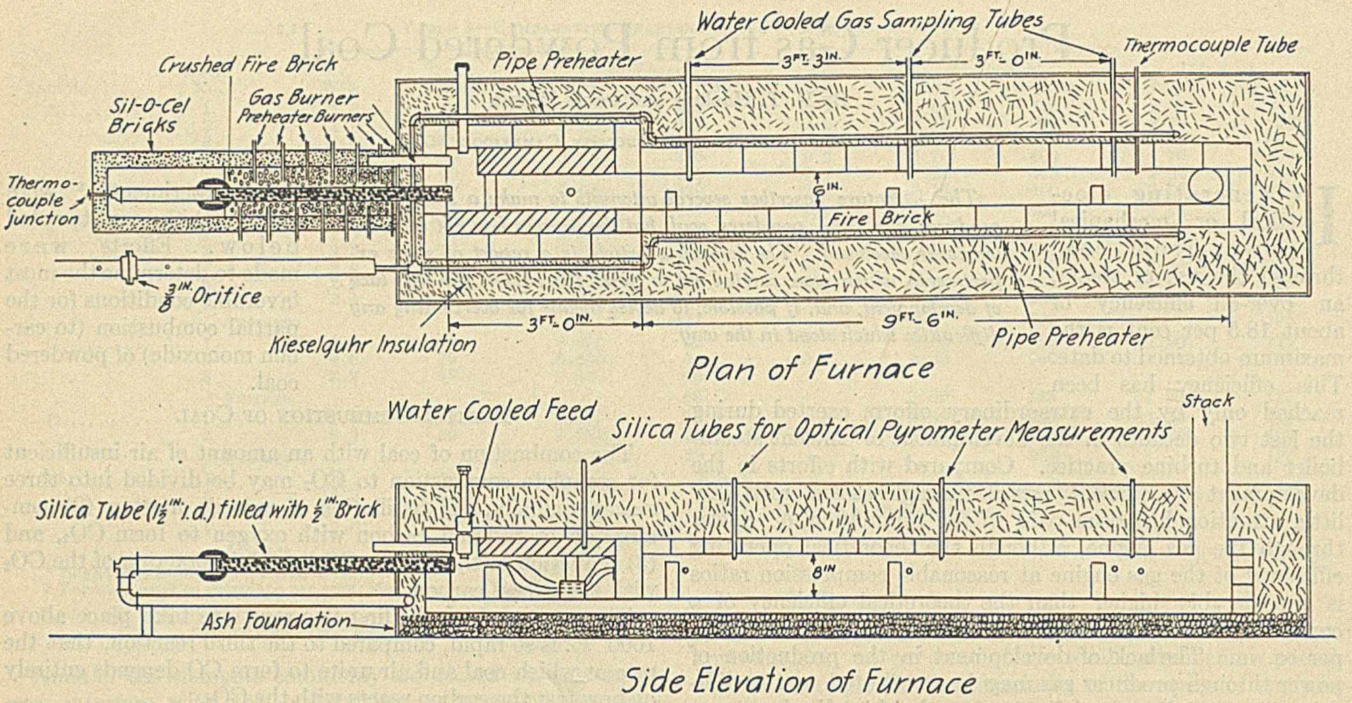
[7] Harris and Sanders, M.S., Chemical Engineering Thesis, M. I. T., **1921**.

[8] Canfield and Didisheim, M.S., Chemical Engineering Thesis, M. I. T., **1922**.

[9] *J. Chem. Soc. (London)*, **1921**.

[10] *Bur. Mines, Bull.* **7** (1911).

[11] *Ibid., Tech. Paper* **137**.



SKETCH OF FURNACE AND PREHEATER

NOTE: Cross-hatched portion shows section of combustion chamber bricked in to increase velocity of gases.

if the carbon is burned with air at a temperature already above the point where CO_2 can exist in appreciable quantities in contact with carbon. Therefore, it would seem desirable to preheat the air for combustion to 1000° C. or over, in order to reduce the time of contact or size of furnace required. Furthermore, the preheating of the air to this temperature would actually lower the temperature of the flame if carbon only burns to the equilibrium ratio of $CO : CO_2$ corresponding to the temperature of the entering air. Thus, the reaction would be hastened and the destructive action of the flame on fire brick minimized by preheating the air to about 1000° C.

TIME REQUIRED FOR REDUCTION

Calculation of the size of furnace required to reduce a given amount of CO_2 to CO by powdered coal shows the great effect reaction temperature has on the size of combustion chamber required. The general rate of reduction equation

$$\frac{d}{dt}(CO) = k_1 (CO_2) - k_2 (CO)^2 \qquad (1)$$

may be simplified by considering the speed of reversal negligible at the temperature in the furnace

$$\frac{dx}{dt} = k_1 \left[m - x\left(\frac{1+m}{2}\right)\right] \qquad (2)$$

Integrating,

$$t = \frac{2.3}{\left(\frac{1+m}{2}\right)k_1} \log \frac{1}{\left[m-\left(1+m\right)x\right]} + C \qquad (3)$$

where t = time in seconds
x = the fraction of CO at the time t
m = the fraction of CO_2 at the start of reduction
k_1 = the velocity constant for the reaction $C + CO_2 = 2CO$, as given in Table I
C = the constant of integration.

Using Equation 3, a furnace as shown in the accompanying drawing was built large enough to burn and reduce 12 lbs. of coal per hour. The sectional area of the furnace was designed to give a gas velocity above the critical range—thus affording turbulent or a churning motion to the powdered-coal-gas mixture. The furnace was built sufficiently long to permit a study of the progressive reactions in the furnace.

COAL FEEDING

Two distinct types of coal feeders were used. In the first the coal fell into an air stream, and after traveling about 8 in. was introduced into the furnace. However, this method of coal feeding permitted less than one-half of the air to be preheated. In the second type of feeder the coal fell directly into the combustion zone, being picked up by all the preheated air. This method of coal feeding had the disadvantage that a considerable portion of the coal settled out in the combustion zone, owing to the low velocity there. A contraction in the cross section of the combustion zone, as illustrated in the drawing, helped prevent the settling of coal and gave a gas richer in carbon monoxide. The advantage in better mixing of the first type of feeder over the second is counteracted by the beneficial effects of higher temperature of entering air in the case of the second type of feeder.

PREHEATING AIR

For the runs in which only part of the entering air was preheated, the preheating was carried out by passing the air through a double row of $^1/_2$-in. pipes in series, laid alongside the flue on each side of the furnace. Where all the air was preheated before entering the furnace, it was passed through 1-in. pipes, as above, and then through an externally heated silica tube filled with crushed fire brick. The air passing through the first preheater was heated to 540° to 775° C., depending on the conditions of the run. In the second preheater, all the air was raised to approximately 475° C. Calculations on runs made with former types of preheater indicate that approximately 12 per cent of the total heat of the chemical reactions ($C + O_2 = CO_2$, $C + {}^1/_2O_2 = CO$) was used to preheat the air. This factor causes a lowering in the temperature of the powdered-coal-gas mixture, and necessitates the use of a larger furnace. This preheating of the air is best carried out by the use of a regenerative checkerwork system *after* the completion of the reduction reaction.

TABLE II

Run	Gas Analysis			Temperatures		Mols Air per Hr.	Lbs. Coal Burned per Hr.	Air Preheated
	CO_2	O_2	CO	Final Sample Point ° C.	Entering Point ° C.			
8*c* (Final)	12.3	2.0	10.4	895	495	0.670	1.96	All
5 (Middle)	10.2	0.6	9.4	865	775	0.577	1.84	Less than one-half
7 (First)	10.4	4.1	6.5					
(Middle)	12.5	1.2	8.3	900	690	0.485	1.16	Less than one-half
(Final)	....	...	...					

TABLE III

Run	Cu. Ft. of Combustion Space per Lb. of Coal per Hr. Calculated	Observed	Ratio of Observed to Calculated
8*c*	0.7	1.2	1.72
5(Middle)	1.0	1.0	1.0
7(First)	0.8	0.9	1.12
7(Middle)	0.9	1.5	1.67
		Average............	1.38

RESULTS

Table II illustrates the type of results obtained with two different coals.

In Run 7 the temperature fell from 1300° C. at the combustion chamber to 900° C. at the point where the final sample was taken. These runs, as well as the others, showed conclusively that a gas richer in CO was obtained the higher the temperature of the entering air. However, it is to be noted that in the case where all the air was preheated, an air temperature of only 495° C. was obtained, whereas 1000° C. was desired. A comparison (Table III) is given between calculated and observed reduction rates by integrating Equation 2 between the limits zero per cent CO and the per cent CO formed in the run, upon introducing the proper fraction of CO_2 initially formed in the run.

The difference beween the calculated and observed capacities may be due to the coal not being at 900° C. (the temperature used for calculation) throughout the run or by incomplete mixing of the coal and flue gas. Although the design of the furnace was changed several times, great difficulty was encountered in maintaining a uniform mixture of coal and gas. Coal dust had a tendency to settle out and the gas stream became stratified. In a number of runs incompletely consumed coal was carried out of the furnace by the gas stream.

CONCLUSIONS

1—It is much more difficult to generate producer gas from powdered coal than the literature would lead one to suspect. However, the problem does not seem hopeless and in view of the possibilities of obtaining cheap power additional work should be carried out.

2—The difficulties seem to be the production of a sufficiently high temperature in the reacting zone, and the maintenance of the necessary intimacy of mixing between the powdered coal and reacting gas.

3—With each increase in the temperature of the incoming air, better results were obtained. It seems desirable to preheat the air to about 1000° C.

4—The maximum amount of CO obtained in any reliable run was 10.4 per cent, although for short periods 12 to 13 per cent was reached.

5—For the condition of the experiments the observed size of combustion space required for reduction of CO_2 to CO by the powdered coal was 1.38 times that calculated by Equation 3.

Note on the Use of Phosphorus in Gas Analysis[1]

By August Holmes

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Pyrogallic acid, widely used for the determination of oxygen in gas, has several disadvantages. It will absorb carbon dioxide if present; if not properly prepared it is liable to give off carbon monoxide; it exhausts its absorbing power for oxygen so gradually that it is difficult to determine when absorption is complete. It has the advantage, however, of being rapid, accurate when freshly prepared, and uninfluenced by traces of illuminants.

It has been the writer's experience that phosphorus is a better reagent for oxygen because, although a little slow, it is never exhausted as long as there is any present. By observing a few points it is quite rapid, and complete oxygen absorption is easily determined by the disappearance of the white fumes. To remove the last traces the sample should be replaced in the measuring pipet, mixed, returned to the phosphorus pipet, and allowed to stand until the disappearance of the white fumes.

After the gas has passed through the bromine water and absorbed the illuminants, the oxygen is easily absorbed by the phosphorus. This is also true for flue gases from boilers and burners, but not for the exhaust from a gas engine, nor the residue from the explosion in a gas analysis. Frequently, the oxygen in these cases is not easily acted upon by the phosphorus, which leads to the conclusion that there is no excess oxygen present. By passing such gases through bromine water, although there will be no change in reading after absorbing the bromine in the caustic potash, it will be found that the oxygen has been activated and is easily absorbed. It is not necessary, however, to pass the entire sample through the bromine water but merely to inoculate it with bromine by passing 2 to 3 cc. into the bromine pipet and then directly to the phosphorus pipet. A rapid absorption of the oxygen takes place at once.

This bromine inoculation has been found advantageous for sluggish oxygen absorption. It is not necessary to pass the gas, after this treatment, through the caustic, since no change in reading takes place. If the room is cold, inoculation assists the absorption.

In case the phosphorus has become contaminated by the illuminants or, more likely, by the cuprous chloride, the black spots may be removed by displacing the water on the phosphorus with concentrated nitric acid or, if the spots are very bad, with concentrated nitric acid to which a little concentrated hydrochloric acid has been added. The acid should, of course, be removed with clean water. The phosphorus will be light in appearance, and very active for some time.

The time required for a complete analysis of illuminating gas for carbon dioxide, illuminants, oxygen, carbon monoxide, explosions for hydrogen and paraffins, and absorption of the excess oxygen is about 20 min. with phosphorus, which is not very long.

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[1] Received February 16, 1923.

A New Specific-Gravity Apparatus for Natural Gas[1]

By T. R. Weymouth, R. P. Anderson, and J. R. Fay

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A new apparatus has been described for determining the specific gravity of natural gas, which comprises an orifice and a capillary tube in the same gas line, with differential gages for each. The method of operating and calibrating this apparatus has been discussed and its field of usefulness compared with that of the well-known effusion apparatus.

THIS new apparatus for determining the specific gravity of natural gas comprises an orifice and a capillary tube in series, and the principle of its construction is based upon two facts, well known to those familiar with the flow of fluids in pipe lines, which may be stated as follows: (1) when a fluid is passed through a thin, sharp-edged orifice, the drop in pressure at the orifice, known as the differential pressure, varies with the specific gravity of the fluid, other factors remaining constant; and (2) when a fluid is passed through a small capillary tube at a low rate, the drop in pressure through the tube is a function of the viscosity of the fluid, but is independent of its specific gravity. It is thus obvious that, for fluids of the same viscosity, the rate of flow of the fluid through the orifice may be kept constant by maintaining a constant differential pressure on the capillary tube, and that any variation in the specific gravity of the fluid will result in a corresponding variation in the differential pressure at the orifice. In other words, the differential pressure at the orifice is a measure of the specific gravity of the fluid and the differential gage scale may be calibrated to read specific gravity directly.

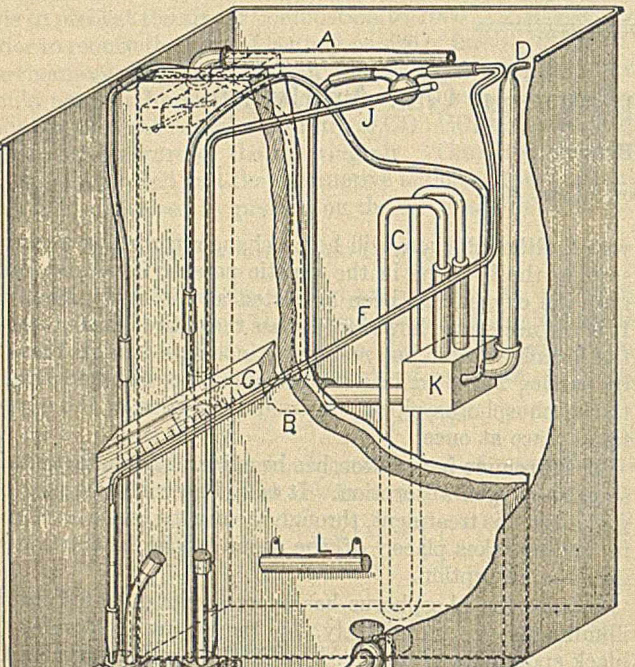

FIG. 1

The first application to be made of these facts has been in the determination of the specific gravity of natural gas. Preliminary experiments with a wet meter and small capillary tubes on natural gases from western Pennsylvania, of widely varying specific gravities, showed that the influence of viscosity upon the differential pressure is practically constant for these gases, and accordingly the apparatus here described has been developed.

DESCRIPTION OF APPARATUS

For convenience in field use, the apparatus has been built in compact, portable form, as shown in Fig. 1. The metal case is 12 in. high by 8 in. wide by 6 in. deep, with a partition through the center from side to side. Back of the partition the orifice and capillary tube are suspended in water for convenient control of temperature, and in front of the partition is a board to support the differential gages for the orifice and the capillary tube. Gas enters through tube A, which contains cotton for removing dust and other foreign matter from the gas, passes through fitting B, which contains an orifice 0.02 in. in diameter, then through a capillary tube, C, and finally out of the apparatus at D. The orifice is connected by copper tubing to differential gage E, read on inclined portion F, with scale G, calibrated in specific gravity. The inlet of the capillary tube is connected by copper tubing to differential gage H. This gage is inclined in the upper portion, J, to increase the accuracy of setting the fluid in the gage for the passage of gas at a definite rate through the orifice. The capillary tube is of glass, has a bore of about 0.04 in., is about 28 in. long, and is cemented in the special fitting K with de Khotinsky cement. One-eighth inch standard brass pipe and fittings are used in the connections to the special fittings for the orifice and the capillary tube. The level L is attached to the board for convenience in setting the apparatus approximately horizontal before use. Xylol is used in both differential gages, which must be filled to the proper point before the apparatus is used.

MANIPULATION

The gas whose specific gravity is to be determined is passed into the apparatus through tube A at a rate which will produce a certain differential on the capillary tube J, and the specific gravity of the gas is read from the scale G. This specific gravity may be termed the *observed* specific gravity of the gas, and must be corrected to obtain the *true* specific gravity if the temperature of the gas passing through the apparatus differs from the calibration temperature, or if the barometric pressure differs from the calibration pressure. The temperature of the water in the bath in which the orifice and capillary tube are suspended and the barometric pressure must be determined at the time when the reading of the observed gravity is made; and by the use of tables or charts the true specific gravity may easily be ascertained.

CALIBRATION

The apparatus in Fig. 1 was calibrated by using natural gases varying in specific gravity from 0.60 to 0.90, as determined by calculation from combustion data. Data have also been secured on the effect of variations in temperature and atmospheric pressure on the reading of the apparatus, and charts for the reduction of observed readings to true specific gravity have been prepared.

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[1] Presented before the Section of Gas and Fuel Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

FIELD OF USEFULNESS

In the natural-gas industry there is need for an apparatus that will give accurate results in the field at all times of the year. The effusion specific-gravity apparatus, now widely employed, gives trouble in cold weather, due to the difficulty of preventing the condensation of moisture in the orifice, and this difficulty is eliminated entirely with this new specific-gravity apparatus. Further advantages of the new apparatus as compared with the effusion instrument are the higher degree of accuracy and the shorter time required for a complete determination. Moreover, since the new instrument gives instantaneous readings, it responds readily to rapid changes in specific gravity, and can be adapted to recording purposes where gases of fluctuating gravities are flowing.

A New Method for the Control of Thermostats[1,2]

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A new method has been outlined for accurately controlling the temperature of a thermostat for long periods of time, which possesses the following advantages: (1) the elimination of sparking at the mercury contact, (2) an oscillating contact obtained without the use of elaborate mechanical equipment, (3) the elimination of the back-lash at the mercury contact, (4) the elimination of excessive wear on the relay points, and (5) a thermoregulator which reacts very quickly to small changes in temperature.

With this apparatus it is possible to maintain water or oil thermostats of capacities varying between 10 and 300 liters constant to 0.001° C. over long periods of time with a minimum amount of attention.

IN THE course of some work on conductivity and viscosity measurements, it was necessary to maintain a thermostat constant to ± 0.001° for several months at a time. The thermostats on the market were found to be inadequate for the purpose, mainly because of oxidation of the mercury surface in the thermoregulator. This oxidation is caused by the small electric arc produced when the contact is made or broken. This difficulty can be eliminated by decreasing the number of contacts per unit of time with a proportionate decrease in the accuracy of regulation or by making the current across these points so small that no arc can be produced. The object of the present paper is to describe a regulating device which combines accuracy of regulation with constancy of regulation for long periods of time.

Constancy of regulation by electrical methods depends mainly on two interdependent devices—the thermoregulator and the controlling mechanism.

DISADVANTAGES OF OTHER THERMOREGULATORS

Many kinds of thermoregulators capable of indicating a change of 0.001° in the bath temperature have been described in the past. Nearly all of them are made of glass and contain either toluene and mercury or mercury only. The contact is usually made between mercury in a capillary tube and a fixed platinum point. It was observed by Gouy[3] that, if the platinum point was made to oscillate up and down for a distance of about 1 mm., more sensitive temperature control was secured than when using the same thermoregulator with a fixed point. In recent articles by White[4] and Sligh[5] the advantages of the oscillating contact are discussed mainly from the theoretical viewpoint. Sligh gives some data for short runs on a thermostat, using first a fixed and then an oscillating contact point, which show that the latter gives a regulation about fifty times as sensitive as the former—i. e., the temperature variation of the first was fifty times as great as for the latter. It is stated that the mercury surface "was in bad condition" but that this had very little effect on the regulation, showing that a dirty mercury surface has less effect on the regulation when an oscillating point is used than when a fixed point is used. However, we found after a day's run, when using the oscillating point, the mercury surface is usually so contaminated with oxide that it has to be cleaned.

To prevent the formation of the oxide film on the mercury, an atmosphere of hydrogen or nitrogen is maintained over the surface. This method is satisfactory as long as the gas is present, but is cumbersome because of the apparatus and care required to maintain the supply of gas. Clark,[6] after filling the space above the mercury surface with hydrogen, seals off the top of the thermoregulator so that no other gas can enter. With the thermoregulator sealed in this manner it is difficult to adjust the temperature and impossible to use an oscillating contact. King[7] claims to have secured satisfactory results by replacing the air above the mercury with an inert gas and then sealing the capillary tube above the contact point with a drop of mercury. This method fails if the regulator is jarred, because the drop of mercury gradually works down to the main body of liquid and so changes the temperature of regulation.

A simpler and more permanent way to prevent this oxidation of the mercury is to use an electrical controlling mechanism, which requires a very small current for its operation and which is so constructed as to be free from inductance or capacity. A properly constructed magnetic relay or solenoid will operate satisfactorily with a current of 0.004 ampere under a 6-volt drop of potential. However, even with this small current an appreciable spark is formed at the mercury surface, owing to the large inductance of the relay coils. A nonmagnetic controlling mechanism in which the expansion of a brass tube, caused by the heating effect of the controlling current, is used to make or break the heater circuit, requires sufficient current to cause considerable arcing at the mercury surface. This arcing can be largely, but not completely, eliminated by the use of condenser of the proper capacity across the contact points.

METHOD OF REGULATION

After trying several different methods we found that the most satisfactory way to overcome these drawbacks is to use a very small current across the mercury contact and then

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 401 from the Department of Chemistry, Columbia University, New York, N. Y.

[3] *J. chim. phys.*, **6** (1897), 479.

[4] *Phys. Rev.*, **15** (1920), 509; *J. Wash. Acad. Sci.*, **10** (1920), 429

[5] *J. Am. Chem. Soc.*, **44** (1922), 60.

[6] *J. Am. Chem. Soc.*, **25** (1913), 1889.

[7] *Ibid.*, **42** (1920), 2058.

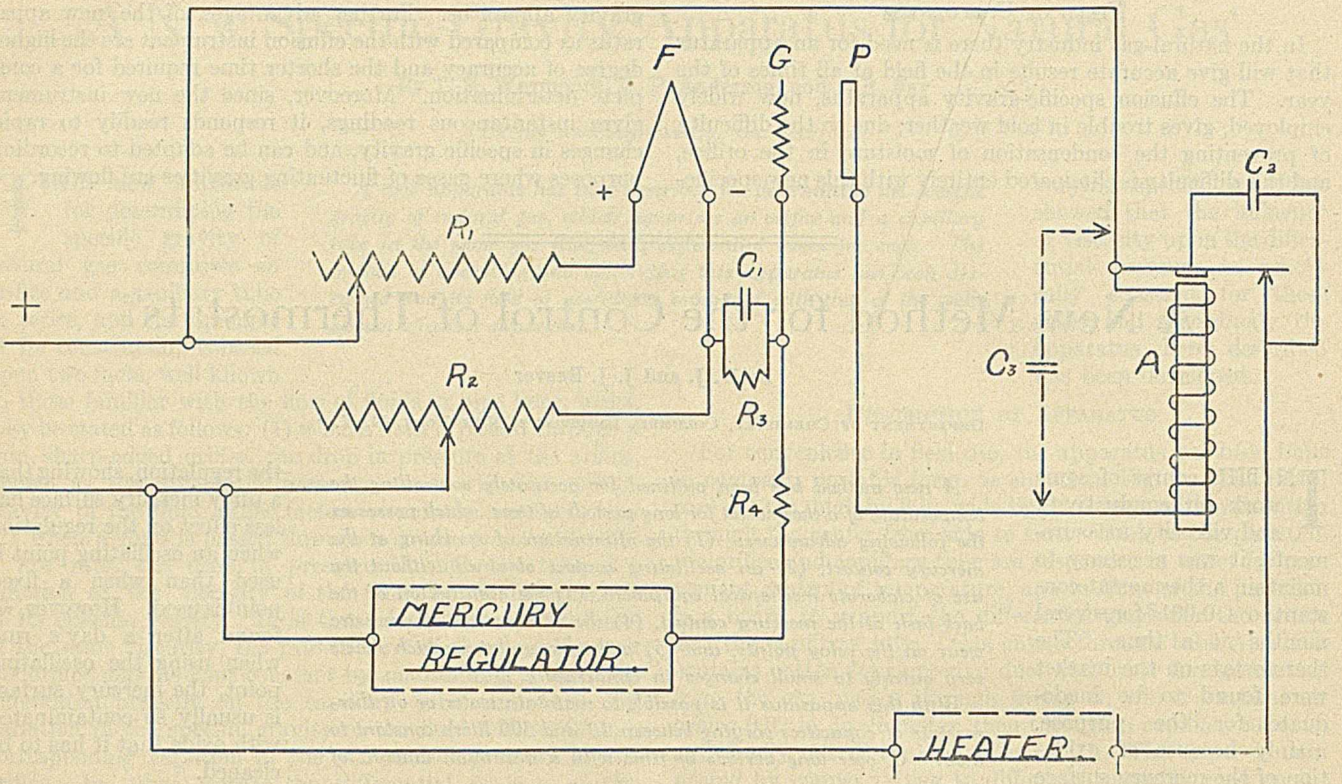

Fig. 1

amplify it sufficiently by means of a vacuum tube to actuate a magnetic relay or other current-controlling mechanism. A description of the method[8] used and some results obtained with different thermostats when using this method of control with an oscillating contact type of thermoregulator is given below.

For a 120-volt, direct-current supply the circuit shown in Fig. 1 is used. R_1 and R_2 are rheostats of about 120 ohms resistance and 2-ampere-current capacity; F is the filament, G the grid, and P the plate of the vacuum tube; R_3 and R_4 are 1-megohm resistance units; C_1, C_2, and C_3 are mica condensers, A is a telegraph relay with contact points capable of carrying 3 amperes in order that the heating coil may be of 250-watt capacity when necessary. (After determining the resistances required to obtain the maximum output of the tube being used, these rheostats can be replaced by fixed resistances made of nichrome or other resistance wire.) When using a General Electric Company UV 201 radiotron tube the drop in potential across R_1 is 96 volts (since this audion tube requires a filament current of one ampere a resistance of 96 ohms will be necessary), across R_2 it is 18 volts, with 6 volts across the filament. With a 1-megohm leak between the grid and mercury contact the current across the latter is approximately 2×10^{-5} amperes—far too small to produce an arc at the contact surface. Under these conditions the output of this type of tube is 0.006 ampere, while a telegraph relay wound with a resistance of 1500 ohms with No. 30 B & S gage copper wire requires between 0.003 and 0.004 ampere for satisfactory operation. With a special low impedence UV 202 radiotron, the drop in potential across R_1 is 64 volts, across R_2 it is 50 volts, with an output of 0.009 ampere when the filament current is 2 amperes. Since these filaments are designed to carry 2.35 amperes the life of the tube can be greatly lengthened by using only 2 amperes. With a Western Electric Company VT 2 or J tube the drop in potential across R_1 is 96 volts, and 18 volts across R_2. With a filament current of 1.3 amperes the output of this type of tube is between 0.008 and 0.01 ampere. There are several other types of tubes on the market at present which can be used in this circuit with but slight changes in the ratio of resistances R_1 and R_2.

If the heater is of 100 watts or less, no condenser need be used at C_2. When 150 watts are used a 0.05 microfarad condenser at C_2 will reduce the sparking at the relay points to a minimum, while a 250-watt heater requires 0.2 microfarad at C_2 to eliminate sparking.

When the thermoregulator is not fastened rigidly to the thermostat, the mercury surface oscillates quite rapidly and these oscillations cause the controlling current to be broken many times a minute. Since this oscillation of the mercury surface increases the sensitivity of regulation, it is not desirable to eliminate it. But with so many contacts per minute the relay points will soon wear out. In order to make the relay act more slowly, a condenser, C_1, of 0.1-microfarad capacity is connected in parallel with the grid leak R_3. This leak is from the grid to the negative terminal of the filament. By varying the capacity of this condenser or the resistance of the grid leak, the speed of the relay can be regulated to any desirable period. For example, with a 1-megohm resistance at R_3 and with the condenser C_1 disconnected, the relay will react the instant the contact is broken in the thermoregulator. If a 0.1-microfarad condenser, C_1, is used along with the megohm leak, the heater light flashes on one-half second after the contact is broken. In other words, the relay points cannot make contact more often than twice a second.[9] This period we found to be ideal for all baths of 30 liters or more capacity, but with the smaller baths it is better to have the period shorter than this. Another method of stopping the

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[8] Patent application covering the new improvements in this method has been filed.

[9] We have found that the grid leaks labeled 1 megohm vary anywhere from $^1/_2$ megohm to 2 megohms in resistance, so if any trouble is experienced with the action of the relay the resistance of the leaks ought to be tested. We have also had trouble with the mica condensers on the market at present, so, in order to make certain of the operation of the relay, all condensers should be tested for short circuits.

"chattering" of the relay is to put an 8-microfarad condenser, C_3, in parallel with the windings of the relay. This method works as well as the first on direct current, but is much more expensive and, moreover, it cannot be used with alternating current.

For a 60-cycle, 110-volt, alternating-current supply the circuit as given in Fig. 1 can be used if the condenser C is eliminated and a 1.0 microfarad condenser, C_3, is connected in parallel with the windings of the relay. If this condenser is not used the relay will chatter, no matter what the grid leak may be. With this added condenser the relay can be operated just as satisfactorily with alternating as with direct current.

THERMOREGULATORS USED

Several different kinds of thermoregulators were used with the foregoing controlling device to test the constancy of regulation over long periods of time. The first one used was made of 0.7 cm., Pyrex glass tubing bent in the form of a spiral just large enough to fit inside of a 12-liter bath. A small U-tube containing a capillary of 1.5-mm. bore was sealed on the upper end of the spiral. After sealing the lower end of the spiral it was filled with toluene or turpentine (turpentine gave satisfactory results at temperatures up to 70° C.) and the U-tube filled with mercury. A small platinum wire sealed in the lower end of the U-tube was used to make one contact, while a fine iron or nickel wire was used to make the adjustable contact in the capillary.

By using iron or nickel wire any back-lash at the mercury contact is eliminated, because neither of these metals is wet by mercury, with the result that the temperature of the make is the same as for the break. Either iron or nickel wire can be used in the thermoregulator when the vacuum-tube controlling mechanism is used, without in the least decreasing the constancy of regulation, as there is no arcing and consequently no corroding of the contact point. If a platinum wire is used in place of the iron or nickel, the temperature of the make is higher (0.002° to 0.003°) than that of the break.

After filling the tube it was placed in the thermostat and then wired to the support of the stirring motor in such a way that the vibrations of the support were transmitted to the regulator. In this way the regulator was given a periodic vibration which caused the mercury surface to oscillate uniformly. It was found that a moving mercury surface gave very sensitive temperature control (within $\pm$ 0.001°), and it has an added advantage over the oscillating point in that it requires no extra equipment.

With the spiral thermoregulator connected as described and containing 125 cc. of toluene and 25 cc. of mercury, the temperature of a 12-liter, asbestos-jacketed, glass jar was maintained at 25° $\pm$ 0.001° C. for a period of 3 mo. under varying room temperatures. These readings were started after the regulator had been in use for 2 wks. When this thermoregulator was operated under the conditions described above, with the exception that it was suspended so as to prevent the mercury from jarring, the temperature variation was 25° $\pm$ 0.02° C. With the toluene in the thermoregulator replaced by turpentine, the temperature of the bath was maintained at 70° $\pm$ 0.02° C. with the oscillating surface. Without the oscillating surface the temperature variation was 0.15° C. From these results it seems that the method of securing an oscillating contact by means of a moving mercury surface is as satisfactory, as far as temperature regulation is concerned, as Gouy's oscillating-point method. It is hardly necessary to emphasize the fact already pointed out in previous papers,[10] that accurate temperature control depends nearly as much upon adequate stirring, proper distribution of heating units and good thermal insulation as it does on a sensitive thermoregulator and proper controlling mechanism.

While a glass thermoregulator gives excellent results when the room temperature does not fluctuate too greatly, a more rapidly acting thermoregulator is necessary when the room temperature fluctuates 5° or more from the bath temperature. It was found that a Monel metal tube filled with mercury responded more rapidly to temperature changes than did a glass thermoregulator of similar design. A thermoregulator was made of 152 cm. of Monel metal tubing 0.7 cm. in diameter and containing about 70 cc. of mercury. In order to take care of the electrical contacts, it was necessary to fasten a glass capillary to the Monel tube. After trying several cements to seal the glass to the metal with no success, we finally succeeded in making a tight joint by nickel-plating the two parts together. The glass was first etched for a length of 3 cm. and then coated with a silver mirror. The mirror was coated lightly with copper, and the glass tube, which just fitted inside the metal tube, was soldered in place. The joint was then plated with a thin layer of copper and this was coated with a heavy layer of nickel. This layer is approximately 1 mm. thick and consequently the nickel sheath is strong enough to hold the glass tube rigidly in place. This regulator maintained a 300-liter bath constant to within 0.001° even when the room temperature was 29° C., and a cooling coil was necessary. In addition to its greater sensitiveness, a Monel metal regulator is very resistant to corrosion and breakage, and is therefore the most satisfactory for use in a water or oil thermostat under the usual laboratory conditions.

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[10] Geer, *J. Phys. Chem.*, **6** (1902), 85.

New Section at Akron

The need for an Akron Section of the AMERICAN CHEMICAL SOCIETY has been felt for some time, since there are more than two hundred chemists in the vicinity, a large percentage of them being engaged in problems relative to the rubber industry. They accordingly felt the need of getting together regularly and bringing in speakers from the outside, who would talk to them and present problems that were confronting other chemists engaged in other lines of chemical work.

On May 3, 1922, the chemists of Akron entertained the members of the Cleveland Section in Akron. E. F. Smith addressed the meeting, which was attended by about three hundred chemists. Talks were also made by C. L. Parsons and H. E. Howe. The meeting was such a decided success that work was immediately started by the men located in Akron toward the formation of an Akron Section.

These efforts were culminated on January 18, 1923, when an organization meeting was held and the following officers were elected:

Chairman: W. W. EVANS.
Vice Chairman: N. A. SHEPARD.
Secretary-Treasurer: W. J. KELLY.
Councilor: R. P. DINSMORE.

The Akron Section extends an invitation to all members of the AMERICAN CHEMICAL SOCIETY to visit with them at any time they may be in the vicinity and meetings are being held.

Plans for Organization of Scientists in Northwest

A meeting of people interested in the advancement of science was held in Spokane on February 9, and was attended by representatives from the science faculties of Washington State College, University of Idaho, State Normal School at Cheney, Whitworth College, Spokane University, North Central High School, and the Lewis and Clark High School. After discussion which brought out the need of an organization with a meeting center in the northwest, a committee was appointed consisting of Dr. M. A. Angell, of Idaho University; Dr. Frederick Heald, of Washington State College; Dr. Geo. W. Hess, of Whitworth College; Miss Elizabeth L. Martin, of Cheney State Normal School; Supt. O. C. Pratt, of the Spokane public schools; and Mr. Frederick Keffer, mining engineer. Letters have been sent out to a large number of scientists residing in the district, asking suggestions as to the type of organization which would best serve the interests of the region.

Causticization of Soda Ash[1,2]

By J. Harrop and H. O. Forrest

Massachusetts Institute of Technology, Cambridge, Mass.

THIS PAPER presents the results of a study of the causticization of sodium carbonate with lime, followed by the separation of the liquor from the sludge by decantation. The variables studied were the amount and character of the lime and the time of causticization. The effects of the variables upon the "free settling"[3] rate and percentage conversion of sodium carbonate to sodium hydroxide were determined.

Throughout the runs the solution to be causticized was maintained constant in soda content at a value of 2.6 *N*, and in the study of the character of the lime and time of causticization the amount of lime used was 10 per cent in excess of that theoretically necessary for the conversion.

Apparatus

The apparatus consisted of a container 5¹/₄ in. in diameter by 7¹/₄ in. deep, equipped with a closed steam coil for heating the solution and a motor-driven, propeller-shaped stirring device. A scale of ¹/₈-in. graduations was fastened to the side of the beaker. This scale, used in determining the settling curves, had a zero mark at a volume of 2000 cc. and a mark of 44 at the bottom of the beaker.

Slaked Lime *vs.* Unslaked Lime

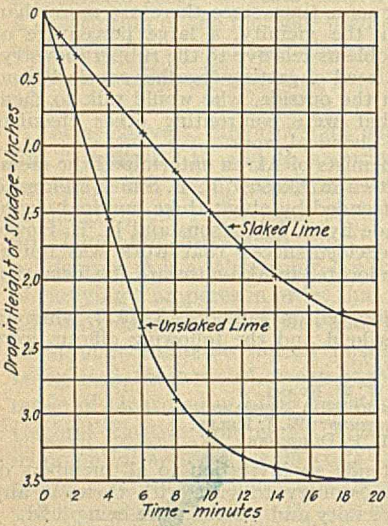

Fig. 1—Settling Curves after Causticizing with Slaked and Unslaked Lime

Two 225-g. samples of No. 2 lime, representing 10 per cent excess of the theoretical amount, were weighed out. One of the samples was slaked before being added to the soda-ash solution and the other was added directly. Both samples were causticized at boiling temperatures for 10 min. and the settling rates and percentage conversions determined. The settling curves are shown in Fig. 1. The free-settling rates for slaked lime and unslaked lime were, respectively, 0.11 and 0.53 in. per min. However, the percentage conversion for the slaked-lime run was 92.2 per cent against 91.7 per cent for unslaked lime, showing that slaking of lime before causticization increases the conversion but slightly, whereas it greatly reduces the rate of settling.

0,15 ? 0,35

Amount of Lime

Samples of No. 2 lime of 150, 175, 200, 225, and 250 g. were weighed out and each used to causticize 2 liters of soda-ash solution, allowing 10 min. for causticizing at boiling temperature. The settling curves and percentage conversion were determined for each run, the results being shown graphically in Fig. 2.

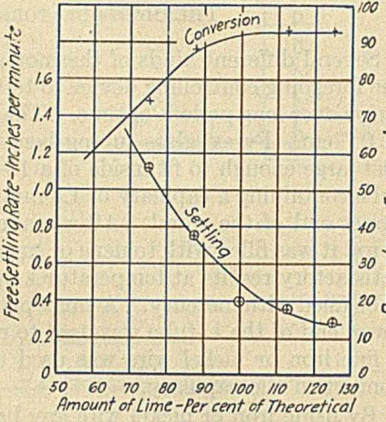

Fig. 2—Relation of Free-Settling Rate and Percentage Conversion to Amount of Lime Used

From this plot it is evident that increase in amount of lime increases the percentage conversion but decreases the rate of free settling, and since, with a given decantation equipment available, production is proportional to the rate of free-settling, the choice of amount of lime must be determined from an economic balance of these factors.

Time of Causticizing

Four samples of 225 g. of No. 4 lime were weighed out and causticized in 2 liters of soda-ash solution for periods of 5, 10, 20, and 30 min. The results are shown graphically in Fig. 3, and it can be seen that with increasing time of causticization the percentage conversion is increased while the free-settling rate is decreased. Here again the economic aspect, as to the proper choice of time of causticizing, comes into play.

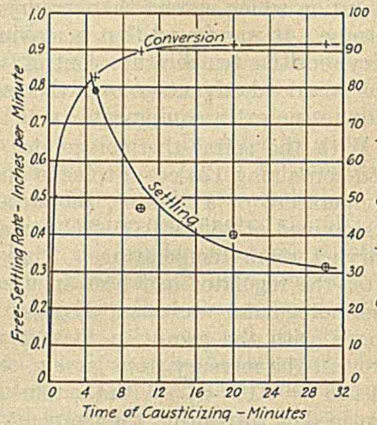

Fig. 3—Relation of Free-Settling Rate and Percentage Conversion to Time of Causticizing

Character of the Lime

In the study of the effect of character of the lime on percentage conversion and free-settling rate, six limes of varying calcium and magnesium content and varying degrees of air-slaking were used. The general tendency, from a study of the results, indicates that the percentage conversion is unaffected by the character of the lime as long as there is present 10 per cent excess lime. On the other hand, the free-settling rate is markedly affected by the character of the lime. For instance, high-calcium limes give better settling rates than limes containing appreciable amounts of magnesium, and air-slaking produces lower settling rates.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 35 from the Department of Chemical Engineering, Massachusetts Institute of Technology. From a thesis submitted in partial fulfilment of requirements for the degree of Master of Science.

[3] "Free settling" conditions are those in which the fall of particles through the solution is not interfered with by other particles.

The physical properties of the lime, such as apparent density and size of particles, influence the free-settling rate—the more granular and compact the particles, the greater the settling rate.

In the plant economics of causticization, three problems frequently arise, namely:

1—With a given equipment, what are the best operating conditions to yield a product of definite amount and concentration?

2—With a given equipment, what are the best operating conditions for maximum production?

3—For the design of a new plant what operating conditions should be chosen?

The first two problems are of immediate importance, because a plant manager always desires to know how to operate his plant at minimum cost and again how to obtain increased production without expending a "cent" for additional equipment. In all three problems, the final operating conditions are chosen after making an economic balance on the factors involved, such as cost data, time of causticization, and amount and character of the lime. This latter information can be obtained from runs made on the given lime, similar to those presented in this paper.

Detection of Sugar in Condensed Waters by Means of Cresol[1]

By G. E. Stevens

The Great Western Sugar Co., Eaton, Colo.

During the war several substitutes for alpha-naphthol as a reagent for the detecting of sugar in condensed waters were experimented with, but no satisfactory reagent was found that would give satisfactory results. The research had to do largely with the higher phenols, such as resorcinol, etc.

It occurred to the writer that the lower phenols, such as creosote, cresol, etc., had possibilities. Along with finding a suitable substitute was a desire to find also a cheap solvent which would eliminate the use of alcohol. With these ends in view several phenols were experimented with, and after various comparisons and experiments cresol was found to give satisfactory results.

The chief difficulty was in finding a solvent that in no wise hindered or affected the color reaction and at the same time was a good solvent. Cresol has a solubility of only 0.3 in water; therefore, if water was to be used as a solvent or vehicle, some substance soluble in water and at the same time a solvent of cresol must be found. Castile soap was found to be a good solvent for cresol in the proportions of 6 g. of soap to 15 cc. of cresol, the soap previously being dissolved in 100 cc. of distilled water. This solution can be made up in liter quantities without apparent deterioration. If solution is not effected on warming and agitation, the addition of a little more soap will complete the solution.

One objection to the use of α-naphthol has been that in most cases β-naphthol is usually present to some extent, which produces a green coloration on the addition of concentrated sulfuric acid. Iron and lime salts also produce various colorations which, if present in sufficient quantities, tend to mask the violet ring, especially in the detection of traces of sugar.

By the use of the cresol solution the foreign color reactions are almost entirely eliminated and a decided color ring is obtained only in the presence of sugar. A solution containing 1 part sugar in 100,000 parts of water, and also a trace of oil, lime salts, iron (held in solution by means of ammonium oxalate), ammonia, and other mineral salts was tested, and the color reaction found to be unaffected to any extent with no foreign colors present sufficiently to mask the test.

The castile soap in the presence of lime salts really acts as an aid, as the milky color produced serves as a good background in making the color reaction more prominent.

Procedure

Put about an inch of the water to be examined in a 6 x $^5/_8$ in. test tube (a 6 x 1 in. test tube is recommended in detecting light traces) and add 5 to 10 drops of the cresol solution and contents thoroughly mixed. Cool the contents if warm and then add concentrated sulfuric acid from a dispensing buret, holding the tube in an inclined position so that the acid will run to the bottom and form a separate layer, and continue to add the acid until the acid layer is $^1/_2$ to $^3/_4$ in. deep. Then roll the tube between the hands and if sugar is present a reddish black to pink color ring will appear, the color depending upon the concentration of the sugar. It is recommended that white translucent screen be placed between the eye and the source of light, as this aids in recognizing more easily the color reaction, especially in faint traces.

Advantages

This solution can be cheaply prepared, the cost for a 100-day campaign would be approximately $1.00. It eliminates high-priced solvents, and is very sensitive, giving a color reaction on standing a half-hour of 1 part sugar in 500,000 to 1,000,000 parts of water. There are no serious foreign color reactions to interfere or mask the test, and the color rings are of such a nature that a rough estimate of parts of sugar present can be estimated. While this method has not been tried out during plant operations, various waters were tested and the writer believes it to be applicable in all respects and to serve the purpose as a possible substitute for the α-naphthol method. The accompanying color chart shows the color reactions of various parts of sugar present in solution. This chart represents merely the colors observed by the writer while making the various tests, and to other individuals the color would probably seem slightly different.

Color Reactions with Known Parts of Sugar in Solution

Parts Sugar in Solution	Color Reaction
1 - 100	Reddish black turning to black
1 - 500	Reddish brown to black
1 - 1,000	Reddish brown
1 - 5,000	Deep red to reddish brown
1 - 10,000	Red to dark red
1 - 20,000	Light red to deep red
1 - 40,000	Pink to light red
1 - 60,000	Pink to light red
1 - 80,000	Light to heavy pink
1 - 100,000	Pink
1 - 150,000	Light pink in few sec.
1 - 200,000	Light pink in 20 sec.
1 - 250,000	Light pink in 30 sec.
1 - 300,000	Light pink in 1 to 2 min.
1 - 350,000	Light pink in 5 min.
1 - 400,000	Light pink in 18 min.
1 - 1,000,000	Light pink in 1 to 2 hrs.

Note: Slight agitation of the contents of the tube hastens reaction in light traces. A very light brown color is to be disregarded and will disappear upon agitation, and a pink color develop, if sugar is present.

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[1] Presented before the Division of Sugar Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

Evaporator Design[1]

Influence of the Properties of Aluminium Sulfate Solutions

By W. L. Badger and J. S. France

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COMMERCIAL aluminium sulfate—commonly but erroneously called "alum"—is ordinarily made by concentrating to such high densities that the resulting solution solidifies, when cold, to a cake hard enough to grind. This calls for concentration to about 60° Bé. The solution is usually boiled in open lead-lined tanks, heated by lead coils. Before attempting to design an evaporator for such work, it was necessary to obtain data on the relation between density and total solids in strong solutions of aluminium sulfate. A difficult point in the process is the fact that these strong solutions contain less than enough water to supply water of crystallization for the salt they contain, and therefore they solidify at rather high temperatures; hence, freezing points were needed. Elevation of boiling point was also of interest in designing this evaporator.

A search of the literature revealed very little information. No data on freezing points or boiling points could be found. All handbooks and reference works quoted determinations of specific gravity by Preuss,[2] who only worked up to 25 per cent solids at 45° C.; and by Gerlach,[3] who worked only at 15° C. The only other information available was a statement[4] that commercial aluminium sulfate for water purification should contain not over 47 per cent water.

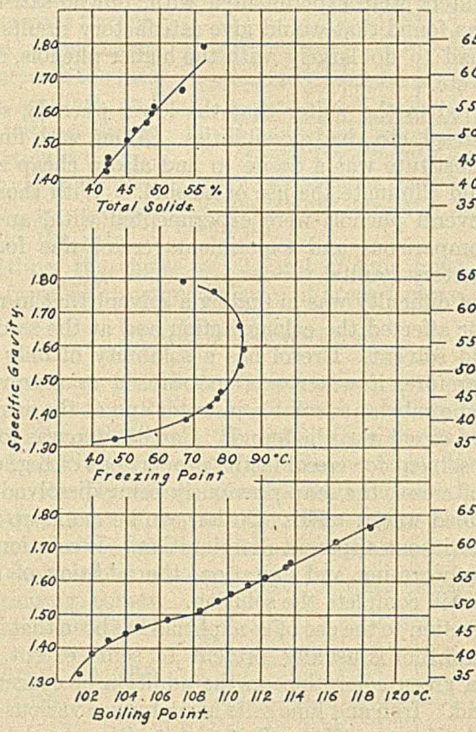
The time available for this work was limited, and approximate results would be of use if they could be obtained at once. It has not been feasible to repeat this work with more care, and the results are therefore published for the convenience of those who would rather have approximate data than none at all. It is hoped that someone may be interested enough to repeat this work more accurately.

Solutions were made from a laboratory grade of aluminium sulfate of better color than the commercial article—hence, probably fairly free from iron—but not an analyzed reagent. The solution was put in a large test tube of Pyrex glass ($2^1/_2 \times 10$ in.) and heated by a glycerol bath. Boiling and freezing points were read with an uncalibrated thermometer, uncorrected for emergent stem. Density was read at or near the boiling point with an uncalibrated hydrometer spindle, and was not corrected for temperature.

The solutions were frozen by bubbling air through them, which probably concentrated them somewhat, but this has not been allowed for, as the samples for analysis were removed before freezing. Analyses were made by heating a weighed sample just below red heat. Even with small samples and large crucibles, the samples puffed up into bulky and friable crusts which extended over the sides of the crucibles and could not be handled without loss. The purpose for which the work was done did not warrant the expenditure of time or funds on a better analysis.

It is believed that boiling points and freezing points have an absolute accuracy of ±1° C., with the results probably low rather than high. Their relative accuracy is considerably greater. Total solids are accurate to ±1 per cent, and density to ±0.05 per cent. Boiling points seem to indicate a change in phase at about 1.50 sp. gr., though this is not confirmed by the other curves. The freezing point of the densest solution means little, as the solution was extremely viscous, and even when hot the hydrometer reading was questionable. One solution gave a total content of 56.5 per cent and a freezing point of 68° C., but it was too viscous to get a density reading. It is believed that it was about 1.79 sp. gr., in which case the curve for total solids is not drawn steep enough. The results are purposely plotted on a small scale, to prevent any tendency to read the curves closer than the accuracy of the work warrants.

It is evident from the data presented that a vacuum evaporator cannot be applied to this problem, since at 55° Bé. the solution freezes at 85° C. These solutions are so viscous near their freezing point that the margin between freezing and boiling points at atmospheric pressure is necessary to permit handling the material. If the solution is boiled at atmospheric pressure, steam of at least 25 lbs. gage would have to be used for heating; and if a greater temperature drop could be obtained, it would be an advantage.



All fittings of this evaporator must be very simple, and the discharge would be best handled by a steam-jacketed pipe leading straight to the cooling floor. One obvious possibility is a multiple-effect evaporator operating with backward feed—i. e., thin liquor fed to the last effect and finished in the first. The objection to this is that the small temperature drop regularly occurring in the first effect of a multiple-effect evaporator will not be sufficient to keep such viscous material moving. The loss of available temperature drop from elevation in boiling point of the solution in the first effect would be too great. Hence, the only practical way of handling this material is to concentrate part way in a multiple-effect, preferably with backward feed, and finish in a single-effect pan, heated by steam at as high pressure as possible.

The properties of solutions of aluminium sulfate will probably not be studied again in the near future, so that the field is open to anyone who cares to repeat this work using more accurate methods.

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[1] Received August 19, 1922.

[2] *Ber.*, **17** (1884), 288.

[3] *Z. anal. Chem.*, **28** (1889), 493.

[4] Anon., *Munic. J. Eng.*, **31** (1911), 263; *C. A.*, **5** (1911), 3487.

The Heat Treatment of China Wood and Linseed Oils[1]

By Charles F. Mabery

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China wood oil polymerizes slowly at temperatures below 150° C. to the condition of saturation in oleic acid, as shown by iodine numbers, more rapidly in a current of air, the oxygen taking part in the change. In a current of carbon dioxide, however, the change proceeds as in absence of air, giving softer products.

Linseed oil is not affected, or only slightly, in absence of air when heated below 150° C. Heated in a current of air, polymerization proceeds slowly at temperatures up to 150° C., more rapidly at 200° C., giving products from which acids may be separately reduced to the condition of saturation of oleic acid, as shown by iodine numbers.

When polymerized slowly in a current of air at 150° to 200° C., both China wood oil and linseed oil are converted into their most cohesive form—a thick, sticky jelly. The solubility of both is greatly reduced when polymerization reaches the solid condition.

THE nature, composition, and changes by heat of China wood oil have received considerable attention within recent years, especially on account of its intense coherent quality when converted by heat into a particular stage of polymerization which renders it adaptable for the formation of strong flexible paint and varnish films, together with similar changes of the longer known linseed oil. Notably, by the work of Fahrion, and Von Shapringer (working under the direction of Dr. Ubbelohde at Karlsruhe), the structure of its principal constituents has been identified. Two of the cleavage products, azelaic acid ($(C_9H_{16}O)_4$ and valeric acid ($C_5H_{10}O_2$), having previously been obtained, Fahrion gives Von Shapringer the credit of identifying the third, succinic acid ($C_4H_6O_4$), which definitely proves the structure of the principal acid constituent, eleostearic, as follows:

$$CH_3—(CH_2)_3—CH=CH—(CH_2)_2—CH=CH—(CH_2)_7—COOH$$

Fahrion calls attention to the incorrectness of Von Shapringer's statement that eleostearic acid is a stereoisomeride of linolic acid of linseed oil, which has been shown to have the formula:

$$CH_3—(CH_2)_4—CH=CH—CH_2—CH=CH—(CH_2)_7—COOH$$

showing that the only difference between the two acids is the position of the double linkage. Von Shapringer found no oleic acid in China wood oil, although earlier work had seemed to show that it contained 25 per cent of this acid. In referring to the uncertain evidence based on the acetyl derivative on which Von Shapringer relied, Fahrion stated that according to his experimental proof this oil contains 10 per cent of oleic acid, besides 2 to 3 per cent of saturated acids, all of which Shapringer overlooked in his separation of eleostearic acid. It is now known that the separation of this acid from oleic acid and its other associates in the wood oil depends on the insolubility in ether of the lead salt of eleostearic acid. Another point of difference between the work of these two experimenters is the action of heat, Von Shapringer asserting that, whether heated in presence of air or not, only polymerization took place, while Fahrion, depending on the uncertain evidence of increase in specific gravity when the oil was heated exposed in air, asserted that oxidation took place, but that the experiments of Von Shapringer were carried on in test tubes that did not allow sufficient exposure to the air.

The last word has been said more recently by Wolff, who has taken up the action of heat on China wood oil from the point of view of colloidal solutions. After heating the oil for 8 hrs. at 200° C., contrary to previous experience, he found that a part of the product to the extent of over 70 per cent is soluble in ether, benzene, and chloroform, and the insoluble part, mixed in varying proportions with linseed oil and heated to 250° C., forms a clear solution which becomes solid on cooling—a jelly-like solid, representing a solid colloidal solution—from which he inferred that by chemical change an equivalent to 10 or 20 per cent of the original oil had been transformed into some sort of a polymerized product which formed with the remaining oil, as in his experiments with linseed oil, a solid colloidal solution; but he insisted that the nature of the change was unknown.

The object of this paper is to define with more precision than heretofore the changes that result in the heat treatment of China wood and linseed oils at moderate temperatures and carefully regulated conditions, and to ascertain the precise temperatures at which the various stages in composition occur from the beginning through the thin and thick jelly consistency to the solid granular end-product. China wood oil is so extremely sensitive to heat—as every manufacturer of paints and varnishes knows—that it must be treated with particular care. The possible changes by heat, all of which have received attention, include polymerization, absorption of oxygen, and the formation of anhydrides, lactones, and loss of carboxyl. The last change requires a very high temperature—in fact, to the breakage point of the molecule—and the formation of lactones is uncertain. The particular changes to receive attention here are polymerization alone and in presence of air. For the former, the oil was heated in tightly closed flasks in an air bath, and also in a current of carbon dioxide, and in the latter, air was drawn through the heated oil.

Table I gives the constants of the two specimens of the crude China wood oil used in this experiment:

Table I

1	2	3
Iodine numbers	178	171
Molecular weight	907	1151
Index of refraction	1.5191	1.15191
Analysis C	77.88	77.50
H	10.91	11.21
O (by difference)	11.21	11.29

As shown in Table II, the action of heat in China wood oil was tried under a great variety of conditions to ascertain just what was due to polymerization, and what to the action of air. With exclusion of air little change was observed below 100° C., but increasing rapidly above this point through the jelly stage, 125° to 150°, between 150° and 200° C., it was quickly transformed into the solid, brittle condition. The close concordance in composition shown in Experiments 1, 2, 3, and 6, indicates that polymerization is the only change, and that it is solely a function of the temperature. It is also apparent that the principal change takes place at the higher temperatures, and in Experiments 3 and 6 that agitation by CO_2 retards solid formation, even retaining the jelly condition in Experiment 6 at the higher temperature, and with the higher degree of saturation shown by its iodine

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[1] Received October 21, 1922.

TABLE II—HEAT TREATMENT OF CHINA WOOD OIL

No.		Time Hrs.	Temp. ° C.	Iodine No.	Change	Index of Refraction	C %	H %	O[a] %	CONDITION
1	Closed	95 48 53	100 125 150	134	44	1.15135	75.54	10.70	11.76	Solid gum
2	Closed	48	150	130	41		77.49	10.87	11.64	Semisolid
3	CO_2	96 48 55	100 125 150	130	48	1.15140	77.28	10.90	11.82	Sticky
4	Air	40 30	90 150	113	65		75.92	10.47	13.61	Solid gum
5	Air	90 96	60 90	103	66	1.4900				Thick sirup
6	CO_2	69 48 48 15	90 125 150 200	65	106	1.5040	77.97	10.78	11.25	Thick jelly
7	Air	72 54	60 90	149	29	1.5150	76.07	10.80	13.13	Thin jelly
8	Air	65	90	141	30					Jelly

[a] By difference.

number. In Experiments 4 and 7, where the oil is heated in a current of air, the effect of oxygen is plainly evident in the analysis by the increased percentage, 13.61 per cent. Since for the addition of one atom of oxygen to the molecule of China wood oil 13.39 per cent is required, it appears that one-bond linkage is affected when polymerization is carried to the solid condition. This difference, 2 per cent, between the composition of this product and that of the oil polymerized with air excluded leaves no doubt as to the different effects on the oil of this variation in treatment. Further evidence also appears in the different solubility of the lead salts. For practical purposes these experiments indicate that the most coherent polymerized condition of China wood oil is obtained by slow heating in a current of air between 125° and 150° C., or at a higher temperature with exclusion of air, preferably by a current of carbon dioxide.

The change in molecular weights by heating is very marked. Two specimens of the commercial oil gave in stearic acid molecular weights of 907 and 1151. The thick sirup in Experiment 5 gave as its molecular weight, 2337. On account of the insolubility in stearic acid of the solid, polymerized forms of the oil, their molecular weight could not be ascertained. The change in air, therefore, includes the absorption of oxygen and polymerization.

SEPARATION OF THE CHINA WOOD-OIL ACIDS

The raw oil saponifies slowly when heated with sodium hydroxide, but the polymerized oils emulsify to such an extent that saponification is prohibited. But when dissolved in alcohol and heated with the solid alkali the oil slowly saponifies. To separate the eleostearic acid from its polymers and other associates in the polymerized oil, it must be converted into the lead salt, insoluble or nearly so in ether, while the lead salts of the oleic and other associated acids are readily soluble. This is best done by adding to the alcoholic solution of the sodium salt an alcoholic solution of lead acetate. On account of a difference in solubility the lead salts of the oil heated with exclusion of air must be treated differently from those of the air-treated oil. The former salts remain in solution in the alcohol, and water does not precipitate them. But when the alcohol is distilled off the salts are left as a sticky mass, which solidifies on stirring. The lead salts of the oil polymerized in air precipitate immediately as a pasty mass, and very little remains in solution. Both lead salts were well washed with ether while in solution, the larger part leaving 25 to 35 per cent of the insoluble salt of eleostearic acid. After decomposition with sulfuric acid, the lead sulfate required long heating and stirring to separate the entangled acid. The washed and dried acids were examined for their iodine numbers, composition by analysis, index of refraction, and molecular weight.

In the following table the numbers correspond to those of the oils in Table II.

TABLE III—CONSTANTS OF ACID OF OIL POLYMERIZED UNDER DIFFERENT CONDITIONS

	CONDITION	Iodine No.	Index of Refraction	Mol. Wt.	C %	H %	O[a] %
1	Closed	114	1.5040	645			
2	Closed	127	1.5030		77.06	10.89	12.05
3	CO_2	84	1.5080		76.19	10.88	12.93
4	CO_2	91		601			
5	Air	82	1.5050		76.32	10.86	12.76
6	Air	138			75.88	10.92	13.10
		Calcd. for $C_{18}H_{32}O_2$			77.14	11.43	11.43

[a] By difference.

The separated acids also show evidence of oxygen addition, especially those from the oils heated with air. The higher percentage of oxygen in the acids from the oils heated in carbon dioxide is difficult to understand, for condensed carbon dioxide from a tank could hardly contain enough air to cause such a change.

The molecular weights of the acids in Experiments 1 and 5, more than twice as large as the theoretical value of the acid of the untreated oil (280), are evidently the result of polymerization. In Experiments 5, 6, and 7 the iodine numbers are reduced to the equivalent of oleic acid, Iodine No. 91—that is, one set of double bonds was involved in these changes. All the treated acids separated were compact solids.

POLYMERIZATION OF LINSEED OIL

Linseed oil, heated to 200° C., showed little or no change, either in closed flasks or in carbon dioxide, and the changes in air were much slower than those of China wood oil. The iodine number of the specimen used was 173. A combustion gave: C, 78.95; H, 11.14; O (by difference), 11.91; and index of refraction at 20, 1.4810. The raw oil heated in air gave the values in the following table:

TABLE IV—RAW OIL HEATED IN AIR

No.	Time Hrs.	Temp. ° C.	Iodine No.	Change	Index of Refraction	C %	H %	O[a] %	CONDITION
1	98 96 50	60 90 120	110	63	1.4900	74.84	10.48	14.68	Sirup
2	88	90	115	58					
3	72 96	60 90	140	33					
4	50	200	111	62					
5	50 22	200 150	90	83	1.4950	75.17	10.78	14.05	Thick jelly
6	223	120	129	42		75.17	10.71	14.12	Jelly
7	15 220	120 150	108	65	1.4910				Thick sirup

By difference.

As in China wood oil, the addition of oxygen forms an important aid in the polymerization of linseed oil, although the change proceeds more slowly, but in prolonged heating to 200° C., as shown by iodine numbers, it is reduced in saturation to the conditions of oleic acid.

THE ACIDS FROM POLYMERIZED LINSEED OIL

For saponification the polymerized oil was dissolved in alcohol and heated with solid caustic soda. To form the lead salts, an alcohol solution of lead acetate threw down the salts as a pasty mass. The acids separated by sulfuric acid collected after long heating as an oily layer that did not solidify—a mixture of polymerized linolic acid with oleic acid and its other associates and isomers.

TABLE V

No.	Bottle No.		Iodine No.	Index of Refraction	C %	H %	O %
1	42	Air	119				
7	79	Air	97	1.4970			
5	78	Air	82	1.5000	75.17	10.78	14.05

Experiments 5 and 7 show that linseed oil at high temperatures and in prolonged heating has its acids reduced to the condition of saturation in oleic acid.

ACKNOWLEDGMENT

The author desires to express his appreciation of the faithful service of his assistant, Mr. George Grossman, during the progress of this work.

Control of the Gelling Point of Glue[1]

With Specific Application to Drying Barrel Linings in Hot Weather

By Robert E. Wilson and William B. Ross

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This article summarizes the results of an investigation designed to determine the cause and most suitable remedy for the difficulties found in drying the glue sizing in barrels during hot weather. Contrary to the general impression, it was found that the cause was not primarily the high humidity of the drying air, nor fermentation of the glue, but lay in the fact that the outside temperature was above the gelling point of the glue (about 80° F. for the solutions used). As a result, instead of a thin film being held in place until dry, the sizing coat continually drained to the bottom of the barrel, and the resulting pool fermented before it had time to dry.

After considering several methods of overcoming this difficulty, it was found that the addition of small amounts of chrome alum to glue solutions was an entirely practicable method of raising their gelling point without injuring any of the other properties of the glue or the resulting films. Extensive data are presented on the gelling point and viscosity of solutions containing varying amounts of glue and chrome alum. Data are also presented on the gradual decrease in the gelling point of various solutions when kept hot.

Special precautions are necessary in adding chrome alum, so as to prevent localized high concentrations which cause irreversible setting, but with proper mechanical arrangements it is entirely possible to obtain satisfactory glue coats by the regular drying schedules with outside temperatures as high as 100° F.

IN THE process of sizing barrels with glue, as practiced extensively in the oil industry, satisfactory drying of the glue film during hot weather has been found almost impossible. The glue, instead of drying on the sides of the barrel, drains down and forms pools in the bottom, and soon gives unmistakable evidence of fermentation. This difficulty has generally been attributed either to rapid fermentation of the glue during hot weather, or to the retardation of the drying caused by the high humidity of the air blown through the barrels.

The brief study described in this paper was undertaken at the request of the Vacuum Oil Company in an effort to determine the cause of these difficulties and the best method of remedying them at the barrel factory in their Rochester plant.

The customary process of applying the second heavy coat of glue sizing to a finished barrel is to pour in hot, concentrated glue solution (generally from 30 to 40 per cent glue at temperatures from 110° to 140° C. depending on weather conditions), rotate the barrel so as to coat all the inside surface, and then drain out the excess glue through the bung for a predetermined length of time. The barrels are then taken to the drying room where a blast of atmospheric air is blown into them for several hours until the surfaces are substantially dry.

The thickness of the glue coat is controlled by noting the average glue consumption per barrel over fairly short periods of time and regulating the temperature or concentration of the glue solution so as to leave in just the proper amount after draining—thus, in winter weaker solutions of glue are used than in summer, in order to obtain the same average thickness of glue coat.

A preliminary investigation of the source of trouble with the drying process in hot weather brought to light the unsuspected fact that neither fermentation nor the high humidity of the air was the primary cause of the difficulty, but that the failure of the glue to gel before the end of the draining process was the real source of trouble. At ordinary temperatures the glue layer on the inside of the barrel cooled sufficiently to gel in a coat of the desired thickness before draining ceased, but during hot weather the film did not gel until after the drying had been in progress for some time and most of the glue had drained down into the bottom of the barrel. The resultant pools naturally dried but very slowly and fermentation generally took place before the drying was completed, but this was entirely a secondary phenomenon.

This explanation was further borne out by the fact that the gelling point of a 35 per cent solution of the glue used was found to be 82° F., just at the point which would have been predicted by the observation that drying was never satisfactory when the temperature in the drying room was above 80° F.

Throughout this paper the "gelling point" is defined as the temperature at which the glue solution just ceases to flow when slowly cooled and stirred with a thermometer. It can

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[1] Received October 23, 1922. Published as Contribution No. 70 from the Research Laboratory of Applied Chemistry, M. I. T.

be determined with surprising accuracy after making a few tests, and can be checked repeatedly by remelting and recooling the same sample. It is parallel to, but generally a few degrees lower than, the "melting point" referred to in the literature of glue and gelatin.

METHOD OF ATTACK

A number of possible remedies for these difficulties were considered, of which three were deemed worthy of investigation, as follows: (1) very rapid drying by the use of hot, dry air before the solution had an appreciable chance to drain, (2) cooling and dehumidifying the drying air so as to keep the glue film below its gelling point, (3) raising the gelling point in some manner above the prevailing summer temperature.

Sufficient work was done to indicate that both the first two methods were practicable, but the operating costs would be rather high, and the cost of special equipment excessive, considering the fact that it would only be required for a very small portion of the year. Effort was therefore concentrated on the third possibility of raising the gelling point so as to permit of satisfactory drying by the existing plant methods at any probable summer temperature.

EXPERIMENTAL WORK ON GELLING-POINT CONTROL

A considerable amount of work has been done on the effect of various electrolytes on the viscosity, jelly strength, rate of swelling, etc., of glue and gelatin, but, strangely enough, little attention has been paid to the effect of salts on the important physical change of passing from a liquid to a jelly. The references are generally obscure and qualitative. Thus, W. Pauli[2] found that chlorides, bromides, and iodides of sodium, potassium, and ammonium lower the melting and gelling points of a 10 per cent jelly, while sulfates raise both points. Coblentz[3] states that alums raise the "setting point" and Wo. Ostwald[4] gives data on the effects of various potassium salts.

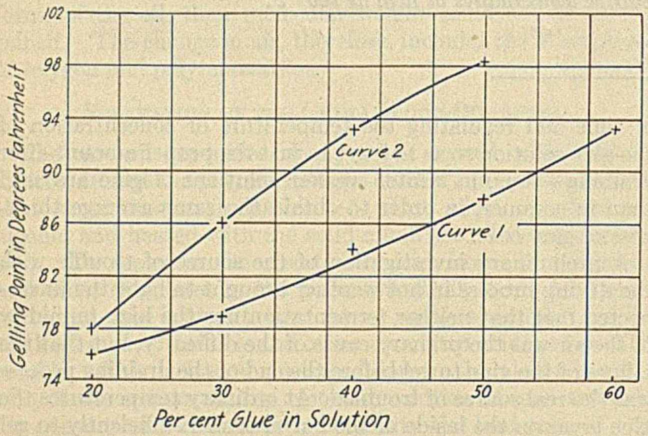

FIG. 1—CURVE 1: VARIATION OF GELLING POINT WITH PER CENT OF GLUE IN SOLUTION. CURVE 2: VARIATION OF GELLING POINT WITH PER CENT OF GLUE IN SOLUTIONS CONTAINING ANHYDROUS CHROME ALUM EQUAL TO 0.8 PER CENT OF THE WEIGHT OF DRY GLUE

Determinations were first made of the gelling point of glue solutions as a function of the concentration of glue, with the results shown in Curve 1, Fig. 1. This curve indicates that gelling point is practically a linear function of the concentration of glue. The glue used in these and all other tests was a high-grade hide glue in flake form. A number of other samples of glue were obtained from different sources and tested to see if a higher gelling point could be secured, but only one equaled, and none surpassed, the sample used in these experiments. It is recognized that the results are quantitatively applicable to only a single sample, but the amount of change of the gelling point of different glue solutions by the addition of a given chemical was found to be similar.[5]

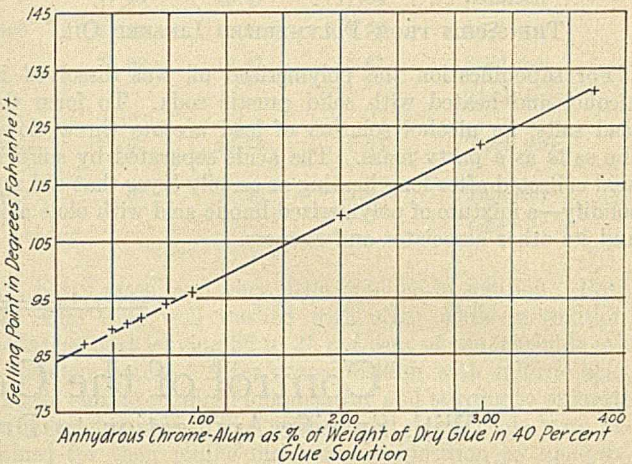

FIG. 2—VARIATION OF GELLING POINT OF 40 PER CENT GLUE SOLUTIONS CONTAINING CHROME ALUM WITH WEIGHT OF ANHYDROUS CHROME ALUM AS PER CENT OF THE WEIGHT OF DRY GLUE

It is evident that a high gelling-point solution could be obtained by using 60 or 70 per cent glue. There are, however, serious objections to the use of such concentrated solutions. The high viscosity of even a 50 per cent solution prevents the application of an even, thin coating on the barrels; this, of course, results in a large waste of glue. Furthermore, a thick film of glue cracks badly during drying, rendering the coating useless.

Attention was next turned to the possibility of controlling the gelling point by the addition of various chemicals. Certain chemicals, like formaldehyde, were found to set the glue irreversibly and these were not considered satisfactory. Most salts either lowered the gelling point or did not have an appreciable effect at moderate concentrations.

It was found, however, that alums, as a class, tended to raise the gelling point quite appreciably, and that chrome alum was remarkably effective in this respect, being by far the most efficient per unit weight of any of a large number of materials tried. It was accordingly the only addition agent of which a detailed investigation was made.

Curve 2, Fig. 1, shows the effect of the presence of 0.8 per cent of anhydrous chrome alum per unit weight of dry glue of the gelling point of solutions of various concentrations. It will be noted that the increase in gelling point produced by even this small amount is quite marked, especially at a high concentration of glue. Fig. 2 shows more detailed data on the addition of varying amounts of chrome alum to 40 per cent glue solutions. Again, the gelling point is practically a linear function of the alum concentration, except that the first small addition is apparently more effective than subsequent ones. By this means it is possible to secure gelling points as high as 130° F.

It should be emphasized that in making these determinations great care must be taken in adding the chrome alum to

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[2] *Pfluger's Archiv.*, **71** (1898), 333.

[3] *Chem.-Ztg.*, **42** (1918), 533.

[4] "Praktikum d. Kolloidchemie," **1921**, 79.

[5] This work was carried out in 1919, before the writers appreciated the important effect of the hydrogen-ion concentration of glue solutions on their physical properties, so that this possible variable was not measured or controlled. However, glue tends to buffer itself near its isoelectric point, and the addition of quite appreciable amounts of acid or alkali had much less effect than that of similar amounts of chrome alum. Furthermore, the more important points were checked up quantitatively with several different lots of glue of the same grade, so there can be little doubt as to the reliability of the results for practical purposes.

the solution. Indeed, at the higher concentrations (above 1 to 1.5 per cent chrome alum) the setting of the gel on cooling is substantially irreversible, and in adding even the lower concentrations great care must be taken to use only dilute solutions of the alum and to add them gradually with vigorous stirring; otherwise, the presence of localized high concentrations will cause the formation of strings, etc., which do not redissolve.

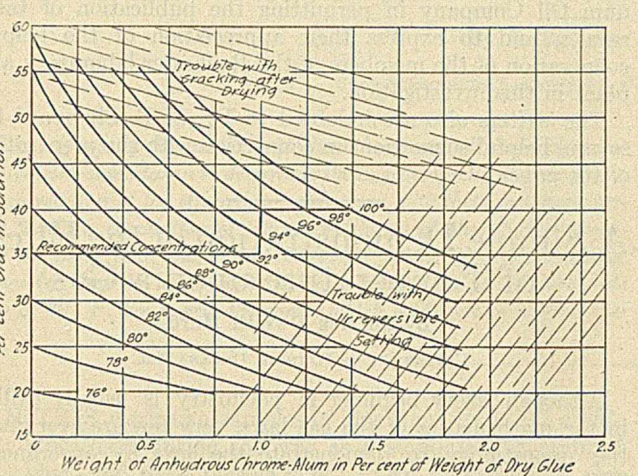

Fig. 3—Gelling Points of Glue Solutions as a Function of the Concentration of Glue and Anhydrous Chrome Alum

In order to cover the whole range of concentrations of glue and chrome alum, the contour chart shown in Fig. 3 was constructed by determining the gelling points of a large number of solutions containing different concentrations of glue and chrome alum.

It will be noted that an infinite number of combinations of glue and alum concentrations are possible for any given gelling point. There are, however, several factors which limit the allowable range of combinations. A high alum content causes irreversible setting, as is indicated by the shaded area on the right of Fig. 3, and high glue concentrations cause cracking of the dried film. On the other hand, low concentrations of either glue or alum fail to give the desired gelling-point raising. The approximate optimum combinations of glue and alum to give any desired gelling point are indicated by a somewhat arbitrary line in Fig. 3. It is possible to reach a gelling point of at least 100° F. without experiencing any difficulty from either irreversible setting or film cracking.

Irreversible setting, which occurs on cooling the solutions containing over 1 to 1.5 per cent chrome alum, is apparently only a continuation of the reaction which raises the gelling point. It does not in any way cause deterioration of the glue, even the films made from very strong chrome-alum solutions being as strong and stable as those of glue alone. It does, however, cause trouble in the plant because the glue which sets on the surface of the solution, around the edges of the pot, or which drains back from the barrels, cannot be remelted and used, and it is therefore considered essential to keep below the alum concentration at which irreversible setting is likely to occur.

To determine about what change should be made in the temperature of the glue solution in order to leave the same amount of glue in the barrel, a few rough determinations were made of the relative viscosity of hot solutions containing chrome alum. It was found that the alum made quite an appreciable increase in viscosity, as has also been pointed out by Bogue.[6] It was found, however, that the effects on gelling point and viscosity were so nearly parallel that the viscosity *at a given number of degrees above the gelling point* was roughly independent of the amount of alum added to a given glue mix. This is very convenient from the standpoint of plant operation, because if the glue must be heated too much or too little above its gelling point, it will not set at the proper time in the draining process.

Fig. 4 shows the relative times of efflux of a variety of different glue solutions, each measured at a temperature 20° F. above its gelling point. Lines of constant gelling point (Fig. 3) are shown for comparison. The approximate constancy of the viscosity (at a given temperature above the gel point) for a given glue content, and regardless of the chrome-alum content, is readily apparent. On the other hand, variations in the glue concentrations have a much greater effect on viscosity than on gelling point. In other words, as the contours in Fig. 4 clearly indicate, if a given gel point is obtained by adding chrome alum to a dilute glue solution, the product is much more fluid at slightly higher temperatures than if the same gel point had been obtained by using a stronger solution of glue with less chrome alum. The independent control of these two properties may be found valuable in a number of applications.

Plant Control of the Process

One of the difficulties in carrying out the method in the plant is to find suitable means of adding the alum so as to prevent the formation of insoluble strings and yet complete the addition within a reasonable time. This was successfully accomplished by rapidly recirculating the hot glue through a small centrifugal pump, and running in a small stream of 1 per cent chrome-alum solution just before the glue entered the pump.

During the large-scale tests in the plant, it was found that the gelling point of both the plain glue and the glue-alum solutions dropped several degrees in 24 hrs. This phenomenon was then studied in the laboratory, with the results shown in Fig. 5.

A large batch of 40 per cent glue solution was made up and the chrome-alum solution added, thus reducing the glue content from 40 to 35 per cent. Two samples of the mix were taken before and after the addition of the alum.

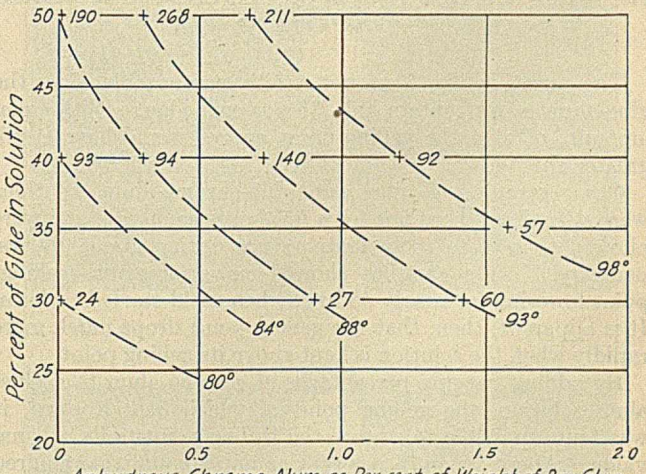

Fig. 4—Comparison of Viscosity of Glue-Anhydrous Chrome-Alum Solutions at 20° F. above the Gelling Point. Dotted Lines Are Equal Gelling Points

These samples were kept at 160° F., one of each kind being stirred hourly for 8 out of each 24 hrs.; the remaining samples were not stirred. Fig. 5 shows the gelling-point characteristics of the samples cited. The drop in gelling point of

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[6] *Chem. Met. Eng.*, **23** (1920), 5

the unstirred samples was considerably greater than the others showing clearly the effect of agitation in keeping up the gelling point.

Of the stirred samples, the one containing chrome alum dropped slightly more rapidly during the first few hours, after which the gelling points of the two were practically parallel for a period of four days. This would seem to indicate that the drop in gelling point is really characteristic of the glue alone. For a given concentration, therefore, the effect of chrome alum is to raise not only the initial gelling point, but the whole curve as well.

The more rapid drop of the unstirred sample containing chrome alum was due possibly to a separating out of a glue-chromium precipitate, thus leaving a solution weaker in glue and in chrome alum. The presence of a visible sediment was noted in this instance.

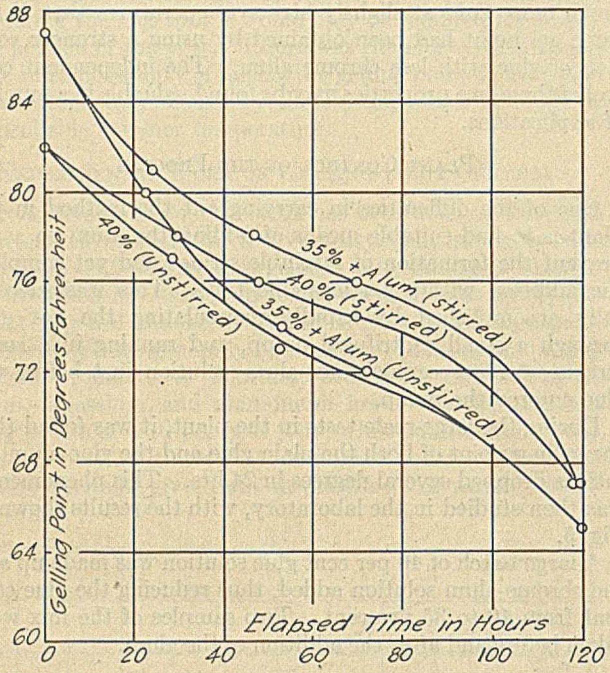

Fig. 5—Drop in Gelling Point of Glue and Glue-Chrome Solutions with Time. Solutions Held at 160° F.

The curves in Fig. 5 are not strictly comparable, since the glue-alum mixes contain only 35 per cent glue. With equal amounts of glue the gelling-point curves would have a still greater spread.

Other samples of glue and glue-chrome-alum solutions were stirred and kept hot for a few hours each day, and were allowed to cool to room temperature during about 16 hrs. per day. These samples showed no appreciable gelling-point lowering for nearly 48 hrs., when mold started to form. It is apparent, then, that the gelling point drops much more rapidly when the solution is kept above its gelling point.

By adding varying percentages of chrome alum to a glue-alum solution, the gelling point of which had dropped, it was found possible to restore the gelling point to its original value. About 70 or 75 per cent as much alum was required to make a given increase in gelling point as was required for fresh glue. Thus for any glue-chrome alum mix, the addition of small amounts of chrome alum with agitation once or twice a day serves to keep the solution up to the required gelling point.

With these precautions and control of the temperature of the solution so as to get the proper thickness of glue coat, entirely satisfactory results were obtained in the plant. The method is now used as standard practice during hot weather and permits rapid drying without draining to the bottom or fermentation, regardless of the temperature.

Acknowledgment

The writers desire to acknowledge the courtesy of the Vacuum Oil Company in permitting the publication of these results, and to express their appreciation of the helpful coöperation of the members of the Rochester laboratory and plant in this investigation.

The writers also are indebted to Dr. S. E. Sheppard for several helpful suggestions in connection with the preparation of the paper.

A Simple Demonstration of the Effect of Temperature upon a Gas[1]

By Charles DeWitt Hurd

University of Illinois, Urbana, Ill.

Although every beginner in chemistry is usually drilled in the mathematics of the gas laws, very few are ever given the opportunity to demonstrate the laws by experiment. This is probably due to the fact that the experiments which would be assigned are quantitative in nature, and as such would involve the use of apparatus somewhat too complex for the novice in laboratory procedure. The two experiments which follow do not aim to prove Charles' Law, since they are qualitative in nature. They do demonstrate, however, that a gas will contract with a decrease in temperature and will expand with an increase in temperature. The apparatus, certainly, would not confuse even a beginner.

Six grams of soap are added to 80 cc. of distilled water in a tall 100-cc. beaker. The mixture is heated nearly to boiling until the soap is entirely dissolved. A test tube is warmed, and at the same time the inner wall of it is lubricated by filling it with the hot soap solution. This soap solution is immediately poured back into the beaker, and a soap film is formed across the mouth of the tube. This can be done easily if the mouth of the tube is dipped just below the surface of the solution and then withdrawn. This film will rise in the inverted tube as the tube cools. It can be made to rise rapidly if the walls of the tube are surrounded by a cold, wet cloth.

This shows the contraction in volume due to a decrease in temperature. It is simple also to demonstrate gaseous expansion due to an increase in temperature. A soap film is formed across the mouth of a cold test tube. If the rounded glass end of the tube is thrust into the hot soap solution in order to warm it, the soap film at the other end will form a bubble.

Received February 20, 1923.

Calendar of Meetings

International Photographic Arts and Crafts Exhibition—Grand Central Palace, New York City, April 21 to 28, 1923.

American Oil Chemists' Society—14th Annual Meeting, Hot Springs, Ark., April 30 and May 1, 1923.

American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

American Association of Cereal Chemists—9th Annual Convention, Sherman Hotel, Chicago, Ill., June 4 to 9, 1923.

American Leather Chemists' Association—20th Annual Meeting, White Sulphur Springs, W. Va., June 7 to 9, 1923.

American Institute of Chemical Engineers—Summer Meeting, Wilmington, Del., June 20 to 23, 1923.

American Society for Testing Materials—26th Annual Meeting, Atlantic City, N. J., week of June 25, 1923.

The Hygroscopicity of Hide Glues and the Relation of Tensile Strength of Glue to Its Moisture Content[1,2]

By E. Bateman and G. G. Town

Forest Products Laboratory, U. S. Forest Service, Madison, Wis.

The purpose of this paper is to show the results obtained from investigations undertaken to determine the hygroscopicity of hide glues; the correlation of the strength of such glues with their moisture content, and the correlation of the susceptibility of glue to decomposition by mold with the moisture content of the glue. The paper shows (a) that the hygroscopicities of a veneer and a standard hide glue at 80° F. are nearly the same, which leads one to suspect that for all hide glues there is a great probability that the same moisture content would eventually be attained in the same humidity and temperature; (b) that the relation between tensile strength of two hide glues and their moisture content is such that at 30 per cent moisture content neither of the two glues is as strong as wood; (c) that the moisture content above which glue will mold and below which molding apparently ceases is approximately 33 per cent.

IN THIS work two samples of glue were used: (1) a hide glue[3] used during the war as a standard for certified glue, and (2) a veneer glue.[4] Two conditions of glue were used: (1) ground, and (2) cast in strips. The first was obtained by grinding in a mill. The degree of fineness was not determined, however. The strips of glue were obtained by pouring a 4 to 1 solution of glue on plate glass, allowing this to dry to such an extent that it could be handled easily without breaking. It was then fastened to a strong wooden frame and allowed to dry in 60 per cent humidity. After drying, these sheets, which were about 18 in. square, were cut up into strips 3 x 1 in. Two $^{1}/_{4}$-in. holes, $1^{1}/_{2}$ in. from either end, $^{1}/_{2}$ in. apart, were bored in the strips. Fig. 1 shows a glue strip before and after breaking.

Table I—Relative Humidities Used in the Work

Solution	Relative Humidity %	How Obtained and Maintained
1	0	Dried in oven of 105° C.
2	0(?)	Dried in vacuum over phosphorus pentoxide
3	30	Humidity regulated room at 80° F.
4	60	
5	75	In glass jar containing Na_2CO_3 solution. Held in a temperature-regulated room at 80° F.
6	86	
7	89	In glass jar containing $CaCl_2$ solution. Held in temperature-regulated room at 80° F.
8	100	In a glass jar containing distilled water. Held in a temperature-regulated room at 80° F.

Two temperatures, 70° and 80° F., were used. The relative humidity of the air in contact with the glues in the various experiments is given in Table I, which also shows the method of maintaining the humidity.

Determination of Relative Humidity

The air in a 4-liter bottle which contained 1 liter of the various solutions shown in Table I was allowed to come to equilibrium. The air was then displaced by exactly 3 liters of the same solution as the bottle contained and at the same temperature. The air thus displaced was passed through a weighed drying bottle containing concentrated sulfuric acid. It was found that a change in temperature of 0.3° C. during any run was sufficient to cause an error in the calculation. Such runs were, therefore, discarded. A considerable number of determinations were made which were acceptable as far as temperature change was concerned, and the

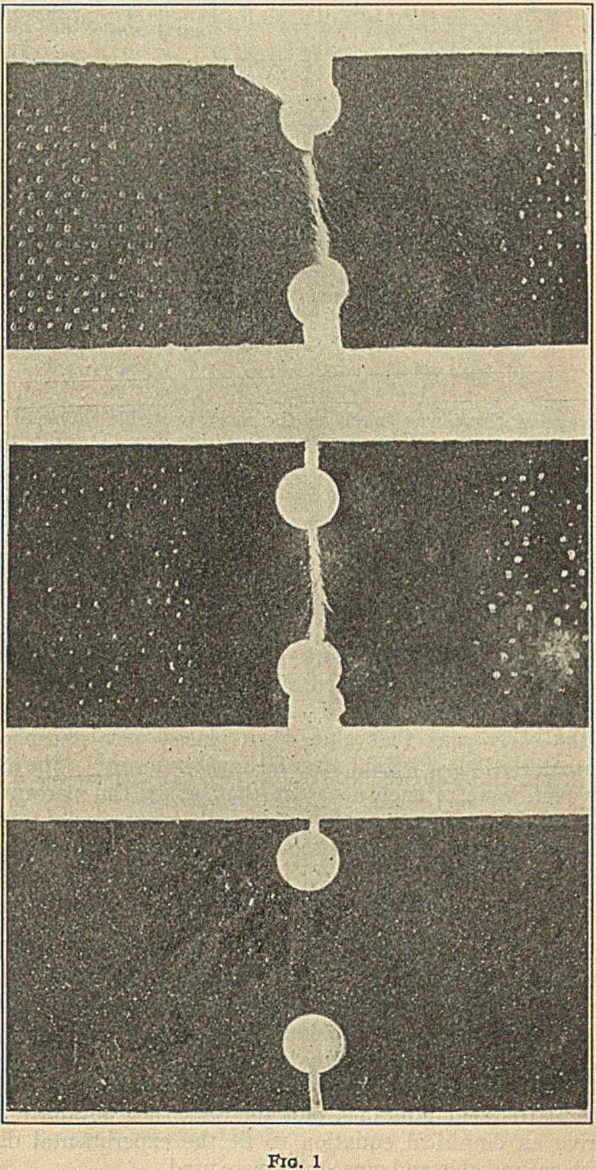

Fig. 1

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This paper was submitted by G. G. Town in partial fulfilment of a minor for the degree of Doctor of Philosophy at the University of Wisconsin.

[3] The standard hide glue had the following characteristics:

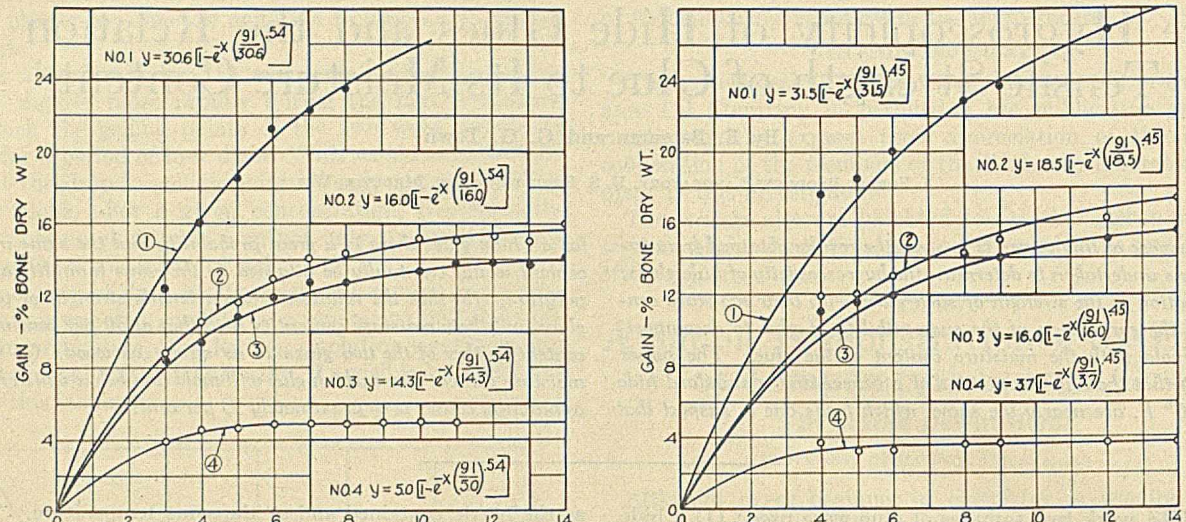
Viscosity at 60° C. of a 5 to 1 solution—142 sec. (Normal Engler 52.8 sec.).

Jelly strength of a 12 to 1 solution—6.5 mm.

Tested by Forest Service jelly-strength tester. *See* Teesdale and Bezeau, "Modern Glues and Glue Handling." Slight grease content, sweet odor.

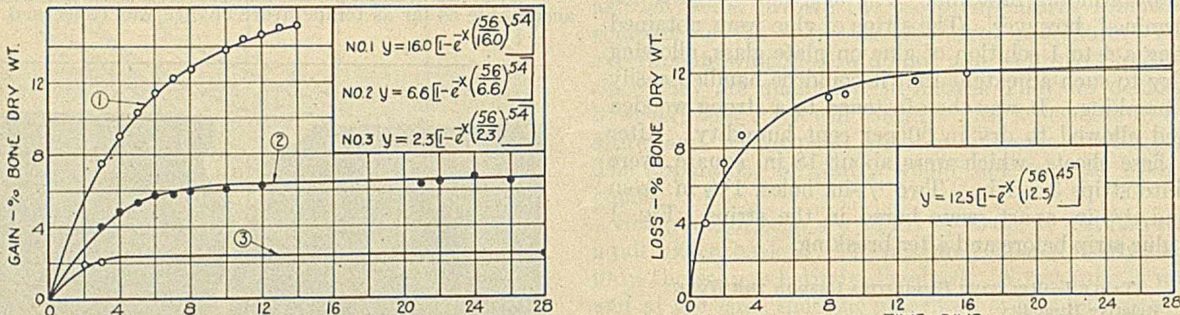
[4] The veneer glue was a low-grade hide glue. It had the following characteristics:

Viscosity at 60° C. of a 5 to 1 solution—114 sec. Jelly strength of a 12 to 1 solution—7.8 mm. Considerable grease content. Sweet odor.



PERCENTAGE GAIN OF HIDE GLUE AT 80°F.
1-IN 100% HUMIDITY 3-IN 86% HUMIDITY
2 " 89% " 4 " 75% "

PERCENTAGE GAIN OF HIDE GLUE AT 70°F
1-IN 100% HUMIDITY 3-IN 86% HUMIDITY
2 " 89% 4 " 75%



PERCENTAGE GAIN OF GROUND HIDE GLUE AT 80°F
1-IN 86% HUMIDITY 2-IN 75% HUMIDITY
3-IN 60% HUMIDITY

PERCENTAGE LOSS OF HIDE GLUE
IN VACUUM OVER P_2O_5 AT 70°F

FIG. 2

average of these was taken as the most probable value of the relative humidity. The results of the humidity determinations are as follows:

Solution	Average Humidity
1	75.2
2	86.0
3	88.8

(A) HYGROSCOPICITY

METHOD USED—The work planned required that dishes containing 10 g. of air-dried glue be left in the various humidities until they reached *constant* weight. It was found in the early runs that glue when placed over phosphorus pentoxide still lost weight after 30 days' exposure. The data, however, were of such a nature that when the percentage loss was plotted against time a smooth curve was obtained. The equation for this curve took the form of

$$y = a\left(1 - be^{-cx}\right)$$

where y is the percentage loss or gain in the time x. When x equals infinity, then $y = a$. Therefore, a is the limit of y, or the amount of moisture which could eventually be lost or gained under the set of conditions used. b and c are constants, while e is the base of natural logarithm.

The final method of conducting the work was to weigh the glue at frequent intervals, plot the data thus obtained, and derive an empirical equation to fit the experimental data. Both ground glue and glue strips were used.

RESULTS—The data giving these weights in detail are shown in Figs. 2 and 3.

The moisture content of glue in equilibrium with the vaious relative humidities was obtained by adding the value of a in the equation for that particular condition to the percentage of moisture in the glue at the beginning of the experiment. The values thus obtained are plotted against relative humidity in Fig. 4, and represent the moisture content of glue in equilibrium with the air of varying humidity.

DISCUSSION OF RESULTS—The curve shown in Fig. 4 shows that the hygroscopicity of the two glues tested is practically the same. This leads one to believe that in all probability the hygroscopicity of hide glue is the same, irrespective of the grade of the glue, since the two glues represent both high- and low-grade materials. The hygroscopicity of glues is greater at 70° than at 80° F., although the difference is not very great.

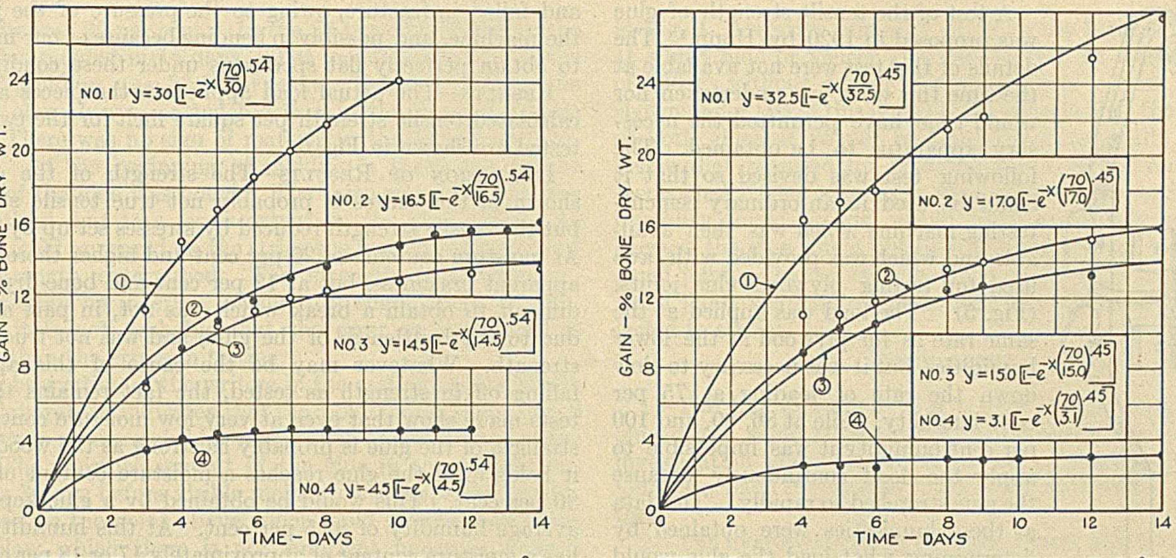
A study of the empirical equations obtained by the two grades and conditions of glue absorbing moisture under different humidity conditions shows that the equation

$$y = a\left(1 - be^{-cx}\right)$$

can be further expanded into

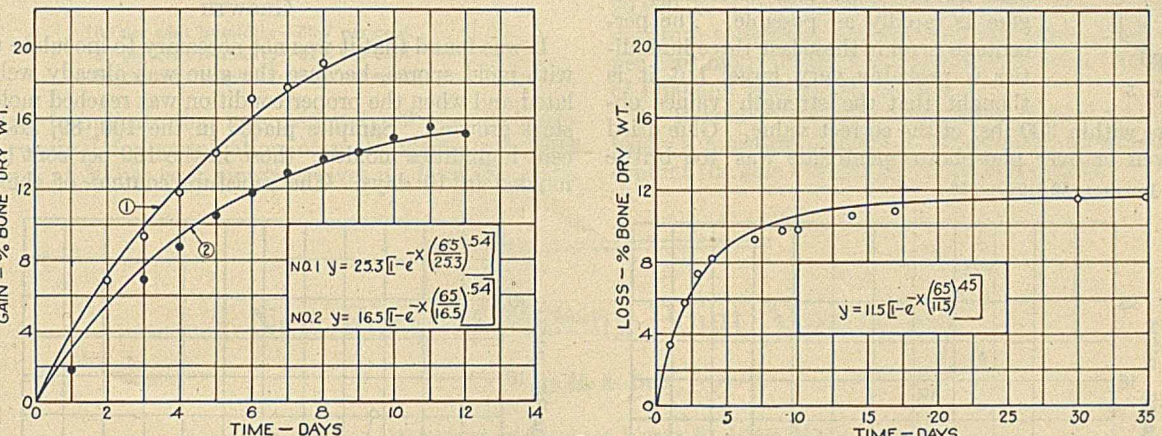
$$y = a\left(1 - be^{-x\frac{K^d}{a}}\right)$$

where K is a constant for the particular grade of glue and its condition, whether ground or sheet, and d a factor for tem-



PERCENTAGE GAIN OF VENEER GLUE STRIPS AT 80° F.
1—IN 100% HUMIDITY 3—IN 86% HUMIDITY
2 " 89% " 4 " 75% "

PERCENTAGE GAIN OF VENEER GLUE STRIPS AT 80° F.
1—IN 100% HUMIDITY 3—IN 86% HUMIDITY
2 " 89% " 4 " 75% "



PERCENTAGE GAIN OF GROUND VENEER GLUE AT 80° F.
1—IN 100% HUMIDITY 2—IN 89% HUMIDITY

PERCENTAGE LOSS OF GROUND VENEER GLUE IN VACUUM OVER P_2O_5 AT 70° F.

Fig. 3

perature. The value of b is constant for both grades of glue and both conditions of surface, and varies only as the temperature, being 0.45 at 70° F. and 0.54 at 80° F. If it is assumed that the value d varies directly as the temperature, the value at 212° F. should be 1.76. Calculations on the loss which should be experienced in 24 hrs. drying in a drying oven checked, with the actual loss within 2 or 3 per cent. This seems to indicate that the value of b is directly proportional to the temperature. The values of K are constant for each condition of each glue. It seems more than likely, however, that this value really contains at least two variables, K_1 and K_2, one of which varies with the grade of the glue, the other with the amount of surface exposed per unit weight. In other words, the relative humidity of the air sets a limit upon the moisture content of the glue. The speed with which this limit is approached depends upon the glue, the ratio of surface exposed, the moisture already present, and the temperature.

(B) Relation of Tensile Strength to Moisture Content

Method of Testing—All previous tests on the strength of glue at the Forest Products Laboratory have been confined to glue joints. This test, while it shows the suitability of a glue for use in a joint, does not tell the strength of the glue itself except in weak glues, because the wood fails before the glue. It was not suitable for this work, which deals with the relation of glue strength to moisture.

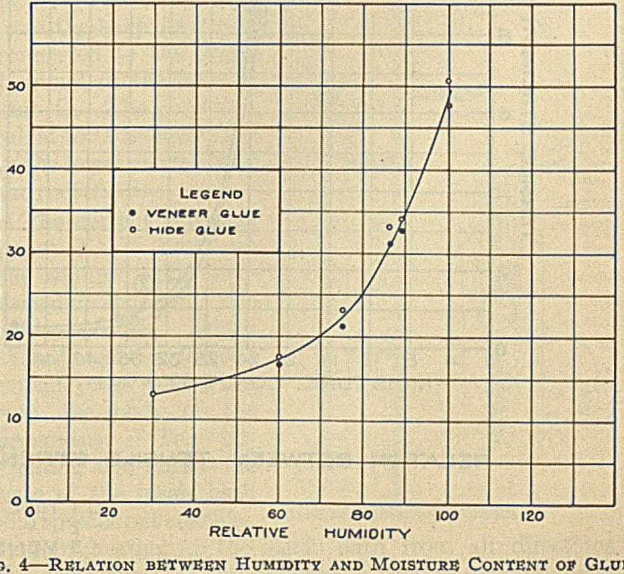


Fig. 4—Relation between Humidity and Moisture Content of Glue at 80° F.

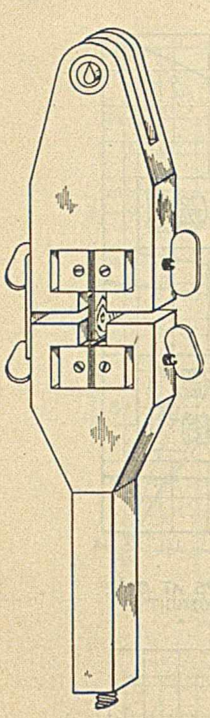


FIG. 5

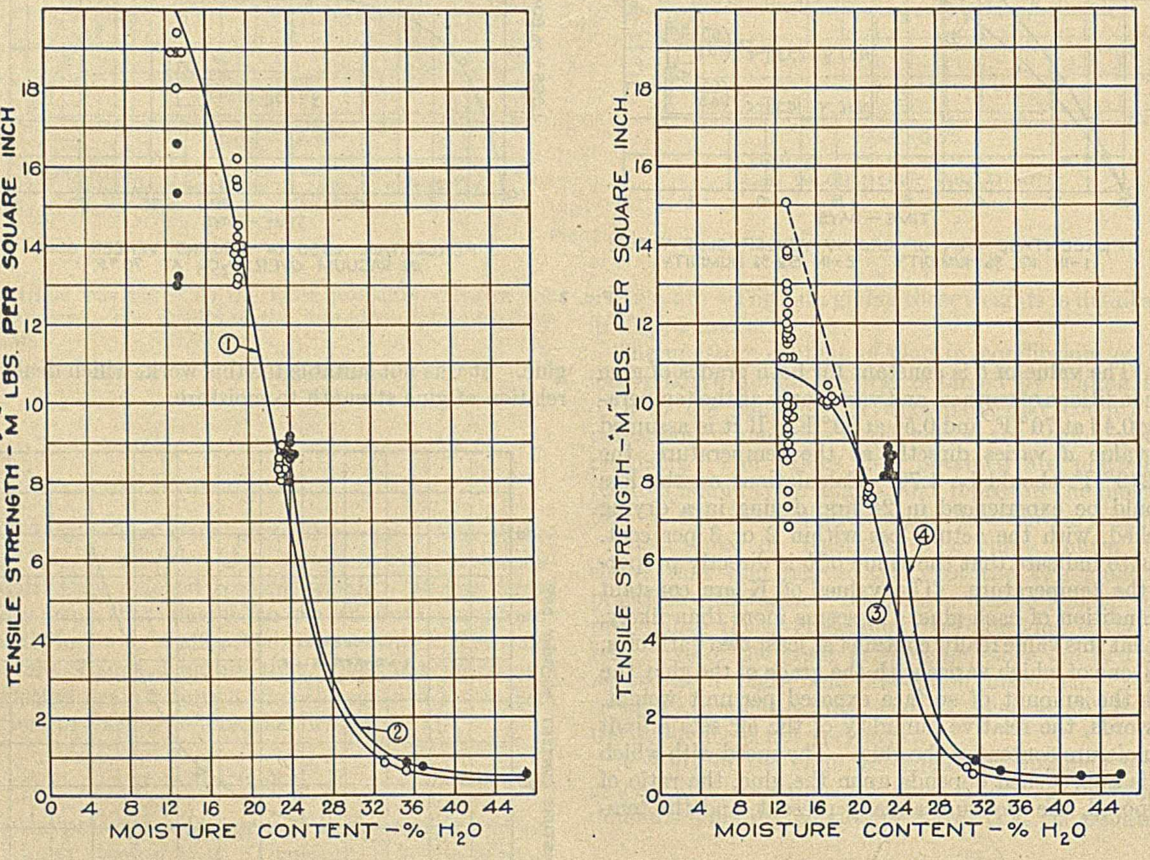
A test of the tensile strength of glue was proposed in 1920 by Hopp.[5] The details of this test were not available at the time this work was undertaken nor would time have permitted the necessary apparatus to be obtained. The following test was devised so that it could be used in an ordinary cement-testing machine which was then available and which was provided with jaws used for testing plywood glue joints. (Fig. 5) The load was applied at the same rate as for plywood at the lower humidities, but it was necessary to slow down the rate of loading at 75 per cent humidity, while at 86, 89, and 100 per cent humidity it was impossible to apply the load continuously because the glue stretched so rapidly. The data at these humidities were obtained by determining what load the glue would lift before breaking and applying this load at the start and stretching the glue as rapidly as possible. The percentage error in these last three humidities is probably very large, but it is thought that the strength values obtained are within 300 lbs. of the correct value. Glue dried in the oven or over phosphorus pentoxide was too brittle and failed in fracture, owing to the pressure of the jaws of the machine, and possibly in bending because of our inability to obtain perfectly flat specimens under these conditions.

RESULTS—The actual load applied to the pieces and the calculated tensile strength per square inch for the two glues tested are shown in Fig. 6.

DISCUSSION OF RESULTS—The strength of the glue as shown in the curves is probably not true tensile strength, but the tensile strength reduced by stresses set up by drying. At moisture contents of 20 per cent and higher there was no apparent brashness, but at 12 per cent and bone-dry it was difficult to obtain a break which was not, in part at least, due to the brittleness of the glue, and was not true tensile strength. Whatever may be the cause of this apparent falling off in strength as tested, the fact remains that the tests made show that even at very low moisture content the strength of the glue is probably as strong as the wood which it holds until the glue reaches a moisture content of about 30 per cent. This would be obtained by a glue kept in an average humidity of 82.5 per cent. At this humidity wood has a moisture content of approximately 17 or 18 per cent.

(C) THE RELATION OF MOISTURE CONTENT TO MOLD GROWTH

It was found that it was not necessary to inoculate the glue with mold spores, because the glue was already well inoculated and when the proper condition was reached mold would start growing. Samples placed in the 100, 89, and 86 per cent humidities molded; those in the 100 per cent humidity molded in 10 days. The moisture content of the glue at



RELATION BETWEEN TENSILE STRENGTH OF GLUE AND ITS MOISTURE CONTENT

NO. 1 HIDE GLUE AT 80°F.
" 2 " " " 70°F.
" 3 VENEER GLUE AT 80°F.
" 4 " " " 70°F.

FIG. 6

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[5] THIS JOURNAL, 12 (1920), 356.

that time was 39 per cent. In the 89 per cent humidity the same glue molded in 14 days. The moisture content at the time of molding was 33.1 per cent. Before molding, the ground glue always matted together in the form of a loose cake. There was no sign of matting in the 75 per cent humidity. At the beginning of molding a sharp rise in the weight of the glue was noted. The same rise in weight was also noticed, but to a lesser extent, in the glue strips. As soon as mold appeared on the strips the test was stopped and their strength determined. The strength data, therefore, may possibly be in error, owing to a slight mold growth, though it is not probable that the error so introduced is greater than the errors in testing.

The observation of the writers in the casting of glue sheets in the laboratory indicates that the mold spores take from 2 to 3 days to produce visible mold growth on the surface of the glue. The moisture content of the glue in the various humidities 3 days before visible mold growth appeared might, therefore, be the point above which mold growth may occur and below which there is not sufficient moisture content to permit growth. The moisture content of the glue in the dishes 3 days before molding appeared is as follows:

100 per cent humidity—33.7 per cent
89 per cent humidity—32.3 per cent
86 per cent humidity—32.8 per cent

This seems to indicate that approximately 32 per cent moisture is required for germination of mold spores. Putting a safe limit at 30 per cent moisture gives us, from the curve in Fig. 4, a relative humidity of 85 as the highest humidity at which hide or veneer glue can be held at a temperature of 80° F. without danger of mold growth. From the data shown under (B) of this report it is apparent that the strength of both glues at 85 per cent has been materially lessened below that required for breaking the wood. From this it seems that if glue specimens were subjected to work at this humidity, mold growth would have practically no effect, because the glue would not be sufficiently strong to hold the glued joint. On the other hand, it might be a factor if the glued joints were stored under high humidities and not subjected to strains.

Conclusions

1—The hygroscopicity of a veneer and a standard hide glue is the same at the same temperatures, as far as the investigation goes. It seems probable, therefore, that all hide glues have the same hygroscopicity at the same temperature.

2—The hygroscopicity of both the veneer and the standard hide glue is greater at 70° than at 80° F.

3—The tensile strength of glue may vary from at least 20,000 lbs. per sq. in. to practically zero, depending upon the moisture content of the glue and the grade of glue. At 30 per cent moisture the two glues tested had a tensile strength of 1700 and 700 lbs. per sq. in.

4—It seems very likely that mold cannot maintain itself below a moisture content of 30 per cent, at which moisture content the glue has already failed in strength.

New Form of Melting-Point Apparatus[1]

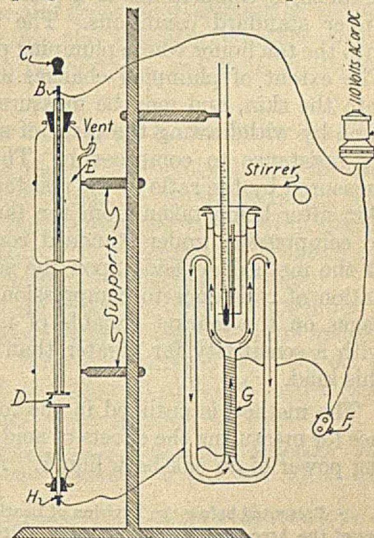
By H. A. Bell

Mallinckrodt Chemical Works, St. Louis, Mo.

This apparatus, which is a modification of the Thiele apparatus, is made of Pyrex glass and is about 12 in. in height. It consists of a sulfuric acid bath, containing the thermometer and the melting-point tube with stirrer, the heat being controlled by a water rheostat. The purpose of the double bath is to prevent any sudden changes of temperature that might cause the sample to melt before the thermometer could register the true temperature; also the direction of circulation is opposite that of a Thiele apparatus. This is to promote more uniform heating of the bath. The middle leg of the apparatus should be somewhat larger than the outside legs, so as not to restrict the flow of the acid. The middle leg is made of $^3/_8$-in. tubing and the outer legs of $^{11}/_{32}$-in. tubing. The middle leg is wound with 50 ft. of No. 34 B & S gage nichrome wire, the ends of which are brought out and attached to brass rings on the outside legs.

The rheostat is composed of a 2- x 20-in. glass tube, having openings at top and bottom to permit the removal or adjustment of the electrodes. A small tube is sealed in the side of the top for the escape of the products of electrolysis. The electrodes should be capable of adjustment of from $^1/_2$ to 16 in. of separation, and are insulated from accidental contact with the operator's hand by inclosing the connecting rod of the adjustable electrode with a small glass tube.

The apparatus is connected to an electric-light plug, or other source of power furnishing 110 volts, by means of a plug, A. One lead from this plug is soldered to the end of the connecting rod of the adjustable electrode B. This rod is incased snugly in a glass tube and capped with a hard-rubber handle, C. The temperature and rate of temperature rise are obtained by varying the distance between the electrodes, D, or by changing the concentration of the salt solution E. The second lead from the light plug is connected to a snap switch, F, and the second lead from the snap switch is connected to the upper terminal of the heating unit G. The lower terminal to G is connected to the lower electrode of the rheostat H.



The current is turned on at F. G heats up the sulfuric acid contained in its core. The acid becomes lighter than the acid in the two outside legs and rises into the body of the apparatus. The circulating acid strikes the base of the inside bath and spreads out conelike, thereby heating up the inside bath from all directions at the same time. The apparatus is easy to operate and gives accurate and consistent results.

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[1] Received February 23, 1923.

Direct Determination of the Plumping Power of Tan Liquors[1]

By John Arthur Wilson and Albert F. Gallun, Jr.

A. F. Gallun & Sons Co., Milwaukee, Wis.

THE DEGREE to which skin is *plumped* in tan liquors is a matter of great practical importance, and concerted efforts have been made to devise a means for measuring the degree of plumping under known conditions. Claflin[2] proposed a method in which a fixed quantity of hide powder was shaken with a known volume of the tan liquor, after which the mixture was filtered and the volume of filtrate taken as a measure of the plumping power of the liquor. Modifications of this procedure have been suggested from time to time, but all methods thus far proposed have been lacking in sensitivity and have failed to make a direct determination of plumping power, relying in each case upon the action of hide powder.[3] The term "plumping" is used by the tanner to indicate an increasing resistance of the skin to compression, which is due to both the swelling of the protein matter of the skin and the changes in properties which this protein matter undergoes during its conversion into leather.

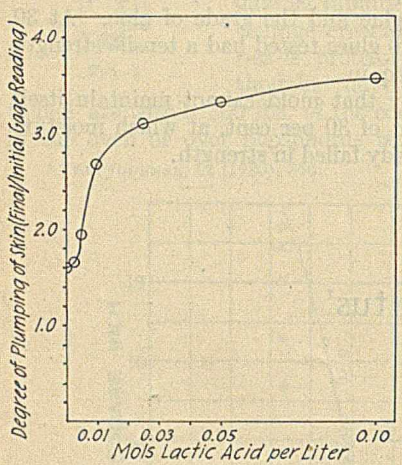

FIG. 1—EFFECT OF LACTIC ACID UPON THE PLUMPING POWER OF A TAN LIQUOR CONTAINING 25 G. OF OAK-BARK EXTRACT PER LITER

In studying the effect of change of hydrogen-ion concentration upon calfskin, the writers[4] devised a method which appears to be capable of measuring the plumping power of tan liquors directly and with great accuracy. The resistance to compression of a piece of skin is first measured under standard conditions. The same piece is then put into the tan liquor whose plumping power is to be determined. The extent of plumping changes as the tan liquor diffuses into the skin, and may be measured for any given lapse of time by withdrawing the piece of skin and again measuring its resistance to compression. The degree of plumping is measured by the ratio of the resistance to compression of the skin after being taken from the tan liquor to its resistance to compression under standard conditions. The sensitivity of the method depends upon the sensitivity of the determination of resistance to compression, and there are thickness gages on the market capable of making this measurement with a sensitivity far greater than is necessary for work of this kind.

The method is outlined in the following description of its use for measuring the effects of acid and salt upon the plumping power of an oak-bark liquor. A piece was selected from the butt of a calfskin, after liming, unhairing, and washing, of as nearly uniform thickness as possible and cut into squares having a side of about 2 cm. These squares were delimed by washing with several changes of 0.01 *M* HCl containing 10 per cent of NaCl, then kept over night in a saturated solution of $NaHCO_3$ containing 10 per cent of NaCl, washed thoroughly, and finally bated for 5 hrs. at 40° C. in a solution of 1 g. per liter of pancreatin, having a pH value of 7.6. The pieces were then washed for 24 hrs. in running tap water, and were kept under distilled water in a refrigerator at 7° C. until used. It was found possible to prepare a month's supply of these squares at one time, there being little or no sign of any decomposition taking place at this low temperature.

The resistance to compression of any piece of skin was measured by means of a Randall and Stickney thickness gage with a flat, metal base, upon which the piece of skin was placed, and a plunger, having a circular base 1 sq. cm. in area, capable of pressing on the surface of the skin under constant pressure. The gage reading was taken, in every case, exactly 2 min. after dropping the plunger onto the skin.

TABLE I—TAN LIQUOR CONTAINING 25 G. OF OAK-BARK EXTRACT PER LITER, AND LACTIC ACID AND SODIUM CHLORIDE AS SHOWN IN TABLE

MOLS PER LITER		GAGE READINGS MM. (AVERAGE OF TRIPLICATES)			Final pH Value at 25° C.
Lactic Acid	Sodium Chloride	Initial	Final	Ratio	
None	None	1.346	2.150	1.60	4.63
0.0025	None	1.411	2.343	1.66	3.94
0.0050	None	1.383	2.699	1.95	3.74
0.010	None	1.433	3.842	2.68	3.47
0.025	None	1.470	4.564	3.10	3.05
0.050	None	1.360	4.497	3.31	2.81
0.100	None	1.434	5.100	3.56	2.52
0.100	0.05	1.456	4.522	3.11	2.49
0.100	0.10	1.458	3.918	2.69	2.47
0.100	0.25	1.461	3.483	2.38	2.43
0.100	0.50	1.420	2.182	1.54	2.37

Eleven tan liquors were prepared as indicated in Table I. The gage readings of pieces of the standard skin were taken and the pieces were then shaken with water to bring them back to their normal shape after being compressed in the gage. They were then put into the tan liquors and allowed to remain there for 24 hrs. at 20° C. In each case three pieces were put into 100 cc. of liquor. The final gage readings were then taken. The results are shown in Table I and in Figs. 1 and 2. The plumping action of acids and the repressing influence of salt are clearly shown.

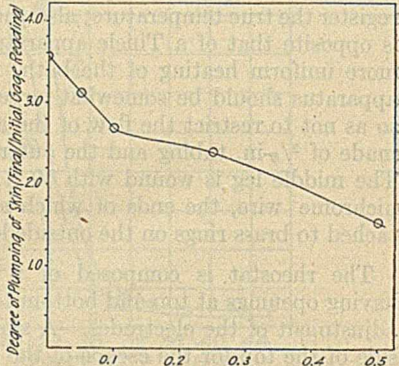

FIG. 2—REDUCTION BY SALT OF THE PLUMPING POWER OF A TAN LIQUOR CONTAINING 25 G. OF OAK-BARK EXTRACT AND 0.10 MOL OF LACTIC ACID PER LITER

This method has the advantage of being able to duplicate exactly the conditions of the tan yard. As the standard, skin may be taken in the condition in which it normally

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] *J. Am. Leather Chem. Assoc.*, **15** (1920), 234.

[3] V. J. Mlejnek, et al., *Ibid.*, **17** (1922), 341.

[4] THIS JOURNAL, **15** (1923), 71.

enters the tan vats. The chief precaution is that all pieces to be compared must be uniform at the time of taking the first gage readings. The pieces may then be put into actual yard liquors. A direct means is thus afforded of rating the plumping powers of tan liquors in actual use on a large scale. Using only ordinary care in the preparation of the test pieces of skin, we found a deviation of only ±0.07 in testing the solutions described in Table I with different pieces of skin; in half the total number of determinations the differences were 0.03 or less. The method obviously may be applied to the determination of plumping power of any kind of solution.

An Improved Method for the Determination of Alpha-, Beta-, and Gamma-Cellulose[1]

By M. W. Bray and T. M. Andrews

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The following improved method for the determination of α-, β-, and γ-cellulose, based upon the titration of organic material in Cross and Bevan cellulose, is more accurate and can be carried out much more rapidly than the gravimetric method. It gives a direct means for the estimation of α-, β-, and γ-cellulose. None of the constants are obtained wholly by difference, as is the case in the gravimetric method. Filtration and washing difficulties of the gravimetric method are practically overcome in the volumetric method. Check determinations can be made without repeating the Cross and Bevan chlorination, as is necessary in the gravimetric method.

The determination of α-, β-, and γ-cellulose is a measure of the resistance of cellulose to the action of 17.5 per cent sodium hydroxide.[2] The application of this determination to pulp cooked by various methods offers a means of evaluating these pulps and possibly a way of showing the relation of one method of cooking to another and of establishing the character of the cellulose resulting from the cooking and bleaching processes.[3] This determination affords valuable data also in the study of decay of wood and wood pulp, showing the change of resistant to nonresistant cellulose during decay.[4]

Practically the first work mentioned on the differentiation of cellulose into α-, β-, and γ-cellulose is that of Cross and Bevan,[5] who used this determination in the estimation of normal celullose. The method for the determination of α-, β-, and γ-cellulose in cellulose obtained by the chlorination method, as worked out in the Cross and Bevan[6] laboratory and described by Jentgen,[7] with but slight modification, has been used in the Forest Products Laboratory for a number of years, in connection with the chemical analysis of American woods.[8] It has also been used in the analysis of cattle food consisting of hydrolyzed sawdust,[9] in the study of decay of wood and pulps,[4] and in the study of the effect of bleaching of pulps.[3]

Gravimetric Method

A number of difficulties and errors are encountered in the gravimetric method of determining α-, β-, and γ-cellulose. This method necessitates careful washing of α- and β-cellulose to completely free them from impurities, and drying without decomposition is very difficult. Cumulative errors introduced in the determination of α- and β-cellulose are included in the determination of γ-cellulose, as this constant is estimated wholly by difference. In order to check the percentages of α-, β-, and γ-cellulose in the gravimetric method, it is necessary to repeat the Cross and Bevan determination, which is a long, tedious process.

The change in the gravimetric method suggested by Opfermann,[10] which consists of washing the α-cellulose with dilute alkali instead of water in separating it from the nonresistant cellulose, gives more concordant results, the separation appearing to be much more complete. This improvement has been used satisfactorily in connection with the authors' volumetric method.

Volumetric Method

Because of the difficulties in the gravimetric method and to obviate the necessity of weighing, the oxidation method proposed by Bronnert[11] for "hemicelluloses" has been extended and modified by the authors to provide a volumetric method of analysis.

Theoretically, cellulose is decomposed as follows upon oxidation with potassium dichromate in sulfuric acid solution:

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O$$

The calculations for the theoretical amount of potassium dichromate necessary for the reaction, together with the method of preparation of solutions, are given in Bronnert's work.

Standardization of Potassium Dichromate Solution

Since the potassium dichromate solution is to be used in oxidizing cellulose from pulps, it is standardized against cellulose obtained by the chlorination method[12] of Cross and Bevan from sulfite pulp. The cellulose equivalent so obtained is used in preference to the theoretical value.

Approximately 1 g. of cellulose (not corrected for ash), dried at 105° C., is taken from a weighing bottle and placed in a 250-cc. beaker. This is triturated with 30 cc. of 72 per cent sulfuric acid and allowed to stand until solution is complete. The sulfuric acid solution is transferred to a

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[1] Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Jentgen, *Z. Kunststoffe*, **1** (1911), 165; Piest, *Z. angew. Chem.*, **26** (1913), 24.

[3] Wells, This Journal, **13** (1921), 936.

[4] Bray and Staidl, *Ibid.*, **14** (1922), 35.

[5] "Researches on Cellulose," **1905-1910**, Vol. III, p. 23.

[6] "Paper Making," **1916**, p. 97.

[7] *Loc. cit.*; *Wag. Jahr.*, **57** (1911), 426; *Z. angew. Chem.*, **24** (1911), 1341; Schwalbe, "Chemie der Cellulose," **1911**, p. 637.

[8] Ritter and Fleck, This Journal, **14** (1922), 1050; Mahood and Cable, *Ibid.*, **14** (1922), 727.

[9] Sherrard and Blanco, *Ibid.*, **13** (1921), 61.

[10] "Die Chemische Untersuchung pflanzlichen Rohstoffe und der daraus abschiedenen Zellstoffe," translated by C. J. West, *Paper*, **8** (1921), 19.

[11] "Die Chemische Untersuchung pflanzlichen Rohstoffe und der daraus abschiedenen Zellstoffe," translated by C. J. West, *Paper*, **18** (1921), 21; Schwalbe and Sieber, "Die Chemische Betriebskontrolle in der Zellstoff und Papier Industrie," p. 151; Schwalbe, "Chemie der Cellulose," **1911**, p. 637.

[12] Schorger, This Journal, **9** (1917), 556.

100-cc. graduated flask. The beaker is washed several times with 72 per cent sulfuric acid to insure complete removal of the dissolved cellulose. The flask is filled to the mark with 72 per cent sulfuric acid and thoroughly mixed. To a 10-cc. portion of the dissolved cellulose, 10 cc. of potassium dichromate solution (containing approximately 90 g. per liter) and approximately 60 cc. of 72 per cent sulfuric acid are added. The solution in the beaker is boiled for exactly 5 min., cooled in ice, and titrated with ferrous ammonium sulfate solution (containing 159.9 g. per liter), using potassium ferricyanide as an indicator. The titration is conducted in the usual way and the point where a drop of the titrated solution gives a blue color with a drop of the indicator is taken as the end-point of the titration. The relative value of ferrous ammonium sulfate solution to the dichromate solution is established by titration in the usual way.

PROCEDURE FOR DETERMINATION OF CELLULOSES

One gram of dry Cross and Bevan cellulose or sample of pulp is weighed into a 250-cc. beaker and triturated with 25 cc. of mercerizing liquid (17.5 per cent sodium hydroxide solution) until the mass is homogeneous, and allowed to stand for 30 min. The contents of the beaker are filtered with suction through an alundum (porosity R. A. 98) or a Gooch crucible. After the insoluble cellulose is sucked practically dry, it is loosened with a glass rod and washed, first with 4 per cent sodium hydroxide solution (50 cc.) and then with approximately 300 cc. of cold distilled water in small quantities.

Since the α-cellulose is dissolved in 72 per cent sulfuric acid, it is not necessary to wash it free from sodium hydroxide, which would be very difficult in cellulose containing a high percentage of β-cellulose. In some cases it is impossible to separate the alkali-insoluble and alkali-soluble cellulose (α- and β-cellulose) by filtration through an alundum crucible, as the cellulose mass becomes very jelly-like[9] because of the presence of β-cellulose. In such cases the alkali-treated cellulose is placed in tubes and centrifuged until the α-cellulose separates at the bottom of the tube. The supernatant liquid is decanted from the α-cellulose and successively washed by decanting and centrifuging, first with 4 per cent sodium hydroxide solution (50 cc.) and then with distilled water, until the total washings approximate 350 cc.

α-CELLULOSE—The alkali-insoluble or α-cellulose is removed from the alundum crucible with a pointed glass rod and placed in a 250-cc. beaker. The filtrate is used for the β- and γ-cellulose determination. It is then dissolved in approximately 30 cc. of 72 per cent sulfuric acid, transferred to a 100-cc. graduated flask by washing successively with portions of the acid, and filled to the mark. A 10-cc. sample is pipetted into a 250-cc. Pyrex beaker, to which are added 10 cc. of standard dichromate solution and approximately 60 cc. of 72 per cent sulfuric acid. The oxidizing mixture is boiled gently for exactly 5 min. and cooled in ice, and the excess dichromate is titrated with ferrous ammonium sulfate solution, as described under "Standardization of Potassium Dichromate Solution."

β- PLUS γ-CELLULOSE—The 350-cc. alkaline filtrate containing the β- and γ-cellulose, remaining from the alkali-insoluble or α-cellulose determination, is diluted to exactly 400 cc. This is divided into two equal parts. One 200-cc. portion, which is left alkaline, is diluted to 150 cc. in a graduated flask. A 25-cc. portion of this solution is pipetted into a 250-cc. beaker. To this are added 5 cc. of the standard dichromate solution and 60 cc. of 72 per cent sulfuric acid. The contents of the beaker are boiled for exactly 5 min., cooled in ice, and titrated as described under the α-cellulose determination. From this titration the sum of the percentages of β- and γ-cellulose is calculated.

γ-CELLULOSE—The remaining 200 cc. of the alkaline filtrate from the α-cellulose determination are acidified with 10 per cent sulfuric acid solution, using one drop of dilute methyl orange as indicator, adding 5 cc. of this acid in excess, and diluting to 250 cc. in a graduated flask. This procedure almost immediately precipitates the β-cellulose. The flask is allowed to stand for several hours, or until the β-cellulose coagulates and settles to the bottom. A 25-cc. portion of the supernatant liquid is pipetted from the flask and treated as described under the β- plus γ-cellulose determination. From this determination the percentage of γ-, or soluble, cellulose may be calculated.

β-CELLULOSE—The percentage of β-cellulose is obtained by subtracting the result of the γ-cellulose determination from the result of the β- plus γ-cellulose determination.

RESULTS

EXPERIMENTS 1 AND 2—Table I gives the results of the analyses of cellulose obtained from Samples 37 and 45, which represent spruce sulfite and aspen soda pulps, respectively. They show how closely duplicate determinations can be made.

TABLE I—VOLUMETRIC ANALYSES OF SPRUCE PULPS

Sample No.	Dry Weight of Sample	α-Cellulose %	β-Cellulose %	γ-Cellulose %
37	1.000	71.5	15.1	11.6
		72.2	15.1	11.6
45	1.000	78.6	17.9	3.8
		78.7	17.4	3.8
2548	0.9473	77.3	12.8	8.1
	0.9473	77.5	12.5	8.4

EXPERIMENT 3—Two portions of spruce sulfite pulp of 0.9473 g. each (dry weight), containing 96.75 per cent of cellulose, were analyzed for α-, β-, and γ-cellulose. These constants were determined in the pulp without first obtaining cellulose by the modified Cross and Bevan method. The results are given in Sample 2548 of Table I.

EXPERIMENT 4—Analyses were made on spruce sulfite pulp (Sample 2548). The results (Table II) show that the volumetric or oxidation method gives results comparable with those obtained by the gravimetric method. Analysis 1 was carried out by the gravimetric method. Analyses 2 to 9 are check volumetric analyses, made on separately chlorinated samples.

TABLE II—COMPARISON OF VOLUMETRIC AND GRAVIMETRIC ANALYSES OF SPRUCE PULP (SAMPLE 2548)[a]

Analysis No.	Dry Weight of Sample	α-Cellulose %	β-Cellulose %	γ-Cellulose %
		Gravimetric Method		
1	1.8925	76.00	16.1	8.0
		Volumetric Method		
2	1.0000	74.6	16.3	8.4
3	0.9575	74.6	17.0	7.8
4	1.0572	77.6		
5		77.0	13.6	8.1
	1.0682	77.0	15.8	8.0
				8.2
6	0.9605	75.0	14.4	8.3
7	0.9624	77.6		
		77.2	13.8	8.9
8	0.9579	76.2	15.5	9.2
				9.4
9	0.9767	75.9	14.2	10.4
	AVERAGE	76.3	15.1	8.6

[a] Complete analysis of this pulp is given in THIS JOURNAL, 14 (1922), 35, Table IV. The data for Analysis No. 1 for α-, β-, and γ-cellulose, in the present paper, were determined after the effect of over-chlorination in the process of isolation of the cellulose was more thoroughly understood and controlled, and therefore differs somewhat from the earlier values.

In THIS JOURNAL, 15 (1923), 19, there appeared a note relative to a new heat- and chemical-resisting enamel. Since then it has been brought to our attention that such white enamels made in other plants have been on the market for some time, and if the impression was given that the enamels there described were the first and only ones with such characteristics, it is an error.—[EDITOR]

The Synthesis of Dicyanine A[1]

By S. Palkin

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

In a previous paper,[2] in which attention was called to the fact that there is no American commercial source of dicyanine dyes, an improved method was described for the preparation of 2,4-dimethyl-6-ethoxyquinoline, one of the principal bases for dicyanine A.

In this paper is described a study of the conditions affecting the synthesis of dicyanine A and an improved process of preparation which yields at least twelve times as much dicyanine A per unit weight of intermediate as that obtainable by the Mikeska-Haller-Adams method.[3]

The process depends on the action of sodium sulfide on α, γ-quinoline intermediates in alcoholic solution, in the presence of small amounts of chloroform.

Dicyanine A, prepared by the method given here, was tested by the Bureau of Standards and found to be an efficient sensitizer.

THE only available supply of the photosensitizing dye, dicyanine, before its preparation in this laboratory, was the German product, "Höchst dicyanine." A method of preparation described by O. Fischer[4] is based on the action of potassium hydroxide on an α, γ-quinoline quaternary salt in alcohol. An improved method, developed by Mikeska, Haller, and Adams,[3] is based on the action of sodium ethylate on the α, γ-quinoline quaternary salt in a medium of absolute alcohol. The yields of dye in both methods are so exceedingly low that unless a large quantity of intermediate is used and great care is taken in the preparation, no solid dye, or a product greatly contaminated with cyanine and tar, can be obtained.

In the preparation of dicyanine by the action of sodium ethylate on α, γ-quinoline intermediate (quaternary salt), at least two types of dyes are formed. One shows a maximum light absorption in the region of 6200 Å. (cyanine), and the other one in the region of 6700 Å. (dicyanine). The relative proportions of these dyes varied in different experiments in which the same intermediate was used. It was obvious that the presence in the original base of other quinolines, such as quinaldines, was not the only or even the principal cause for the formation of contaminating dyes. In order to determine their effect on the speed of reaction, relative tendency toward predominance of cyanine or dicyanine, tar formation, etc., it was therefore decided to test the influence of the following factors—kind of solvent used, concentration of OH-ion, type of alkali, catalysts, water, oxygen, time, and temperature.

No space will be taken for detailed description or for recording results of the numerous qualitative experiments made other than to call attention to the important features.

Variation of Solvent

The first set of experiments involved the variation in the type of solvent. Of the solvents tried—methanol, ethyl alcohol, amyl alcohol, chloroform, pyridine, quinoline, acetone—only chloroform showed any marked effect on the reaction, either when used by itself or in alcoholic solution. Two distinct effects were obtained—the speed of reaction was greatly increased, and cyanine was formed almost to the exclusion of dicyanine. All the other solvents either were no better than, or were inferior to, alcohol, so that the next set of experiments was made with ethyl alcohol as the medium, to test the effect of different alkalies and salts giving an alkaline reaction on hydrolysis. Alcoholic solutions of the following were tried—sodium acetate, potassium acetate, sodium hydroxide, potassium hydroxide, potassium sulfide, and sodium sulfide. Striking results were observed with sodium sulfide. The speed of reaction was markedly increased and the presence of *three* types of dyes was observed spectroscopically—the two previously described and a third showing a maximum in the region of 7200 Å. Of these, dicyanine (6700 Å.) predominated. As 95 per cent alcohol seemed to be somewhat superior to absolute alcohol for this work, and as heat hastened the reaction without apparently introducing injurious factors, as a basis for further study 95 per cent alcohol was used as the medium and sodium sulfide as the alkaline salt, and heat was applied to the reaction.

The first few quantitative experiments (recorded as b, H_1 and H_2 in Table I) showed that the yield of dicyanine was from two to three times as large as that obtained with sodium ethylate,[3] and their quality as observed spectroscopically was about the same. At this point the general plan of study that had been outlined was suddenly interrupted. Accidentally, recovered alcohol was used in some of the experiments instead of the pure 95 per cent alcohol. As recorded in Experiments K_1 and K_2, the yield of dicyanine was decidedly increased. Since the number of impurities known to be present in the recovered alcohol used was rather large, it was some time before it was experimentally proved that this increase was due to a small amount of chloroform. This was somewhat startling, in view of the early experiments which showed clearly that chloroform inhibited the formation of dicyanine to the extent that cyanine was the predominating product. That this was true only when sodium ethylate was used is clearly shown in Experiments G, E, F, C, D, and A, Table I. The yield of dye obtained by the use of sodium sulfide and chloroform was over twelve times that obtained by the Mikeska-Haller-Adams method.

Table I—Comparison of Dicyanine Yields when Sodium Ethylate Is Used, and when Sodium Sulfide Alone and Sodium Sulfide with $CHCl_3$ Is Used

	Intermediate[a] G.	Alcoholic Solution of Na_2S Cc.	Sodium Ethylate	Chloroform Cc.	Time Hrs.	Temperature °C.	Yield Dye G.	Quality
b	1	25	..	..	1	60–70	0.085	Good
H_1	2	45	..	..	2	65–70	0.090	
H_2	2	45	..	..	2	65–70	0.090	
K_1	2	45 (recovered alcohol)	..	Present as impurity	2	65–70	0.575	
K_2	2		..		1/2	65–70	0.400	
G	1	25	..	Few	1	65–70	0.165	
E	1	25	..	..	1	65–70	0.050	
F	1	25	..	2	1	65–70	0.175	
C	1	25	..	2	20	20–25 (room temp.)	0.360	
D	4	100	..	4	1/2	60–70	1.250	
A	1	..	Equiv. of 0.0345 g. Na in 25 cc. alcohol	2	1/2	60–70	None	Solution almost all cyanine

Average obtained by Mikeska-Haller-Adams method: 0.025 g./g. intermediate.

[a] The term "intermediate" used in this and subsequent tables refers to 2,4-dimethyl-6-ethoxyquinoline ethiodide.

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[1] Presented before the Division of Dye Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This Journal, **14** (1922), 704.

[3] *J. Am. Chem. Soc.*, **42** (1920), 2392.

[4] Fischer, Bauer, Scherbe, and Müller, *J. prakt. Chem.*, **98** (1918), 204.

The investigation, therefore, resolved itself into a determination of the optimum conditions for the preparation of dicyanine by the action of alcoholic sodium sulfide and chloroform on the quinoline intermediate.

The general method used in all of the experiments was as follows:

An alcoholic solution of sodium sulfide of the desired concentration was prepared by boiling a weighed amount of $Na_2S.9H_2O$ in 95 per cent alcohol for 2 min. After the hot solution was cooled to the reaction temperature it was filtered, a given volume was poured into an Erlenmeyer flask, and the 2,4-dimethyl-6-ethoxyquinoline ethiodide was dissolved in it. A given volume of chloroform was then added quickly, and the whole was warmed in a thermostatic bath for the time and at the temperature indicated with each experiment. The reaction mixture was then cooled and filtered by suction, and the precipitate was washed, first with 10 cc. of 95 per cent alcohol for each 1 g. of ethiodide used, then with 15 to 20 cc. of U. S. P. ether to remove the alcohol, and finally with enough water (usually from 20 to 50 cc.) to remove all salts, including sodium sulfide. The crystals of dicyanine were then washed with 5 cc. of 95 per cent alcohol to remove the water, and with from 15 to 20 cc. of U. S. P. ether to remove the alcohol, and the air-dried crystals were weighed. The absorption spectra were determined on a 1 in 200,000 alcoholic solution, using a Hilger spectroscope with the Nutting photometer.

The absorption maxima are stated in terms of specific coefficient of extinction, E, where $E = -\log \frac{(Ic)}{(I)}$.[5]

In the concentration of sample used in the experiments (1 to 200,000), the values of the maxima, E, obtained are functions which vary directly with the concentrations of dicyanine and cyanine, respectively, and represent approximately accurate data on the *relative* content of dyes contained in the samples analyzed.

Photosensitizing tests were made in the Bureau of Standards in accordance with their usual methods.

The preparation of definite concentrations of alcoholic sodium sulfide offered some difficulty. Care was taken, however, to use the same alcoholic sulfide solution for any given set of experiments where variables were introduced other than sulfide concentration. Where sulfide itself varied, the other conditions were made empirically uniform for the experiments of that set. Titration of aliquots of the alcohol-sodium sulfide solution, after dilution with water, were made with 0.5 *N* HCl, using methyl orange as indicator. These served as checks for the preparation of subsequent experiments where similar concentrations of sodium sulfide in alcohol were desired.

EXPERIMENTS TO DETERMINE PROPORTION OF CHLOROFORM

The following experiments were made to determine the optimum proportion of chloroform to be used in the reaction:

TABLE II—VARIATION IN AMOUNT OF CHLOROFORM

Uniform Conditions: 1 g. intermediate, 25 cc. Solution A[a] heated 1 hr. at 50° C.

			Absorption Spectrum Maxima at		After Purification	Absorption Spectrum Maxima at	
No.	Chloroform Cc.	Yield Dye G.	6720Å. (Dicyanine)	6200 Å. (Cyanine)	Yield G.	6720 Å. (Dicyanine)	6200 Å. (Cyanine)
1	1	0.320	....	....	0.175	....	....
2	2	0.290	1.01	0.62	0.175	1.40	0.33
3	3	0.235	0.95	0.55	0.155	1.20	0.22
4	4	0.195	....	....	0.140	....	....
5	5	0.150	....	....	0.110	....	....
16[b]	0.5	0.255	1.12	0.55	.....	....	....
17	0.75	0.265	1.16	0.62	.....	....	....
18	1.0	0.280	1.04	0.5	.....	....	....
19	1.25	0.305	1.06	0.66	.....	....	....
20	1.5	0.315	0.98	0.48	.....	....	....
21	2.0	0.285	1.16	0.64	.....	....	....

[a] 20 g. $Na_2S.9H_2O$ boiled in 200 cc. of 95 per cent alcohol for 2 min. Filtrate = Na_2S, Solution A.

[b] New solution of sodium sulfide used in Nos. 16 to 21, inclusive.

The products obtained from Experiments 1 to 5, inclusive, were subjected to further purification by boiling in chloroform and filtering, with the view to concentrating the dicyanine in the insoluble portion and removing most of the more soluble cyanine. As evidenced by spectroscopic examination (Experiments 2 and 3), much higher concentration of dicyanine with respect to cyanine was obtained, but, contrary to expectations, the sensitization test by the Bureau of Standards (Example 2, Table VIII) showed the purified product to be somewhat less effective, as compared with unpurified dicyanine. Crystals obtained from the chloroform-soluble portion (No. 3, soluble portion, Table VIII) gave no better results photographically. The relative concentration of dicyanine with respect to cyanine (determined spectroscopically) is apparently not an absolute criterion of its effectiveness as a sensitizer. This is borne out by further experiments such as Nos. 7 (Table II), 54, and 55 (Table VI). All these proved to be good sensitizers, though they contained relatively less dicyanine and more cyanine than No. 2, Table II.

VARIATION OF SODIUM SULFIDE

As the best proportion appeared to be about 1.5 cc. of $CHCl_3$ to 1 g. of ethiodide, the next set of experiments were carried out using that concentration of chloroform, and varying the concentration of the sodium sulfide. The results are shown in Table III.

TABLE III—VARIATION IN CONCENTRATION OF ALCOHOLIC SODIUM SULFIDE SOLUTION

Uniform Conditions: 1 g. intermediate, 25 cc. alcoholic sodium sulfide,[a] 1.5 cc. $CHCl_3$, heated 1 hr. at 50° C.

				Absorption Spectrum Maxima at	
No.	$Na_2S.9H_2O$ Used per 30 Cc. G.	Yield Dye G.	Physical Appearance	6720 Å. (Dicyanine)	6200 Å. (Cyanine)
25	1	0.070	....	1.24	0.44
26	2	0.150	....	1.25	0.62
27	3	0.185	....	1.15	0.62
28	4	0.240	....	1.24	0.60
29	5	0.315	....	1.25	0.72
30	6	0.325	....	1.25	0.72
31	7	0.350	....	1.22	0.47
32	9	0.390	Difficult to filter	1.25	0.68
33[b]	10	0.260	Dark dull	1.28	0.62
34	12	0.255	Dark dull	0.90	0.60
35	15	0.348	Dark dull	1.00	0.58

[a] Sodium sulfide solutions were prepared by boiling $Na_2S.9H_2O$ in 30 cc. of 95 per cent alcohol for 2 min., cooling and filtering.

[b] Second layer of aqueous sulfide separated in Nos. 33, 34, and 35.

The proportion of chloroform and sodium sulfide, as determined by the results in Tables II and III, was 1.5 cc. of $CHCl_3$ and that concentration of sodium sulfide obtained from boiling 25 g. of $Na_2S.9H_2O$ in 100 cc. of 95 per cent alcohol (approximate average Nos. 31 and 32). These gave the best average results, considering both yield and quality of the dye, and were based on the use of 1 g. of the intermediate.

VARIATION OF INTERMEDIATE

In the next set of experiments the concentration of ethiodide intermediate in the alcohol was varied, while the ratio of chloroform to ethiodide was maintained approximately the same. The results are indicated in Table IV.

TABLE IV—VARIATION IN CONCENTRATION OF INTERMEDIATE WITH RESPECT TO SULFIDE-ALCOHOL SOLUTION

Uniform Conditions: Each experiment, 25 cc. of Solution C,[a] proportion of $CHCl_3$ to intermediate = 1.5 cc., 1 g.; time = 1 hr.; temperature = 50° C.

						Absorption Spectrum Maxima at	
No.	Intermediate G.	$CHCl_3$ Cc.	Yield Dye G.	Yield per G. Intermediate G.	Physical Appearance	6720 Å. (Dicyanine)	6200 Å. (Cyanine)
36	0.5000	0.75	0.100	0.200	Bright green crystals	1.18	0.55
37	1.0000	1.5	0.320	0.320	Bright green crystals	1.08	0.52
38	2.0000	3.0	0.595	0.300	Bright green crystals	1.20	0.65
39	3.0000	4.5	0.970	0.325	Bright green crystals	1.05	1.00

[a] Sodium sulfide solution, C = 25 g. $Na_2S.9H_2O$ per 100 cc. of 95 per cent alcohol and filtering.

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[5] Schook, *Met. Chem. Eng.*, **11** (1913), 494.

Taking into consideration both the yield and quality of the dicyanine product, it appeared that a variation from the original concentration of 1 g. of ethiodide to 25 cc. of alcohol afforded no advantage.

VARIATION OF TEMPERATURE

The next set of experiments was conducted under the most favorable conditions established in Tables II, III, and IV, with respect to concentration of reagents, while the temperature was varied from 40° to 80° C. The results are indicated in Table V.

TABLE V—VARIATION IN TEMPERATURE

Uniform Conditions: 1 g. of intermediate, 1.5 cc. of $CHCl_3$, 25 cc. of Solution D,[a] period 1 hr.

No.	Temperature ° C.	Yield Dye G.	Physical Appearance	Absorption Spectrum Maxima at 6720 Å. (Dicyanine)	Absorption Spectrum Maxima at 6200 Å. (Cyanine)
40	40	0.330	Good	1.08	0.70
45	60	0.290	Good	1.06	0.50
46	B. p. (approx. 80° C.)	0.310	Very dull	0.84	0.55
48	40	0.310	Good bright	0.95	0.60
49	50	0.315	Good bright	1.25	0.65
50	60	0.280	Good bright	1.20	0.55
47[b]	Room temp.	0.215	Bright	1.02	0.75

[a] Alcoholic sodium sulfide solution, D = 25 g. of $Na_2S.9H_2O$ per 100 cc. of 95 per cent alcohol.

[b] Allowed to stand 20 hrs. as yield was too small in 1 hr.

No advantage was gained by using a temperature below or above 50° C. where short periods of time were involved.

VARIATION OF TIME

The following experiments were then carried out, using the optimum conditions derived from the foregoing experiments, while the time of reaction was varied.

TABLE VI—VARIATION IN TIME

Uniform Conditions: 1 g. of intermediate, 25 cc. of Solution E,[a] 1.5 cc. of $CHCl_3$, temp. = 50° C.

No.	Time Hrs.	Yield Dye G.	Appearance	Absorption Spectrum Maxima at 6720 Å. (Dicyanine)	Absorption Spectrum Maxima at 6200 Å. (Cyanine)
51	$\frac{1}{2}$	0.305	Bright green	1.28	0.60
52	$\frac{3}{4}$	0.315	Dark green	1.10	0.60
53	1	0.325	Dark green	1.02	0.60
54	$1\frac{1}{2}$	0.325	Bright green	1.00	0.42
55	2	0.300	Dark green[b]	1.05	0.40
116[c]	3	0.370	Dark green	....	....
117[c]	3	0.435	Dark green	....	....
118[d]	$2\frac{1}{2}$	1.600	Dark green	1.1	0.62
110[e]	$\frac{1}{2}$	0.250	Dark green	1.25	0.52
111[e]	2	0.360	Dark green	0.85	0.62

[a] Sodium sulfide solution, E = 25 g. of $Na_2S.9H_2O$ per 100 cc. of 95 per cent alcohol.

[b] Washed with ether; ether-soluble matter considerable.

[c] Solution F = new sodium sulfide solution used in Nos. 116 and 117.

[d] Expt. 118, used 4 g. of intermediate, 100 cc. of sodium sulfide solution.

[e] New solution of Na_2S.

As evident from Table VI, the slight increase in yield obtained by prolonging the heating to several hours was not worth while because of the inferiority of the product thus obtained. The highest concentration of dicyanine was given in Experiment 51, where the period of heating was $\frac{1}{2}$ hr. Experiments 110 and 111 showed the same tendency.

It was already evident from a few sporadic experiments (No. 47, Table VII) that good results could be obtained by allowing the reaction mixture to stand for a day at room temperature. As shown by the experiments in Table VII, a greater yield of dye may be obtained thus, while a variation in the chloroform concentration (within reasonable range) appears to have little effect.

TABLE VII—EXPERIMENTS OVER LONG PERIOD OF TIME AT ROOM TEMPERATURE WITH VARIATION IN $CHCl_3$

Uniform Conditions: 1 g. of intermediate, 25 cc. of sodium sulfide,[a] temp. = room temperature, period 22 hrs.

No.	Alcoholic Na_2S Soln. Cc.	$CHCl_3$ Cc.	Yield Dye G.	Appearance	Absorption Spectrum Maxima at 6720 Å. (Dicyanine)	Absorption Spectrum Maxima at 6200 Å. (Cyanine)
104	25 H_1[a]	1	0.450	Bright green	1.12	0.78
105	25 H_1	$1\frac{1}{2}$	0.450	Bright green	1.02	0.75
106	25 H_1	2	0.430	Duller green	1.00	0.55
107	25 H_2[a]	1	0.350	Bright green	0.70	0.64
108	25 H_2	$1\frac{1}{2}$	0.350	Dull green	1.10	0.85
109	25 H_2	2	0.370	Bright green	1.11	0.85
7	25 Soln. A	2	0.355	....	0.90	0.54
3a	Special Soln. 25	2	0.300	....	1.15	0.68
5a	Special Soln. 25	...	0.085	....	1.20	0.60

[a] Sodium sulfide solution, H = 50 g. of $Na_2S.9H_2O$ per 200 cc. of 95 per cent alcohol; designated, H_1 when hot solution was used; designated H_2 when cold solution was used.

Although the investigation was largely confined to dicyanine A IV, experiments were made with dicyanine IV and A VI, using the corresponding intermediates. The foregoing method was found applicable to these, although the yields were not as good as that obtained with A IV.

SENSITIZATION TESTS

As the reports obtained from the Bureau of Standards on the practical performance of the dyes are very comprehensive, only such data are recorded (Table VIII) as will bring out important features.

ACKNOWLEDGMENT

The author wishes to express thanks to Dr. W. F. Meggers and Mrs. F. J. Stimson, of the Bureau of Standards, for their valuable coöperation.

TABLE VIII—SENSITIZATION TESTS MADE BY THE BUREAU OF STANDARDS

No.	Description	Solubility	Quality as Sensitizers	Speed	Behavior up to 7500 Å.	Behavior up to Beyond 7500 Å. to 9000 Å.
4	Sample prepared by old method		Equivalent to Höchst			
2	No. 2, Table II, after purification with $CHCl_3$	Not readily soluble	Fairly good sensitizer	Not as good as No. 3		
3	Obtained from $CHCl_3$ soluble portion of No. 3, Table II			Not as good as No. 4		
7	Table VII		Very satisfactory	3 times as fast as No. 4	As good as Höchst	As good as Höchst
3a	Table VII					
5a	Table VII			2 times as fast as No. 4		
16	Table II			$2\frac{1}{2}$ times as fast as No. 4		
51	Table VI		Same as No. 16			Not quite as good as Höchst
54	Table VI					
55	Table VI		Same as No. 5a			
118	Table VI		Between Nos. 54 and 55 (up to 7500 Å.)		Less than No. 55	Quite as good as Höchst (No. 7 somewhat superior in monochromatic work)

Vapor Pressures of Carbazol, Observed and Calculated[1,2]

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A table of vapor pressures for carbazol between the temperatures 250° and 355° C. has been given.

The boiling point of carbazol has been determined and found to be 354.76° C. instead of 351.5° C., as given in the literature.

Interpolation formulas have been derived for vapor pressures and latent heat of vaporization.

IN a former paper by the authors[3] was given a résumé of the literature on vapor-pressure methods and a detailed description of the static method and apparatus used, in making vapor-pressure determinations on naphthalene, anthracene, phenanthrene, and anthraquinone.

The work done on carbazol as reported in this paper consisted of (1) purifying the compound, and (2) determining the vapor pressures at brief temperature intervals from slightly above the melting point to a few degrees above the boiling point, using the same apparatus as described in the previous paper.

In the purification of carbazol, a mixture containing 82 per cent of this compound was used as a starting material. In order to remove the anthracene, phenanthrene, and other impurities, this material was washed three times with benzene at 50° C., each time keeping the mixture well agitated for 30 min. or more. After the third washing the residue was dissolved in boiling benzene, the solution was cooled to room temperature, and the crystalline material filtered off and dried. A melting point of 243° C. was obtained. The material of this melting point was then recrystallized from toluene. These well-dried crystals melted at 244.8° C. Three more recrystallizations from toluene did not change this melting point.[4]

TABLE I

B. P., 354.76° C.

Temp. °C.	Vapor Pressure Mm.	Temp. °C.	Vapor Pressure Mm.
252.61	70.1	309.85	303.7
258.28	82.9	310.81	307.6
259.43	85.3	311.73	317.8
261.99	92.8	315.77	348.4
266.13	103.4	320.85	385.5
270.15	114.9	322.80	401.2
274.34	128.6	326.60	436.6
276.31	135.2	332.65	491.2
281.93	156.6	343.42	610.9
288.02	181.0	348.05	669.4
290.09	191.0	348.26	672.1
291.25	197.2	350.05	693.0
292.65	202.2	354.28	753.4
294.40	212.8	354.49	759.4
298.16	231.5	354.72	761.3
302.71	260.6	357.31	797.8
307.18	286.5	357.71	807.2

TABLE II

B. P., 354.76° C.

Temp. °C.	Vapor Pressure Mm.	Temp. °C.	Vapor Pressure Mm.
250	65.0	305	271.4
255	75.9	310	303.8
260	87.9	315	339.4
265	101.1	320	378.5
270	115.7	325	421.1
275	131.9	330	467.7
280	149.7	335	518.2
285	169.4	340	573.0
290	191.2	345	632.1
295	215.3	350	695.8
300	242.0	355	763.9

Using this purest sample four analyses were made for nitrogen. An average result of 8.22 per cent was obtained. The calculated per cent of nitrogen present in carbazol is 8.38.

This material was therefore accepted as pure and was used for the vapor-pressure determinations. The pressures observed during three experimental runs are tabulated with their corresponding temperatures in consecutive order in Table I. Using these results, a curve was drawn and readings taken from it at 5 degree temperature intervals. These readings are recorded in Table II and represent the interpolated values obtained from the curve.

Since no data on the vapor pressures of carbazol over the range of temperature covered in these tables seem to be available, the authors have no way of comparing these results with those of other investigators. It should, however, be pointed out that the literature gives the boiling point of carbazol as 351.5° C. The samples the authors worked with all failed to show a pressure of 760 mm. until the temperature of 354.76° C. was reached.

An interpolation formula that will fit these values may readily be derived from the Clapeyron equation of state—likewise an expression for the latent heat of vaporization.

The relation between pressure, temperature, and latent heat of vaporization may be expressed by the equation

$$\frac{dP}{dT} = \frac{L}{\frac{RT^2}{P}} \tag{1}$$

where $\frac{dP}{dT}$ denotes change of pressure with temperature, L is the molar heat of vaporization, T, absolute temperature, and R, the gas constant, 1.9885.

Integrating this equation between limits we get

$$\ln\frac{P_2}{P_1} = \frac{L}{R}\;\frac{1}{T_1} - \frac{1}{T_2} \tag{2}$$

Changing over to $\log_{10}$ and solving for L, Equation 2 becomes

$$L = (\log p_2 - p_1)\;T_1T_2\;\frac{2.303\;R}{T_2 - T_1} \tag{3}$$

by which we are enabled to determine the change in L with temperature and pressure.

The values for L were calculated for a number of temperatures and pressures, and plotted on coördinate paper. Over the range of temperature investigated the curve for L was a straight line expressed by the equation

$$L = 22799 - 13.0\,T \tag{4}$$

Substituting this value for L in Equation 1 and integrating, we obtain

$$\ln p = -\frac{22799}{RT} - \frac{13.0}{R}\ln T + C$$

which, when changed over into $\log_{10}$ by dividing by 2.303, becomes

$$\log p = 24.2313 - \frac{4570.3}{T} - 5.0288\log T$$

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[1] Presented before the Division of Dye Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Published as Contribution No. 65 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] THIS JOURNAL, **14** (1922), 58.

[4] Since this paper was written occasion arose for the purification of more carbazol. The method used was the same except that three crystallizations were made and all from benzene. The melting point obtained was the same as that recorded above.

This equation will give results for p that are in good agreement with the observed values, as the following table will show:

Temp. ° C.	Pressure Obs. Mm.	Pressure Calcd. Mm.	Temp. ° C.	Pressure Obs. Mm.	Pressure Calcd. Mm.
260	87.9	88.0	340	573.0	573.0
280	149.7	150.1	350	695.8	694.3
300	242.0	242.4	355	763.9	764.1
320	378.5	380.5	...	.....	.....

In order to determine whether this compound behaves as a normal liquid, the entropy of vaporization was calculated at about 260° C. where the concentration of the vapor is 0.00507 mol per liter (approx.).[5] This result gave 14.9 against about 13.7, the average obtained by Hildebrand for about 15 liquids. From this observation it seems a bit questionable whether carbazol ought to be considered as a normal liquid.

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[5] *J. Am. Chem. Soc.*, **37** (1915), 970.

The Analytical Detection of Rancidity[1]

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The only sound basis for the analytical detection of rancidity is an accurate knowledge of the nature of rancidity, its cause, and the chemical changes incident to its development. Unless applied in the light of accurate knowledge, analytical tests are apt to be misleading.

Rancidity may be defined as a characteristic, spontaneous change which takes place in fats. This definition is not wholly satisfactory, as it includes certain conditions which are commonly called rancidity but are not in fact true rancidity. A notable example is the so-called rancidity of butter. Investigation has shown that this, in most cases at least, is really a decomposition of the milk proteids present, with or without accompanying hydrolysis of the fat. The rancidity of pure, dry fats is of a different nature and is the result of a different series of changes. For the purposes of this paper, the term "rancidity" will be used only in reference to changes in the fat itself, and not at any time to alterations in any substance with which the fat is mingled, or to hydrolysis.

When a rancid fat is examined, the first points which attract attention are the characteristic odor and taste. When well developed and not obscured by odors and flavors due to other causes, they afford a sufficient means of recognition and further tests are not needed. In case of fats originally of good quality and which have not absorbed extraneous odors and flavors, there is but little, if any, need of analytical tests, but it is not always such fats which are sent to the laboratory for judgment. Rancidity is often only one of several factors which must be considered in deciding whether or not a fat is fit or unfit for food.

Characteristics of Rancidity

While changes in the ordinary characteristics are without value in detecting rancidity, they are of some interest and will be briefly considered.

Changes in the free acid are of particular interest. It was formerly supposed that rancid and acid fats were identical, but it is now known that these conditions bear no relation to each other. Determination of free acid is, therefore, without value for the recognition of rancidity. The changes in the percentage of free acid during the development of rancidity are, however, of interest. If a clear, sweet fat is allowed to develop rancidity and the free acid is determined at regular intervals, it will be noted that during the first few weeks the precentage of free acid remains stationary, or perhaps shows a slight increase. Then a sudden drop is noted, the percentage of free acid falling off 0.2 to 0.4, or even more. Coincidently the physical signs of rancidity begin to appear. Following this reduction in the percentage of free acid there begins an increase in acidity. In one particular instance, an acidity of 0.45 per cent at the beginning of the experiment dropped to 0.23 per cent and then rose to 3.05 per cent after one year's exposure.

The iodine number suffers a reduction. In one set of fats the reduction varied from approximately 4 to approximately 7 per cent during one year's exposure. The variation in the iodine number is insufficient for the recognition of rancidity.

The heat of combustion decreases and the specific gravity and viscosity increase. These changes are not of analytical value.

After the fat has become badly rancid there is an increase in the saponification number due to the formation of acids of lower molecular weight than those occurring in the original fat.

The percentage of unsaponifiable matter increases. In moderately rancid fats the increased amount of unsaponifiable matter may interfere with the detection of phytosterol by methods dependent upon saponification of the fat and extraction of the unsaponifiable matter.

Causes of Rancidity

As the ordinary characteristics cannot be depended upon for the detection of rancidity it is necessary to resort to special tests. Before considering these, however, it is desirable to examine into the causes of rancidity and the character of the changes involved. It is now common knowledge that rancidity is due to spontaneous oxidation. While its development is influenced by several factors, it is due wholly to oxidation and can occur only in the presence of oxygen. The relation between oxygen and rancidity has been noted by numerous observers and has been clearly pointed out by the author.[2] The exact nature of the changes involved, their origin, and the character of the products formed are less clearly known. It is possible at the present time, however, to formulate an hypothesis which appears to be in accord with the facts and in harmony with accepted theories of organic chemistry. This hypothesis is originally due to Vintilesco and Popesco,[3] who observed that fats of good quality when exposed to light and air become rancid without increase of acidity. This fact led them to assume that fats are able to fix oxygen from the air without previous hydrolysis. It seemed to Vintilesco and Popesco that the oxygen ought to be easily displaced from such fats by readily oxidizable substances, particularly in connection with peroxi-

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[1] Presented before the Division of Agricultural and Food Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

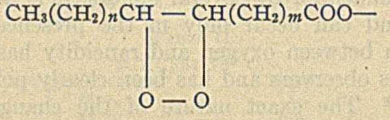
[2] Kerr, This Journal, **10** (1918), 471; *Cotton Oil Press*, **5** (1921), 35.

[3] *J. pharm. chim.*, **12** (1915), 318.

dases—or, in other words, that rancid fats ought to contain loosely combined or labile oxygen. Experimental confirmation was obtained, rancid fats being found to give a reaction when mixed with a readily oxidizable substance (tincture of guaiac) and a source of peroxidase (solution of hemoglobin). Fresh, sweet fats did not give the reaction but developed the power of reacting after a comparatively short exposure to light and air. Vintilesco and Popesco therefore concluded that the primary distinction between sweet and rancid fats lay in the presence of loosely combined or labile oxygen in the latter.

The authors' experiments have confirmed and extended the experimental bases of this hypothesis. The presence of labile oxygen in rancid fats has been confirmed by experimental tests. The authors have found that rancid fats contain oxygen in such a form as to react with tincture of guaiac and hemoglobin, and that the peroxidase of the hemoglobin can be replaced in the reaction by other peroxidases, particularly that of horse-radish. They have found further that, when a rancid fat is shaken up with water and the clear water extract is added to a dilute solution of ferric chloride and potassium ferricyanide, a slight reaction is obtained. If an alcohol extract of the rancid fat is substituted for the water extract, an intense precipitate of Prussian blue is obtained. Sweet fats give no such reaction. The reagent described is a standard reagent for the detection of peroxides and is sensitive to minute traces of water-soluble peroxides. It may be considered proved, therefore, that rancid fats contain bodies similar in chemical composition and behavior to the organic peroxides, and that these bodies are of such high molecular weight and so closely related to the fatty acids as to be insoluble in water. The slight reaction obtained when fats are extracted with water is attributed to molecular interchange between these bodies and the water with formation of minute amounts of hydrogen peroxide, rather than to the existence of soluble peroxides in the fat. It is noteworthy that the appearance of the hemoglobin-guaiac reaction and the peroxide reaction are the first deviations from normal which are observed when fats are allowed to become rancid.

This fact, taken in connection with the well-known fact that only those fats which contain glycerides of unsaturated acids become rancid, leads directly to a more complete hypothesis regarding the beginning of rancidity. This hypothesis is that the first step in the development of rancidity is the entrance of one molecule of oxygen into a molecule of an unsaturated fatty acid, either free or combined, the oxygen molecule attaching itself at the point of double linkage and forming a compound characterized by the peroxide grouping at that point. An illustrative structural formula is presented herewith:



$$\mathrm{CH_3(CH_2)_nCH - CH(CH_2)_mCOO—} \quad (\mathrm{O—O} \text{ bridging the two CH groups})$$

Only a single molecule of acid is shown. It makes no difference for the purpose in hand whether it is or is not combined with the glyceryl radical to form part of a glyceride. Certain evidences, particularly the peculiar behavior of the free acid noted when fats become rancid, the fact that fats of high acidity turn rancid most readily, and the solubility of the compounds giving the peroxide reaction in alcohol, indicate that uncombined acid is attacked at the beginning. As it is not possible to remove rancidity even in the incipient stages by treatment with caustic alkalies and removal of all free acid, it is probable that the combined acids are attacked at the same time.

The formation of such a compound as indicated in the illustrative formula is suggested as the initial step in the development of rancidity. Such a compound would necessarily be unstable and would certainly be a potent carrier of oxygen. The intimate contact between such a compound and the unchanged glycerides would naturally favor the entrance of oxygen into the glycerides and so bring about reactions which could not be caused by the free oxygen of the air. The formation of such a compound in such a situation and in the presence of a supply of free oxygen would naturally be followed by active oxidation. It is well known that rancid fats do take up oxygen and do contain a variety of products all of which are capable of being derived from the constituents of the fat by oxidation. Among these may be mentioned aldehydes, ketones, fatty acids of lower molecular weight than those originally present in the fat, esters of the same, alcohols, oxy- and hydroxy-acids, lactones, anhydrides, and peroxides. All of these may be derived from such a compound as the one illustrated, by molecular rearrangements, with or without further introduction of oxygen from the air.

ANALYTICAL TESTS

It has been pointed out in support of our tentative hypothesis that the first analytical indication of rancidity is that the fat gives the reaction proposed by Vintilesco and Popesco and similar reactions indicating the presence of labile oxygen. The analytical use of this test has been investigated.

Briefly described, this test consists in shaking 10 cc. of the suspected fat with 10 drops of an aqueous solution of hemoglobin, 5 drops of an alcoholic solution of guaiac (5 g. guaiac in 100 cc. of 70 per cent alcohol) and 10 cc. of distilled water. The development of a blue color after standing for a short time indicates rancidity. A saturated salt solution may be substituted for the distilled water. The effect of the substitution is to make the development of the color more rapid and to confine it to the fat layer. The addition of 10 cc. of alcohol to the mixture after shaking, or the substitution of alcohol for the distilled water, makes the test more sensitive, intensifies the color, and causes the reaction to take place in a shorter time. A preparation of horse-radish may be substituted for the hemoglobin with satisfactory results.

This test has been tried out on a considerable number of fats, both rancid and sweet. All fats which were clearly rancid gave good reactions. The reaction was negative with most fats which were unquestionably sweet. Numerous fats which were not recognizable as rancid by any other means gave positive reactions. From experimental study of some of these, as well as the theoretical considerations outlined above, it is thought that the earliest stages in the development of rancidity in these fats had set in; but as they were not recognizable as rancid it is evident that this test is too delicate for use as a standard of edibility or fitness. Attempts to measure its intensity were not successful. Neither the intensity of the color nor the amount of fat required to give the reaction in dilution with nonreacting fats bears any relation to the degree of rancidity.

It was found further that the power of reacting was destroyed by heating the fat, by extracting it with hot water, and by shaking it with a solution of sodium sulfite.

It has been found that this test, unlike the Kreis test, is applicable to crude and to freshly refined cottonseed oil. Fresh, sweet, crude cottonseed oil was found to give no reaction. When exposed to the air it gave a positive reaction. That this was due to the development of rancidity was shown by the fact that a strong and unmistakable rancidity developed on continued exposure.

The value of this test for analytical purposes is limited on account of its hypersensitiveness, the absence of any quantitative character, and the ease with which the fat may be rendered nonreactive, but it is of possible utility in the examination of cottonseed oil. It is of interest chiefly as giving light on the origin and mechanism of rancidity, as it apparently depends on the first formed and most unstable compound associated with that condition.

Issoglio[4] found that the development of rancidity led to the formation of volatile substances which could be separated by distillation with steam and determined by oxidation with potassium permanganate, and which increased in amount as rancidity developed. He proposed a method for the recognition of rancidity based on this observation. A study of this method, previously published,[2] led to a modification which has proved to be more rapid and satisfactory than the original method. The modification consists in extracting the fat with hot water instead of distilling it with steam.

Twenty-five grams of the fat are weighed into a 200-cc. Erlenmeyer flask and 100 cc. of distilled water added. The flask is alowed to stand on the steam bath for 2 hrs., with occasional shaking. At the end of this time the water is separated from the fat by filtering through a filter paper closely fitted to the funnel and thoroughly wetted. The whole contents of the flask is poured on the wet paper. The water containing the soluble matters extracted from the fat runs through, while the fat is completely retained. The filtrate is caught in a 100-cc. graduated flask. After cooling, the flask is made up to the mark, shaken thoroughly, and 10 cc. taken for titration. This aliquot is mixed with 50 cc. distilled water, 10 cc. of 20 per cent sulfuric acid added, 50 cc. of 0.01 *N* potassium permanganate solution run in, the mixture heated to boiling, and boiled 5 min. under a reflux condenser. After cooling, 50 cc. of 0.01 *N* oxalic acid solution is run in and the excess titrated with 0.01 *N* potassium permanganate. The oxidizability value, representing the number of milligrams of oxygen required to oxidize the water-soluble constituents of the fat, is calculated by multiplying the number of cc. of 0.01 *N* potassium permanganate required in the experiment, less that required in a blank test, by 80, and dividing by the weight of fat taken.

This test is really a measure of the water-soluble, oxidizable bodies present. The amount of these is not necessarily in direct proportion to the degree of rancidity, as part of them are continually being lost by volatilization. As they are readily removed by washing or by blowing with steam, the test is of little value unless the history of the sample is known.

Fahrion[5] has called attention to the presence of oxidized fatty acids in rancid fats. These acids are distinguished from the unchanged fatty acids by the fact that they are insoluble in petroleum ether. The Fahrion method is as follows:

Saponify approximately 3 g. of the oil with alcoholic potash and drive off the alcohol by evaporation. Dissolve the soap in 50 to 70 cc. of hot water and transfer to a separatory funnel. When cool add 100 cc. of petroleum ether. Acidify the solution with hydrochloric acid, shake carefully, and let stand over night. Draw off the water solution and filter off the petroleum-ether solution from the precipitate of oxidized acids. Wash these with petroleum ether several times and dissolve in the smallest possible amount of warm alcohol. Transfer the alcoholic solution to a tared dish, evaporate off the alcohol, and weigh. Do not allow the temperature of drying to exceed 95° C.

This method was tested with sweet and rancid fats. Traces of fatty acids insoluble in petroleum ether were found in all cases. These amounted to mere traces in fresh, sweet fats. The highest percentage of oxidized acids found in a sweet fat was 0.17. A sample of lard condemned as rancid, although not badly so, was found to contain 0.55 per cent, a distinctly rancid sample of linseed oil 0.87 per cent, a badly rancid lard 5.25 per cent, and an extremely rancid sample of soy-bean oil 27.95 per cent. Unlike the volatile bodies on which the oxidizability value depends, the oxidized acids accumulate and are not lost by volatilization. This test has the advantage of depending upon the most stable and the most difficult to remove of all the known products of rancidity. It has been found that the oxidized acids, in part at least, are combined with glycerol, so that removal without saponification of the fat is not possible. This test is, of course, without value in the case of castor oil and other oils containing glycerides of hydroxylated fatty acids.

KREIS TEST

The most valuable and generally applicable test for the detection of rancidity is the Kreis test. As a paper dealing with this test has previously been published[2] it will not be described at length here. It consists in shaking a portion of the suspected fat with concentrated hydrochloric acid and an ether solution of phloroglucin. A red or pink color indicates rancidity. It is due to the presence in rancid fats of bodies which are capable of uniting with phloroglucin in the presence of strong hydrochloric acid to form unstable, red-colored compounds. The exact nature of these bodies is not known, but they are thought to be of the nature of aldehydes and ketones. This view finds support in the fact that certain bodies containing aldehyde and ketone groupings form red compounds with phloroglucin under similar conditions. Particular examples mentioned in this connection are cinnamic aldehyde and vanillin. Experience with the Kreis test has confirmed the conclusions previously advanced—namely, that all rancid fats react, that the intensity of the reaction is roughly but not exactly proportional to the degree of rancidity, and that sound, sweet fats do not react except in certain special cases, of which crude cottonseed oil is a notable example. The Kreis test is used as a routine test in the meat-inspection laboratories of the Bureau of Animal Industry. Details of the test follow:

To 10 cc. of the suspected oil or melted fat in a large test tube (8 x 1 in.) add 10 cc. of HCl (sp. gr. 1.19). Close the tube with a rubber stopper and shake vigorously for approximately 30 sec. Add 10 cc. of a 0.1 per cent solution of phloroglucin in ether, close the tube, and shake as before. Allow it to stand and separate. A red or pink color in the acid layer indicates rancidity.

The depth of color is roughly but not exactly proportional to the degree of rancidity. To determine the intensity of the reaction the original fat is diluted with an oil or fat which does not react, preferably white mineral oil or liquid petrolatum, U. S. P., and the intensity judged by the degree of dilution at which a reaction ceases to be observed. In judging this point, a recognizable red or pink shade is regarded as a reaction, a faint orange or yellow is not so regarded. The intensity of the reaction is reported in terms of the highest dilution at which a reaction is obtained. For example, if a fat is found to react when so diluted that there is 1 part of the fat in 20 parts of the mixture but not in higher dilution, it is reported as reacting in dilution 1 to 20.

The principal utility of the Kreis test in inspection work is in distinguishing fats which have an "off" or disagreeable odor and flavor due to other causes than from rancid fats. As the test appears some time before rancidity becomes evident to taste and smell, it should have considerable commercial utility in giving warning of the development of rancidity.

In using analytical tests for the recognition of rancidity, it must be kept in mind that it is a condition and not a definite substance for which the fats are being tested. All the analytical tests depend upon the presence of one or more of the individual products associated with the condition or formed during its development. The tests are, therefore, to be regarded only as more or less valuable aids to judgment, and not as a means of dispensing with judgment. If employed without intelligent understanding of their purposes and limitations they are apt to be misleading, but if used with discretion and sound judgment they are of much value. The Kreis test in particular is recommended as the most practical and reliable, as well as the best adapted for general use.

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[4] *Ann. chim. applic.*, **1916**, 18.

[5] *Chem. Umschau Fette, Oele, Wachse u. Harze*, **16** 1920, 158.

The Determination of Ash in Cuban Raw Sugar[1]

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In common with others, the writers have been accustomed to determine ash in sugar and sirups from refinery and experimental work by direct incineration. For most purposes there is a strong tendency in the literature in favor of the sulfate method. The fact that Bates[2] *used the sulfate method in his standardization of commercial white sugars led the writers to investigate to what extent the use of the sulfate method was justified and also the relation of sulfate-ash results to those by direct incineration. In this work the sulfate method has been compared not only with the ordinary direct-incineration method, but also with various modifications of that method. All determinations in this work were on a 96° Cuban raw sugar.*

The work of the writers indicates:

1—The direct-incineration method is simpler and more rapid than the sulfate method.

2—A modification of the usual sulfate method, in that the requisite dilute sulfuric acid is added to the sugar before heating, gives more foaming than the standard sulfate procedure, but is more rapid as a whole and gives equivalent results.

3—The greater tendency to foam over with direct incineration can very easily be avoided by preliminary heating on a hot plate.

4—Of the various modifications of the direct-incineration method tried, the benzoic acid modification is rapid, but gives a fluffy ash, easily lost; the vaseline oil modification is a good preventive of the foam-over trouble; ammonium carbonate causes loss by spattering; ignition with sand reduces foaming, but prolongs the carbon combustion and gives low results; zinc oxide prevents foaming and evidently retains volatile ash constituents, giving results between the direct-incineration and the sulfate methods; lixiviation methods show no advantage over ordinary direct incineration.

5—No difficulty due to gradual increase in weight is experienced in weighing the ash from ordinary direct incineration.

6—The conclusion of Meyer, that porcelain dishes could be substituted for platinum without sacrifice of accuracy in the sulfate method of ash determination, is confirmed for porcelain crucibles. It is also found that porcelain crucibles, used so extensively now, are as accurate as platinum for ordinary direct incineration.

7—The value for sulfated ash on this sugar, even with the customary 10 per cent correction, is about 34 per cent higher than the ash by direct-incineration methods, or actually, when no correction is made, a total of 49.80 per cent higher than by direct incineration.

8—No such undue loss in weight of ash upon ignition was experienced as was mentioned by Landolt.

The various methods proposed for the determination of ash may be classified as: (1) sulfate methods, (2) direct-incineration methods, and (3) conductivity methods.

Previous Work

Sulfate Methods—When the term "ash" is employed in the literature without qualification, sulfated ash is generally understood. The advantages claimed for the method are—quicker carbonization and combustion of carbon than by direct incineration, practically no danger of loss by volatilization through prolonged heating, or too high temperature; also the ash constituents converted into sulfates do not gain weight during weighing.

The custom of subtracting 10 per cent of the sulfated ash from its total, to convert to true ash or back to the direct-incineration basis, is known to apply only in accidental cases. For beet sugar this factor has been found to be 12 to 15 per cent, and for cane sugar from 6 to 26 per cent.[3] It would be more accurate to multiply the sulfated ash by 0.7 than by the factor now used by the sugar trade (0.9) for raw sugars.[4]

Either porcelain or platinum dishes can be used for the determination.[5] Silica dishes, owing to their excessive weight for their capacity and their continual loss in weight, are not recommended.[6]

Direct-Incineration Methods—It is claimed that the ordinary direct incineration has these disadvantages—the difficulty in obtaining a carbon-free ash, and danger in expelling volatile salts.

The loss on heating ordinary direct-incinerated ash as determined by Landolt[7] is as follows:

Weight of Residue G.	Loss on Heating for			
	30 Min. G.	60 Min. G.	90 Min. G.	120 Min. G.
0.01	0.002	0.004	0.006	0.008
0.02	0.002	0.004	0.007	0.008
0.03	0.002	0.005	0.008	0.010
0.04	0.003	0.006	0.009	0.012
0.05	0.004	0.007	0.011	0.015
0.06	0.004	0.008	0.013	0.017
0.07	0.005	0.010	0.015	0.019
0.08	0.001	0.010	0.016	0.020

We found no difficulty from this source in our work.

The following may be considered as modifications of the direct-incineration method in that the salts present are not converted to any form other than the original except by heat.

Oxalic Acid Modification[8]—It is claimed that adding oxalic acid assists the incineration of sugar in much the same manner as does sulfuric acid. This method gives results agreeing with the ordinary incineration method. Unless sprinkling is resorted to, from two to five times the weight of the sample of oxalic acid must be used, which introduces a chance for error.[9]

Quartz-Sand Modification[10]—Ignition of the sample with quartz sand is stated to give a carbon-free ash, containing sulfate and chlorides as present in the original sample. The determination may be made as quickly as by the sulfate method. Platinum vessels are perceptibly attacked. It is suggested that gold-plated vessels be used.

Benzoic Acid Modification[11]—Benzoic acid in alcohol solution is added to the sugar after caramelizing. The vapors evolved leave the carbon in a very porous condition, thus making it possible to conduct the ignition at a relatively low temperature, with a minimum expenditure of time.

Zinc Oxide Modification[12]—Zinc oxide is mixed with the sugar or molasses by the use of alcohol. The weight of zinc oxide used must be deducted from the ash.

Vaseline-Oil Modification[13]—This modification largely prevents foaming. The carbon is somewhat harder to burn out than in other methods of incineration. The use of a mixture of air and oxygen to hasten the combustion is suggested.

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[1] Received November 24, 1922 Presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 25 to 29, 1921.

[2] U. S. Bureau of Standards.

[3] Ogilvie and Lindsfield, *Intern. Sugar J.*, **20** (1918), 114; *C. A.*, **12** (1918), 1424.

[4] Violette, *Ann. chim. phys.*, [5] **3** (1874), 489; *J. Chem. Soc. (London)*, **28** (1875), 384.

[5] Meyer, *Deut. Zuckerind.*, **33** (1908), 301; *C. A.*, **2** (1908), 1903.

[6] Vorbuchner, *Oesterr.-ung. Z. Zuckerind. Landw.*, **39**, 423; *C. A.*, **4** (1910), 2888.

[7] *J. prakt. Chem.*, **103** (1868), 29.

[8] Grobert, *J. Chem. Soc. (London)*, **58** (1890), 670.

[9] Stift, *Ibid.*, **60** (1891), 1297.

[10] Albert and Hempel, *Deut. Zuckerind.*, **16** (1891), 1069; *Analyst*, **16** (1891), 200.

[11] Boyer, *Compt. rend.*, [3] **190** (1890); *J. Chem. Soc. (London)*, **58** (1890), 1472.

[12] Allen, "Commercial Organic Analysis," **1**, p. 346.

[13] Weichman, "Sugar Analysis," p. 118.

Lixiviation Modification[14]—By extracting the soluble matter from the carbonized sample with water, igniting the carbon and other insolubles separately, then adding the water extract, evaporating and igniting, it is presumed that the salts are obtained nearly as they exist in the original sample. The method is troublesome, and its advantage is questionable.

Weichman[15] modifies this further by adding ammonium carbonate during the evaporation of the water extract, thus obtaining carbonates—if the subsequent ignition temperature is not too high. This is the so-called "carbonate" ash.

CONDUCTIVITY METHODS—With the Kohlrausch method for conductivity, by standardizing against products of known ash content the ash of an unknown sample can be computed after measuring its conductivity.[16]

The obvious criticism of these methods is that only the soluble ash can be measured in this way.[17]

MISCELLANEOUS METHODS—Landolt's method[18] consists in precipitating the organic acids with basic acetate of lead, and then decomposing these insoluble lead salts with hydrogen sulfide and titrating the acids liberated with potash. The potash consumed is supposed to be a measure of the ash, and the potash salts obtained are claimed to more closely approximate the salts present in the sugar than the other forms of ash.

Langier's method[18] consists in directly incinerating a sample of sugar, then adding to this ash the ether extract of the organic acids from the same quantity of sugar as has been ashed, evaporating to dryness and weighing. Langier thought that by this method he actually reconstructed the salts present in the sugar. He demonstrated that multiplying the potassium carbonate equivalent of the organic acids by two gave the amount of organic salt from which it was derived.

EXPERIMENTAL

Various methods, as given in the literature for determining the ash in commercial sugars, were tried out to determine how the results obtained by the different methods would compare with the results obtained by the sulfate method and with those obtained by ordinary incineration. This made possible a general comparison of the results obtained by the different methods. With this object in view, a large dried sample of Cuban raw cane sugar "96° polarization" was ground to a fine powder and intimately mixed, and from this the samples were taken for the different ashing methods. To serve as a check on the results obtained, sufficient sugar for five determinations was taken from the large sample for each method.

This small sample was again intimately mixed to insure uniformity. Two determinations on this small sample were always made by the sulfate method. This "sulfated-ash method" was conducted for our work as follows:

THE SULFATE METHOD—The procedure of the Great Western Sugar Company was used. Samples of from 2 to 4 g. were weighed out in 5.5 x 3.6 cm. porcelain crucibles. Enough water was added to reduce the samples to the consistency of a thick sirup, which then was evaporated on an electric hot plate until the bubbles started to puff up in the crucibles. At this point the crucibles were removed and concentrated sulfuric acid was added a drop at a time around the edges of the crucibles until the entire mass was black and ceased to boil.[19]

The samples after acid treatment were then placed on the hot plate and the excess sulfuric acid driven off. The crucibles were then heated in a gas muffle furnace until the carbon was completely consumed. After cooling, the ash was resulfated with 3 or 4 drops of dilute sulfuric acid (1:10). The excess acid was driven off by heating on the hot plate and then igniting at a dull red heat in the muffle furnace for a few minutes. One-tenth the weight of the ash obtained was deducted from its total weight before calculating the per cent of ash. The presence of sand or clay in sensible quantities must be estimated and deducted from the total ash before making the correction of one-tenth. This was accomplished by dissolving the ash in hydrochloric acid and weighing the insoluble residue. The determination showed the absence of any weighable quantity of sand or clay in the sulfated ash. Approximately 2 cc. of sulfuric acid were added to each sample in sulfating the ash. To determine if this quantity of sulfuric acid contained any weighable matter after igniting under conditions of the ash determinations, 5 cc. of the acid were evaporated to dryness and heated as above, and no weighable residue was obtained.

The results obtained by this method are given under "Sulfated Ash (Uncorrected)" in Table I. It is well known that this sulfate method gives more excessive ash values than are corrected for by the commonly used 10 per cent deduction, and that the actual excess over direct-incineration values varies with different kinds of sugar products. It is probably a reasonable assumption, however, that in a refined white sugar, such as was in hand by Bates, the excess would be consistent. The use of the sulfate method takes advantage also of the high burned ash actually weighed so as to minimize manipulation errors with such low values as the ash of white sugar.

THE DIRECT-INCINERATION METHOD—Samples of 2 to 5 g. of the sugar were weighed into 5.5 x 3.5 cm. porcelain crucibles and heated on an electric hot plate until carbonized. The samples were then ignited to a white ash at a low red heat in the muffle; then they were again ignited for 10-min. periods until constant weight was obtained. This practice was followed in all methods tried. The heating on hot plate causes the carbonization to start locally on the bottom of the crucible and not through the entire sample at once, which would cause a foam-over. This modification in technic very effectively prevents foam-overs. The sugar or sirup would foam up to within a centimeter of the top, and rarely go farther or overflow this because of small fumerole-like streams of steam and smoke, which at about this point would burst through the hot, viscous, foaming mass, releasing the pressure beneath the advancing foam-wave. Further attention was thus unnecessary, until the mass had become sufficiently dried out to be quiescent, whereupon the crucible was placed in muffle furnace until ashed. Some further slight foaming took place at the higher temperature, but distillation to dryness (charring) proceeded too rapidly to bring on overflowing again. (Method 2, Table I)

TABLE I

No.	METHOD	Ash Found % (Average)	Sulfated Ash on Same Sample (Uncorrected) % (Average)
1	Direct incineration	0.508	0.761
2	Benzoic acid	0.496	0.753
3	Vaseline oil	0.510	0.776
4	Ammonium carbonate	0.543	0.753
5	Quartz sand	0.474	0.729
6	ZnO	0.554	0.742
7	Lixiviation	0.512	0.756
8	Modified sulfate ash	0.696	0.756

THE BENZOIC ACID METHOD—A solution of 25 g. of benzoic acid in 100 cc. of 90 per cent ethyl alcohol was used. Samples of from 2 to 4 g. of sugar were weighed and placed in porcelain crucibles and moistened with 1 cc. of water. The crucibles were heated slowly in order to caramelize the sugar without carbonizing it; 2 cc. of the benzoic acid solution were next added and the crucibles warmed until all the alcohol was evaporated. The temperature was then raised until the sugar was converted into carbon. The heating on the hot plate was continued until no more fumes were given

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[14] Great Western Sugar Co., "Methods of Sugar Analysis," **1920**, p. 10; Allen, "Commercial Organic Analysis," 4th edition, Vol. 1, p. 346.

[15] "Sugar Analysis," p. 119.

[16] Main, *Intern. Sugar J.*, **11** (1909), 334; *C. A.*, **3** (1909), 2249; Lange, *Z. Ver. deut. Zuckerind.*, **60** (1910), 359; *C. A.*, **4** (1910), 1554.

[17] Trenkler, *Oesterr.-ung. Z. Zuckerind. Landw.*, **39** (1910), 437; *C. A.*, **4** (1910), 3308.

[18] Blyth, "Foods: Their Composition and Analysis," p. 135.

[19] In most of the methods given in the literature, the sugar was merely weighed out, moistened with a few drops of water (if the sample was dry) and a few drops of sulfuric acid, and the incineration then carried out. It is evident that this procedure does not give the opportunity that the formation of sirup does for uniform contact with sulfuric acid as in the method of the Great Western Sugar Company.

off. The incineration was then accomplished in a muffle furnace at a low red heat until a white ash was obtained. Ashing 20 cc. of the benzoic acid solution gave no weighable residue. (Method 2)

THE VASELINE-OIL INCINERATION METHOD—Samples of sugar of from 2 to 4 g. each were put in porcelain crucibles and saturated with vaseline oil, b. p. 385° C., and then heated on the hot plate until fuming ceased. The carbonized mass was burned to a white ash in a muffle furnace. Ashing 10 cc. of the oil gave no weighable residue. (Method 3)

THE AMMONIUM CARBONATE INCINERATION METHOD—From 2- to 4-g. samples were weighed and placed in porcelain crucibles and heated on the hot plate until the mass was carbonized. The soluble salts were extracted from the carbonized mass with boiling water. The carbonaceous residues were ignited in the muffle furnace until a white ash was obtained. The aqueous extract of soluble salts was added to the respective samples of ash obtained by igniting the carbon. The solutions were then evaporated to dryness, moistened with ammonium carbonate, and heated in the muffle until the ammonia was completely driven off. The results are reported as carbonate ash and given under Method 4.

QUARTZ-SAND INCINERATION METHOD—Porcelain crucibles containing about 5 g. of pure, washed sea sand were ignited to constant weight. The weighed samples of sugar were placed in the crucibles containing the sand, and the sugar and sand intimately mixed with a glass rod. The samples were then heated on the hot plate until the mass was carbonized and finally in the muffle to a white ash. (Method 5)

ZINC OXIDE INCINERATION METHOD—Porcelain crucibles containing about 0.2 g. of pure zinc oxide were ignited to constant weight. The weighed samples of sugar were added to the zinc oxide in the crucibles. After the addition of the samples of sugar, 5 cc. of denatured alcohol were added to each sample, and the zinc oxide was thoroughly incorporated in the sugar by mixing with a glass rod. The adhering particles of sugar were washed off with alcohol. The samples were then heated on the hot plate until all the alcohol was volatilized and the sugar carbonized, and finally in a muffle furnace until a white ash was obtained. (Method 6)

COMBINED LIXIVIATION AND INCINERATION METHOD—A lixiviation method for determining sugar ash is used by Osborn.[14] In the work of the writers, weighed samples of sugar were placed in platinum crucibles and heated on the hot plate until the sugar was carbonized. The mass was crushed to a fine powder by means of a glass rod and heated again at a dull red heat until carbonization was complete. After cooling, 20 cc. of water were added to each and the crucibles heated for about 15 min. on the hot plate, the volume of the solution being kept approximately the same by the addition of more water. The solutions were then filtered through ashless filter paper into small beakers. The carbon was washed into the filter and washed with hot water to remove any adhering solution. After the crucibles had been heated until dry, the filter papers with carbon were placed in the platinum crucibles and ignited over a full flame of a Bunsen burner until free from carbon. When the ignition was complete, the crucibles were cooled and the solutions of water-soluble salts added to the ash in the crucibles. The solutions were then evaporated to dryness on the hot plate and gently heated in the muffle furnace to remove all moisture. The method as given in the literature calls for the use of platinum crucibles, stating that the use of porcelain or silica ware is inadmissible. (Method 7)

PROPOSED MODIFICATION OF THE SULFATE METHOD—To save what seemed to be a needless expenditure of time in the sulfated-ash method, as given in the various references, a modification is here proposed. The standard method calls for the addition of water to the dry sample of sugar until it is reduced to the consistency of thick sirup. It is then evaporated until bubbles start to puff up in the crucible, after which the concentrated sulfuric acid is added. It is proposed in the new method to eliminate the addition of water to sugar and also the evaporation to foaming, but to add a portion of the water to the sulfuric acid to secure the benefit of better contact between sugar and acid than can be obtained even by preliminary solution plus subsequent addition of concentrated acid. In the new method, the sulfuric acid of the proper concentration is added to the sample of sugar which has not been treated with water and is then heated on the hot plate until completely carbonized. The approximate concentration of acid to be added is determined by adding the required amount of water to the sample as in the standard sulfate method and determining the loss in water that takes place on evaporating to the consistency called for in the standard sulfated-ash method before adding the required volume of concentrated sulfuric acid. The amount of water found to be present gives a dilution to the acid, to be added to the sugar, corresponding to about two parts by volume of concentrated sulfuric acid to one part by volume of water. The modified method, therefore, consists in weighing samples of sugar in porcelain or platinum crucibles and adding 2 cc. of sulfuric acid (2 : 1), as calculated above, heating the samples on the hot plate until completely carbonized, and finally igniting into a white ash in the muffle furnace. After cooling, 3 or 4 drops of the sulfuric acid (2:1) are added to each sample of ash and heat applied until the excess of sulfuric acid is driven off and then put in the muffle furnace at a low red heat for about 15 min. In the old sulfate method one was not always sure that sulfuric acid came into contact with all of the at times voluminous carbonaceous material in the crucible. With the new method, there is no doubt of it. There has also been in use the suggestion of adding concentrated sulfuric acid directly to the sugar as weighed, or after moistened with a few drops of water. This has been modified, however, to the sirup plan, probably because of the difficulty of getting all the acid in touch with ash in presence of the great bulk of carbon being formed. (Method 8)

PLATINUM *vs.* PORCELAIN CRUCIBLES—To determine if the results obtained on sugar-ash determinations would be the same if 3.4 x 5.5-cm. platinum crucibles were used instead of the porcelain crucibles used in this work, and in much commercial work to-day, comparative determinations were made using porcelain and platinum crucibles by the direct-incineration method and the usual sulfated-ash method. The results of these determinations are given in Table II.

TABLE II—COMPARISON OF PORCELAIN *vs.* PLATINUM

METHOD	Porcelain % (Average)	Platinum % (Average)
Direct incineration	0.503	0.506
Sulfate (usual)	0.762	0.770
Sulfate (modified)	0.774	0.769

The time required to obtain white ash after the sample had been put in the furnace was from 15 to 30 min.

IGNITION LOSS OF ASH—As soon as white ash was obtained, the crucible was cooled in a desiccator and weighed. Then the ash was reignited for about 10 min. and reweighed.

With the direct-incineration and sulfated-ash methods there was very little change in weight after the first ignition. There was quite a little change in weight with some of the samples using the other methods. (Table III)

DISCUSSION OF EXPERIMENTAL RESULTS

The results given are typical. The sulfated-ash method has the advantage of increasing the weight of the ash and thus making easier the weighing of small quantities. In other

TABLE III—IGNITION LOSS OF ASH BY THE VARIOUS METHODS OF DETERMINING ASH IN COMMERCIAL SUGARS

	Per cent Ash				
	(1) Direct Incineration				
Ignition	1	2	3	4	5
1	0.501	0.502	0.517	0.513	
2	0.501	0.502	0.517	0.513	
	(2) Benzoic Acid Method				
	0.524	0.500	0.589	0.536	0.556
2	0.520	0.500	0.579	0.532	0.552
3	0.516		0.572	0.494	0.492
4	0.516		0.564	0.494	0.460
5			0.524		0.460
6			0.512		
7			0.512		
	(3) Ignition with Vaseline Oil				
1	0.593	0.510	0.511	0.515	
2	0.557	0.510	0.511	0.515	
3	0.505				
4	0.505				
	(4) Ignition with Ammonium Carbonate				
1	0.553	0.606	0.687	0.586	
2	0.549	0.564	0.613	0.538	
3		0.543	0.538	0.538	
4		0.543	0.538		
	(5) Ignition with Silica (Sand)				
1	0.955	1.05	0.478		
2	0.474	0.472	0.478		
3	0.474	0.472			
	(6) Ignition with Zinc Oxide				
1	0.577	0.574	0.633		
2	0.553	0.554	0.602		
3	0.553	0.550	0.560		
4			0.560		
	(7) Lixiviation Method				
1	0.589	0.510			
2	0.574	0.510			
3	0.515				
4	0.515				

respects it has no advantage over the direct-ignition method, and requires somewhat longer time for completing the determination. The results obtained show that with the sugar used in this work the deduction necessary to convert the sulfated ash to actual ash obtained by direct incineration is as high as ever reported.

As already noted, Violette[3] has called attention to the fact that the customary coefficient of 0.9 for conversion of sulfated ash to direct incineration or so-called "carbonated" ash is too high. He suggests 0.7 for crude sugar. The results of the writers are in the same direction. They find 0.66 most suitable for the purpose. This means that instead of deducting 10 per cent, a 33.25 per cent deduction is necesary in sulfated ash from Cuban 96° raw sugar to convert to direct-incineration results. This means that the sulfate-ash results as obtained before the usual 10 per cent deduction are really 49.80 per cent higher than the direct-incineration results.

The direct-incineration method has the advantage in that the results are more quickly obtained than by the sulfated-ash method or any other methods used in this work. No more difficulty was encountered upon weighing this ash than with the sulfate ash.

It is claimed that with direct-incineration methods there is danger from losing ash by volatilization, and that constant weight is practically impossible to obtain. It was the practice of the writers to ignite to a white ash (15 or 30 min. after placing in muffle) and then to weigh. The ash was then ignited for 10-min. periods until constant weight was obtained. In all cases constant weight was actually obtained. With the ordinary direct incineration, constant weight was obtained in all cases at the first ignition. The modifications of the direct-incineration method were more troublesome in bringing to constant weight. The sulfate method gave more trouble in this respect than the direct-incineration methods.

In the benzoic acid method the decomposing benzoic acid produced abundant vapors which rendered the mass extremely porous and thus hastened the complete ignition of the carbon. But the ash, obtained was very fluffy and much harder to weigh than the sulfated ash, as it took up moisture. The results obtained vary somewhat, the low figures being probably due to some of the ash being carried out of the crucibles in the process of heating. The results usually check those by direct incineration.

The use of vaseline oil in the determination of sugar ash has the advantage of preventing, to a large extent, the frothing which takes place on heating the samples of sugar on the hot plate, but has no other advantages. It exactly checks the direct-incineration results.

No advantage in the use of ammonium carbonate in the determination of sugar ash was observed, and great care was required to evaporate the solution of ash and ammonium carbonate to dryness on account of the tendency to spatter. The results run higher than those by direct incineration.

On igniting the sugar with sand, the weight of the sand, together with the adhesion of the sirup formed by the melting of the sugar, prevented any frothing, but caused some trouble on carbonizing the sugar on the hot plate. The samples of ash obtained by this method required a little longer to ignite to constant weight, probably because of the presence of the sand preventing a free circulation of air. As has been shown, the results obtained by this method are slightly lower than those obtained by direct ignition, but the percentage of ash determined on this sample by the sulfated-ash method is also lower, indicating that the sample of sugar used for this method contained a slightly lower ash content than the sample in which the ash was determined by incineration. There are indications, therefore, that the sand-ignition method catches slightly more ash than the direct-incineration method.

The use of zinc oxide in determining sugar ash prevented any frothing on heating the sugar. The results, which are higher than those obtained by direct incineration and correspond closely with those obtained by heating the ash with ammonium carbonate, are probably due to the incorporation of the ash in the zinc oxide, thus preventing the volatilization of some of the more volatile salts or acid radicals in the sugar ash.

No advantage in the use of the lixiviation method was observed. It checked the direct-incineration values, showing that the burning off of carbon in the direct incineration does not lose any ash that the lixiviation method would save.

Our modified sulfated-ash method has the advantage of considerably shortening the standard sulfated-ash method, and gives results which check within the limits of experimental error with the results previously obtained by the standard sulfated-ash method on the same sample of sugar. There was more tendency for the sugar to froth by the use of this method with diluted sulfuric acid, but this tendency was very much suppressed by changing the concentration of the sulfuric acid to 1 part by volume in 2 parts by volume of water.

The results of the comparative test on the use of platinum and porcelain crucibles as found in this work confirm the statement by Meyer,[4] in which he proposes the use of porcelain dishes instead of platinum after making one thousand comparative determinations and finding the results to be the same.

Our experiments indicate that for both the sulfate method and the direct-incineration method, the results with platinum and with porcelain are practically identical.

ACKNOWLEDGMENT

The writers are indebted to several sugar men for samples of raw sugar and for laboratory courtesies, and to Mr. Lawrence E. Stout, Mr. Y. L. Pun, and Mr. H. T. Ruff of this laboratory, and to the Engineering Experiment Station of this university for assistance in the preparation of this article.

The Action of Shortening in the Light of the Newer Theories of Surface Phenomena[1]

By Washington Platt and R. S. Fleming

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In the type of baked products discussed, shortening acts by interposing itself in layers between the particles of dough, thereby preventing the dough from forming one continuous mass. This structure can be seen microscopically in both dough and baked products.

An important factor in causing the difference between the shortening powers of different fats is the plasticity of these fats at the temperature of mixing (about 80° F.). For fats that are not plastic in the dough the relative shortening power is given by their content of unsaturated glycerides. This is in accord with the present ideas regarding the orientation of molecules and the energy relations at interfaces. For plastic fats the shortening power is determined both by the plasticity and by the unsaturated glyceride content.

The parallelism between shortening and lubrication is pointed out.

OF the fats and oils prepared as food products in a practically pure state, such as lard, cottonseed oil, etc., a large proportion is used as shortening in baked products. The literature on fats and oils is, of course, voluminous; yet, when the problem of the action of shortening in baked products was first attacked by one of the authors in 1914, nothing could be found in the scientific literature relating to the mode of action of shortening in these products. There was no clear-cut definition of shortening power, no method of measuring the shortening power, and no explanation whatever of the action of shortening.

Shortening is used in such very different products as bread, soda crackers, sugar cookies, drop cakes, pound cakes, etc. The shortenings commonly used are butter, lard, lard compound, cottonseed oil, and coconut oil. Though the baked products and shortenings vary greatly, the fundamental effect of the shortening is in all cases the same—it makes the finished product more tender and easy to break. Beyond this fundamental effect, the action of each shortening differs considerably from the action of the others. In particular, it is well known in the trade that some fats and oils have much more shortening power per pound than others. The great practical importance of this fact to manufacturers of shortening and to bakers is evident.

An investigation of the problems pertaining to shortening was, therefore, begun by one of the authors. Considerable practical work was done and a machine was constructed for measuring the shortening power of fats in terms of the breaking strength and crushing strength of standard cookies. As far as is known, this was the first machine ever constructed for the measurement of shortening power. This work was interrupted by the war.

This investigation was continued and much extended by C. E. Davis. His paper, "Shortening: Its Definition and Measurement,"[2] describes in detail his improved machine for measuring the shortening power in terms of the breaking strength of biscuits. In the present paper, the definitions as given by Davis, with some modifications, will be used—viz., "Shortening is any fat or fixed oil used as an ingredient in baked products. That material has the greatest shortening power which, when baked in a dough under standard conditions, gives to the product a minimum breaking strength and a minimum crushing strength." In this paper also the word "fats" will be used in the general sense including the fatty oils. A more general description of the action of shortening in baked products was given in a recent paper by one of the authors.[3]

Since the inauguration of this work, important investigations have been published by Langmuir[4] and by Harkins[5] and his co-workers on the structure of the surfaces of liquids. These papers, demonstrating the orientation of the molecules at the surface and discussing the surface tension, work of adhesion, etc., at the interface between liquids, throw important light on many of the fundamental problems relating to shortening and lubricants. The present paper is an effort to connect these more recent discoveries in the domain of pure science pertaining to surface phenomena with the well-known industrial problems of shortening, and to show some of the practical applications of the newer work.

Shortenings are used in such various baked products as bread and pound cake in amounts from 2 to 100 lbs. to the barrel of flour. From this it will be seen that, though the fundamental principles are the same, the details of the action of shortening are quite different in different baked products. In order to present a clear-cut problem, the remainder of this paper will be confined entirely to the action of shortening in sugar cookies.

The consideration of the action of shortening in sugar cookies will be further confined to its *physical* effect on the structure and physical properties of the dough and finished biscuit. It is evident that shortening has also an important influence on the taste, digestibility, nutritive value, and keeping qualities of biscuits, but these points are outside the sphere of the present paper.

Sugar cookies include the various light-colored cookies sold under various names, such as raisin cookies, sugar cookies, etc., and also the dark-colored ones containing molasses, such as ginger snaps. They are common articles of diet with the American people, and are chosen as typical of the variety of baked products made from a stiff dough in a slow mixer, as contrasted with products, such as drop cakes, made from a liquid dough by beating up the fat in a fast mixer. Such sugar cookies contain from 25 to 40 lbs. of shortening and from 75 to 125 lbs. of sugar to the barrel.

Description of Dough during Mixing and Baking

In order to form a clear idea of the present problem, it is necessary to examine in some detail the ingredients used in making a sugar cookie and the conditions which exist during the mixing and baking of the dough. A typical formula is that used by the author and described by Davis:[2]

	Pounds
Flour, medium winter patent	196
Shortening	35
Sugar	80
Water	43.8
Ammonium bicarbonate	0.5
Monocalcium acid phosphate	0.3
Sodium bicarbonate	1.5

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[1] Presented before the Division of Agricultural and Food Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This Journal, **13** (1921), 797.

[3] *Chem. Age*, **30** (1922), 157, 203.

[4] *Met. Chem. Eng.*, **15** (1916), 468; *J. Am. Chem. Soc.*, **39** (1917), 1848.

[5] *J. Am. Chem. Soc.*, **39** (1917), 354, 541; **42** (1920), 700; **43** (1921), 35.

The shortening, sugar, water, and salt are mixed together in a dough-mixer, the arms of which make 16 revolutions per minute. The effect of this mixing is to form a sirup from the sugar and water. Some of the sugar, however, remains undissolved in suspension in this sirup; the salt dissolves completely. The shortening exists in fine globules, well distributed through this sirup. The continual motion of the mixing arm keeps these globules from collecting as a layer of oil at the surface, though this motion is not sufficient to emulsify any considerable portion of the fat.

Toward the end of this preliminary mixing ammonium bicarbonate dissolved in a small portion of the water is added. The temperature of the mixture may be from 40° to 100° F., depending on the temperature of the flour to be added and the season of the year. In the hot weather an effort is made to keep the dough cool.

All the ingredients are then mixed together at 16 r. p. m. for 20 to 40 min. The friction of mixing develops heat, so that the temperature of the dough rises from 5 to 10 degrees. The final temperature of the dough is from 75° to 80° F.

The addition of the flour changes the mixture from a sirup containing fat globules and sugar in suspension to a semisolid, pasty mass of dough. All the ingredients but one—the shortening—are either soluble in water or miscible with it.

Flour is 70 to 75 per cent starch in the form of granules, which remain as solid particles throughout the process of mixing and baking. The proteins of flour are principally glutenin and gliadin. Although these are both insoluble in water, they both absorb water. The gliadin forms a gluelike mass which comes in contact with the firmer particles of glutenin during the mixing, and forms the gluten of the dough. This gluten exists as strands and layers extending throughout the mass. Further mixing brings these particles of gluten into contact with one another. They stick together and are then stretched apart and brought into contact with other strands of gluten. In this way the gluten develops and becomes stronger, tougher, and more coherent. The network of gluten forms the skeleton of the dough and of the finished biscuit. In this network are held the starch grains.

In the mass of dough described above, there are numerous minute air holes. During the process of mixing and baking, bubbles of gas are likewise formed. Except for these small holes, a dough made without shortening is practically a continuous mass. The conditions are favorable for the gliadin and glutenin to adhere to one another and also for the strands of gluten to cohere, forming a strong, tough, continuous mass throughout the dough. The strands of gluten and the starch grains are both soaked in the solution of sugar and chemical leavening agents and are thoroughly wetted by it.

On baking such a dough made without shortening, the temperature of the dough rises and steam is given off, so that the sugar solution becomes highly concentrated, approaching the condition of hard-boiled candy. At the temperature of baking this concentrated sirup is soft and plastic, like hot candy boiled to a corresponding degree of concentration. On cooling, however, such a sirup hardens to a solid, hard candy-like material. Imbedded in this are numerous starch granules, which are partly ruptured but, in general, retain most of the structure intact. Through this candy-like material there also extends a network of gluten. During the baking this holds the air, gas, and steam in the dough, causing it to rise to a certain extent, carrying up the saturated sugar sirup. Later, this gluten cools and sets in this partially risen condition, thereby contributing to the final structure of the biscuit. Such a biscuit baked without shortening is, therefore, essentially a continuous mass of hard candy, containing starch grains and a network of gluten. Although there will be spherical holes in this mass filled with gas, yet the mass will be continuous around these holes, just as a mass of concrete is continuous around the stones which it contains. A biscuit baked without shortening does, in fact, exhibit exactly the structure described above. Such a biscuit is so hard and strong that it cannot be broken with the teeth.

ACTION OF THE SHORTENING

From these considerations it will be easier to understand the fundamental action of shortening in a dough or biscuit. On mixing, the fat is mingled very intimately with other ingredients of the dough. Unlike any other ingredient present, however, it remains always distinct and does not dissolve. During the mixing the fat spreads over the fresh surfaces of the dough which are constantly being formed, coating them with grease. When a fiber of gluten comes into contact with a second fiber of gluten, the shortening prevents these two fibers from cohering as firmly as they would, were the intervening film of shortening not present. In like manner the shortening often penetrates between the starch grains. The dough may be compared roughly to a *sponge* of a very fine texture, of which the gluten, starch grains, and sugar solution form the solid structure, while the shortening is held as liquid in the pores.

In warm weather, under certain conditions part of the fat will run out of the pores of such a sponge of dough and will collect in larger and larger pools. Some of the fat is also frequently squeezed out as it passes through the roller, on being rolled out into sheets preparatory to being cut out and baked as biscuit. This tendency to separate from the dough is very objectionable from a practical point of view. It is much more common in some shortenings than in others. The reason for this difference will be considered.

Profound changes occur in the biscuit during baking. As the air already present and the gas derived from the sodium and ammonium bicarbonates expand with the rising temperature, steam is formed throughout the biscuit and is given off as vapor. The mixture of sugar solution, starch, and gluten becomes much softer with the rising temperature and the whole spongy mass expands with the gases.

It is evident from these considerations that the shortening breaks up what would otherwise be a continuous mass in the dough or finished cookie. It forms innumerable, minute, fat-filled *cracks*, or breaches of continuity, throughout the structure of the biscuit, so that the biscuit consists of many minute particles, which are separated from the adjoining particles by a thin layer of shortening. The reason for using shortening is similar to the reason why candy manufacturers wrap caramels in paraffin paper. Without the paraffin layer between them, the caramels would all stick together and form one large, solid mass. Paraffin, however, does not mix with or dissolve in a thick sugar solution such as caramel, and therefore acts much like shortening in dough by forming a layer which keeps the lumps of caramel apart.

MICROSCOPIC EXAMINATION

In order to determine the state in which shortening exists in dough and in the finished biscuit, these products were examined microscopically. Three different stains were used—namely, osmic acid (Kolossow's stain), Alcanna tincture, and Sudan III. The last stain was used dry and dissolved in the fat before mixing it into the dough.

It was found that unless unusual precautions were taken erroneous ideas were formed concerning the state of the fat. If either dough or baked cake was examined by mounting the specimen on a slide in water or other liquid and covering with a cover glass in the usual way, the fat was invariably seen in the form of globules of various sizes. This would lead one to believe that the fat existed in globular form in the dough and cake. Further examination disclosed the fact that these globules did not exist in the original specimen, but were formed on the addition of liquid to the specimens in mounting. The liquid softened the more-or-less solid walls surrounding the layer of fat, and also supported the fat on all sides, allowing the layers to draw up into globules, owing to the surface tension of the fat. When the specimens were mounted dry and the staining or mounting liquid was then allowed to run under the cover glass, it was possible to see these globules form under the microscope.

Two methods were used to avoid this change in the fat when mounting for microscopic examination. The first of these was to mount the specimen dry. This was especially successful in the case of dough. With careful manipulation it was found possible to spread the dough in the form of a thin film on the slide, placing the cover glass in position and examining in this way. In this case the Sudan III was used to stain the fat before mixing into the dough. The shortening showed up very plainly as thin layers extending between the starch granules and, in many cases, completely enveloping each granule. It was evident, however, that the shortening did not penetrate between *every* granule, nor was every granule enveloped in fat. It was also evident that the thickness of this film varied in different places. In some places a minute pocket or lake of shortening could be seen, and under certain conditions this lake would connect and drain into larger and larger pools of shortening. In the baked cookie the fat exists in similar layers, extending throughout the mass.

Another method of observing the condition of the shortening is to place the specimens, slides, stains, etc., in cold storage and carry out the whole work in the ice box at 46° F. In this case, the Alcanna tincture can be used both as a stain and as a fluid in which to mount the specimen. At the temperature of the ice box, the shortening is so stiff that it does not change its condition upon addition of the liquid. Furthermore, the alcohol of the tincture has such a slight solvent power upon the sugar composing the cake that the structure of the latter is not appreciably changed. At this temperature several hours are necessary for the fat to be stained by the tincture. The results obtained by this method confirm those obtained by staining with Sudan III.

The shortening is seen in layers as described. However, when the fat is added to the dough in an emulsified condition, as is the case with the butter fat in whole milk and the oil of egg yolks, this emulsified condition persists to a large extent in the dough and finished biscuit.

The fundamental action of shortening, as described above, pertains to all forms of shortening. The fact that the action of shortening is "physical" rather than "chemical" is shown by the fact that shortening effect can be obtained with petroleum jelly, such as vaseline. The physical properties of this product are somewhat similar to those of lard, though in chemical composition the two have nothing in common. The similarity of the action of shortenings to the action of lubricants is at once apparent. In both cases the action consists in a thin film of oil holding apart solid masses, and it is evident that oil must not only penetrate between the masses, but it must adhere to them so closely that it will not be squeezed out by pressure. The adherence of the oil film to the masses of dough or metal is evidently a factor of prime importance in considering both shortening and lubricants.

In the lubrication of journals the rotation of the shaft in the bearing continually carries in a film of oil, which has an important effect upon the lubrication. There is little of this effect in the action of shortening. The action of shortening is more nearly similar to the action of the lubricant in separating two pieces of metal under the conditions of static friction.

REASONS FOR THE DIFFERENCE BETWEEN SHORTENING POWERS OF VARIOUS FATS

It is well known to bakers that some fats have a much greater shortening power per pound than others. The common fats, arranged in decreasing order of their shortening power, are lard, lard compound, cottonseed oil, butter, coconut oil. Below these in shortening power are vaseline and purified petroleum oils, such as Nujol.

Many factors are involved in the action of shortening. In the first place, dough is a very complex mixture of colloids and crystalloids, partly in solution and partly in suspension. The action of mixing brings about complicated changes in the structure of the gluten and the intermingling of the fat. These conditions are further modified during baking. In such a system it is evident that no one property can possibly explain the whole action of shortenings. It should be possible, however, to find some of the important factors and to discard those which seem to be of comparatively minor importance.

Viscosity evidently plays a part. A very viscous shortening would evidently spread less easily through the dough, but would run out of the dough less readily. It is of minor importance, however, as some petroleum oils may have the same viscosity as edible oils and yet show an enormous difference in shortening power.

The surface tension of the oil against air is a factor, yet not one of prime importance, as oils having small differences in surface tension show large differences in shortening power. The surface tensions of various oils at 0° C., as given by Harkins, Davies, and Clark,[6] are as follows:

	Dynes /Cm.
Glyceryl tributyrate	31.8
Glyceryl tricapronate	31.5
Glyceryl tricaprylate	30.1
Glyceryl tricaprinate	29.3
Glyceryl trilaurinate	32.9
Glyceryl tripalmitate	34.6
Glyceryl tristearate	35.2
Glyceryl trioleate	37.2
Butter	33.1
Margarine	34.8
Liquid paraffin	32.38

The melting point is also a factor. Fats of such high melting points that they are perfectly solid, such as the completely hydrogenated cottonseed oils, cannot spread through dough, and therefore have little shortening power. Within the ordinary range, the melting point is important. Other things being equal, a melting point about that of lard is desirable. Even this factor, taken alone, is of comparatively minor importance, as coconut oils can be prepared of the same melting point as butter or lard, but these coconut oils will, nevertheless, be much inferior in shortening power.

A somewhat related quality is plasticity throughout the range of temperatures encountered in the dough mixing. This quality cannot be deduced merely from the melting point of the whole fat. It seems to depend upon the range of melting points of the component glycerides, to some extent upon the mechanical treatment of the fat, and upon other factors not yet understood. A fat that will remain plastic throughout the mixing has much greater shortening power than one that is either solid or liquid. The plastic fat tends to spread in fine layers through the dough without running out, and will hold air better than others. Plasticity has, therefore, a most beneficial effect on shortening power. Although the meaning of the term is understood, no work seems to have been done upon the measurement of the plasticity of shortenings. General suggestions of much interest are made in Bingham's recent book.[7] Well-made lard compounds are the most plastic, with lard next, and butter a poor third. Oils are, of course, not plastic. The fact that

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[6] *J. Am. Chem. Soc.*, **39** (1917), 541.

[7] "Fluidity and Plasticity," New York, **1922**.

they have great shortening power shows that plasticity is only one of the important factors.

Insight into another important factor is given by a study of the action of oil films on water. While these conditions are quite far removed from those existing in dough, they give a good opportunity to form some understanding of the forces existing when oil comes into contact with water or water solution.

The action of oil films on water has been described by many observers.[8]

The study of the orientation of molecules at oil-water surfaces and the difference between the attraction of different glycerides for water throws much light upon the action of shortening, and probably is an explanation of one important difference in the shortening power of different oils. This orientation of the molecules has been clearly demonstrated by the work of Langmuir[4] and of Harkins and his co-workers.[5] Langmuir's work consists in the formation of monomolecular films on water. When these are formed the force necessary to compress them, the area covered per molecule of oil, and the thickness of the film can be measured. He shows that at the interface between water and another liquid the molecules of the other liquid arrange themselves in a definite fashion. The polar groups in the molecule are attracted to water, while the nonpolar groups extend into the body of the nonaqueous liquid. For example, in the case of palmitic acid, floating upon the water, the carboxyl end of the molecule is attracted toward the water and may even be said to be dissolved in the water, while the hydrocarbon tail of the molecule is naturally more attracted by the oily layer, and hence extends into it. As Wilson and Barnard[9] have strikingly expressed it, "In such a position, the molecule is most comfortable." It was found that in the monomolecular layer of palmitic acid the molecules stand up straight, perpendicular to the water surface. The esters of such acids occupy the same relative position and cover the same surface as acids. Glyceryl tripalmitate occupies approximately three times the surface per molecule as palmitic acid, and forms a layer of approximately the same thickness. It was found that lauric, palmitic, and stearic acids each occupy practically the same area of interface per molecule. The thickness of the film, however, varies in accordance with the number of carbon atoms in the hydrocarbon tail. The same can be said of the glycerides of these acids.

When we come to an unsaturated acid, such as oleic or its glyceride, we find quite different conditions. Here, not only the carboxyl end of the molecule, but also the double bond near the middle, is attracted to the water surface. As a result, such molecules are partly drawn down along the surface of the water, and therefore each molecule of oleic acid occupies a much larger surface of the water than a molecule of palmitic acid or other saturated fatty acid. Langmuir gives the following measurements:[10]

	Cross Section Sq. Cm.	Length Cm.
Palmitic acid	21×10^{-16}	24.0×10^{-8}
Stearic acid	22×10^{-16}	25.0×10^{-8}
Tristearin	66×10^{-16}	25.0×10^{-8}
Oleic acid	46×10^{-16}	11.2×10^{-8}
Triolein	126×10^{-16}	13.0×10^{-8}

Further experiments show that the presence of two double bonds in the fatty acid molecule, as in the case of linoleic acid, does not cause it to occupy any more space than a molecule with one double bond, such as oleic acid.

Langmuir states in his conclusions, "The saturated fatty acids (from palmitic to cerotic) cover approximately equal areas per molecule (21×10^{-16} sq. cm.), irrespective of the length of the hydrocarbon chain. The glycerides cover about the same area as the fatty acids obtainable from them. . . . The unsaturated fatty acids all cover much greater areas per molecule than the saturated. The double bond in oleic acids is thus apparently drawn down onto the water surface. It is interesting to note, however, that linoleic acid, with its two double bonds, does not cover any greater area per molecule than oleic acid. It may be that the double bonds attract one another to some extent in place of the water."

The principles apparently have a bearing on shortening power. Shortenings containing double bonds should cover a greater aqueous surface and adhere more closely to such surfaces than shortenings without double bonds. The iodine number as such cannot be taken as an indication of the shortening power from this point of view, since glycerides of linoleic acid containing two double bonds (Iodine No. 173) do not cover any greater surface than glycerides of oleic acid containing but one double bond per molecule (Iodine No. 86). For this reason, other factors being equal, shortenings should be arranged in the order of their percentage of unsaturated glycerides. While this percentage can only be given approximately, the results of the analyses given by Lewkowitsch[11] and others give the following figures for fats and oils, arranged in the order of their percentage of unsaturated glycerides:

	Approximate Percentage Unsaturated Glycerides
Cottonseed oil	75
Lard	60
Lard compound	60
Butter	38
Coconut oil	5
Liquid paraffin	0

It is striking that this order is exactly the same as the order of the shortening power of these same fats, as found by practical experience, with the exception of the two plastic fats, lard and lard compound. Here another factor, plasticity, enters, giving to these fats, which are the only ones to remain plastic in sugar-cookie doughs, a greater shortening power than would be expected if only their content of unsaturated glycerides were considered.

Similar conclusions regarding the main cause of the differences in shortening power may be drawn from the work of Harkins and his co-workers. They determined the surface tension of oils and other substances in contact with their own vapor, their interfacial tension against water, and deduced from this the work of adhesion, according to the equation of Dupre[12]—namely:

$$-W_a = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2}$$

where W_a is the work of adhesion involved in the approach of two unlike surfaces, $\Delta\gamma$ is the decrease in free energy during their approach, γ_1 and γ_2 are the free energy (numerically equal to the surface tension) before their approach, and $\gamma_{1,2}$ is the free energy of the interface between the liquids.

These workers published these and other data for a large number of liquids. They show that although the surface tension against air or their own vapors for unsaturated glycerides is not markedly different from that of the saturated glycerides or from that of liquid paraffin, yet other figures, such as total energy of the surface, work of adhesion, etc., show a marked rise for esters of glycerides containing double bonds. These authors state, "The presence of double bonds increases the cohesional work very slightly and the adhesional work very greatly."

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[8] *Nature*, **78** (1891), 437; Rayleigh, Scientific Papers, London, **1890-2**; Hardy, *Proc. Roy. Soc.*, **84B** (1911), 220; *Ibid.*, **86A** (1912), 610; Devaux, Smithsonian Inst. Rep., **1913**, 261; Labrouste, *Compt. rend.*, **158** (1914), 627; Marcelin, *Ann. Phys.*, **1** (1914), 19.

[9] THIS JOURNAL, **14** (1922), 683.

[10] *J. Am. Chem. Soc.*, **39** (1917), 1865.

[11] "Chemical Technology and Analyses of Oils, Fats and Waxes," New York, **1921**.

[12] "Théorie Mécanique de la Chalem," Paris, **1869**, p. 69.

It seems from this work that the presence of double bonds in shortening not only enables the fat to cover more surface per molecule, but that such double bonds also cause the shortening to actually *adhere* to the surface more closely so that it requires more pressure for two layers of dough to break through the intervening layer of the unsaturated shortening.

The deductions from Harkin's work, like those from that of Langmuir, indicate that one of the important factors regarding the shortening power of any fat is its content of unsaturated glycerides.

The difference between the shortening power of hydrocarbon oil, such as Nujol, and commercial shortenings is very marked, and the difference between area covered per molecule, work of adhesion, etc., is equally marked and fits in exactly with the theory. It is only fair to state here that while these principles seem of general application, the determinations of the area per molecule, work of adhesion, etc., for commercial shortenings, do not seem to show all these variations in the same way as the purified glycerides. This has been pointed out by Langmuir[13] and is being given further study.

The parallelism between shortening and lubricants has been mentioned above. It was recognized by practical men that oils, such as lard oil or cottonseed oil, had a property of "oiliness" which was much greater than the "oiliness" of coconut oil, and that this in turn was greater than the "oiliness" of hydrocarbon oils. It was also found that this property of "oiliness" was not due primarily to viscosity or to surface tension. Earlier writers recognized that this was an important and little-understood property of oils and that animal and vegetable oils were superior in oiliness to mineral oils and hence were better lubricants, other things being equal.

This matter has been explained by Wilson and Barnard[9] in a very recent paper. They used, among other methods, the determination of the coefficient of static friction to determine the oiliness of the oil. They have connected the superior oiliness of fatty oils with the attraction of polar groups in the oil for metal, just as the present authors connected the superior shortening power of some fats with the attraction of such polar groups as double bonds for water solutions. The conclusions of Wilson and Barnard for lubricants are closely parallel with those of the present authors for shortenings. Bingham[7] follows the same reasoning.

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[13] Private communication.

Graphic Representation of Water Analyses[1]

By W. D. Collins

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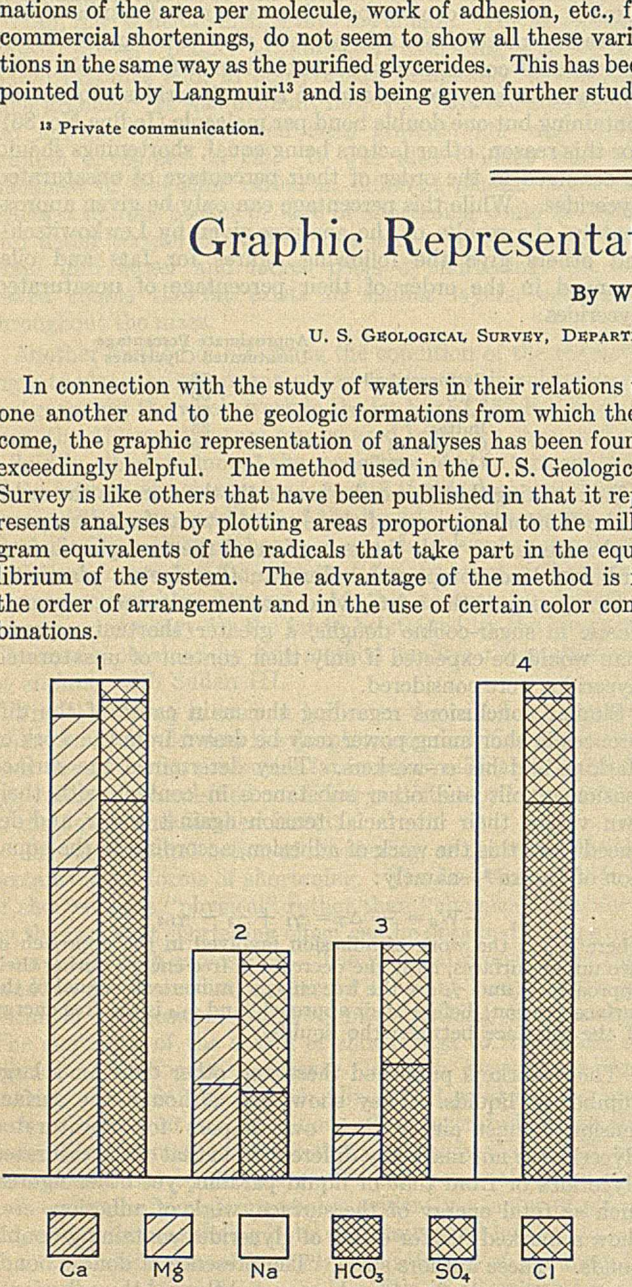
In connection with the study of waters in their relations to one another and to the geologic formations from which they come, the graphic representation of analyses has been found exceedingly helpful. The method used in the U. S. Geological Survey is like others that have been published in that it represents analyses by plotting areas proportional to the milligram equivalents of the radicals that take part in the equilibrium of the system. The advantage of the method is in the order of arrangement and in the use of certain color combinations.



Analyses of Raw and Treated Water

The accompanying figure shows in graphic form the four analyses given in the table. Printing in the text necessitates the use of patterns which are harder to make and less useful than colors for showing the quantities of the different radicals. In regular practice colored crayons or pencils are used as follows:

Calcium	Red	Chloride	Light green
Magnesium	Orange	Sulfate	Light blue
Sodium	Yellow	Bicarbonate	Violet or purple

Potassium is included with sodium, nitrate with chloride, and carbonate with bicarbonate. If it is desired to represent separately the quantities of these radicals, black lines are drawn across the areas in which they are included so as to show potassium and nitrate at the top and carbonate at the bottom of the diagram.

The inevitable error in balance of an analysis may be indicated by inequality of length of the basic and acid columns, but it is generally better to distribute the error between the calcium and bicarbonate so as to make the columns of the same height. If silica is shown, it is represented by a black area extending across the top of the two columns. Suspended matter in an unfiltered water is shown by a brown or sepia area, frequently several times the combined width of the acid and basic columns. The areas for silica and suspended matter are each calculated on the basis of a combining weight of 30.

Analyses of Raw and Treated Water

	1[a]	2[b]	3[c]	4[d]
Parts per million				
Ca	65	19	8.4	Trace
Mg	20	9	0.9	Trace
Na	8	16	45	120
HCO_3	240	53	70	240
SO_4	54	64	54	54
Cl	6	6	6	6
Milligram equivalents				
Ca	3.24	0.95	0.42	....
Mg	1.64	0.74	0.07	....
Na	0.34	0.69	1.94	5.22
HCO_3	3.93	0.87	1.14	3.93
SO_4	1.12	1.33	1.12	1.12
Cl	0.17	0.17	0.17	0.17

[a] Raw water.
[b] Water treated with alum, lime, and soda ash for a public supply.
[c] Water treated hot with lime and soda ash to reduce the hardness to 25 p. p. m.
[d] Water softened by an exchange silicate.

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[1] Published by permission of the Director, U. S. Geological Survey.

Losses in the Refining of Edible Oils[1]

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In practice, two distinct kinds of losses attend the refining or purification of any product. First, there is the production of waste, representing the impurities removed. In most cases, these can be put to some use, and are then called by-products. In the refining processes of edible oils (as well as in most other refining operations) there occurs another form of loss—actual disappearance of materials—so that there is a shrinkage or difference between the weight of material received by the refinery and the total amount finally delivered. It is with this shrinkage or physical loss, and not with directly financial or depreciation losses, that this article is concerned.

EACH kind of edible oil presents a different series of problems with respect to losses, and will be discussed separately. For example, coconut oil is usually filtered at the mill, and for this reason and the fact that copra meat is exceptionally fibrous, it reaches the refiner in a much clearer condition than the other oils. Cottonseed, corn, soy, and peanut oils made in the United States average approximately the same moisture and "meal" content (the latter usually called "gasoline insoluble," from the laboratory method used to determine it). Imported peanut and soy oils are similar in moisture content, but contain less insoluble matter, a condition due probably to longer settling. Coconut oil may run slightly higher in moisture but lower in insoluble matter.

PROCESS LOSSES

The next encounter the refiner has with losses occurs in the processes used for eliminating these impurities. Treatment with an alkali is the first operation. This is commonly looked upon as a process which merely removes the free fatty acids; but this is not its only purpose, and perhaps not always the most important. Sodium hydroxide removes not only the free fatty acids, but also the phosphatides and coloring matter, and is used universally on cottonseed, soy, and corn oils. Sodium carbonate will remove the free fatty acids, but relatively little of the coloring matter and phosphatides. Lime cannot be used at this stage on account of emulsion troubles, but it is interesting to note that in the case of cottonseed oil it removes some of the color which is unaffected by any of the soda alkalies, fuller's earth, or bleaching carbon. This can be shown by first refining and bleaching cottonseed oil, and then treating with lime and noting the color of the oil before and after the lime treatment. Hulme discovered that treatment of cottonseed oil with a boric acid solution precipitates a colored body, and this body has been found by the writer to be a phosphatide.

BORIC ACID AND CAUSTIC SODA PRECIPITATIONS

The study of a number of oils showed that the removal of the phosphatides lowered the free-fatty-acid content in each case 0.2 per cent, indicating the acidic character of the protein, or, possibly, that it is joined to a fatty acid radical.

SUMMARY OF BORIC ACID PRECIPITATE FROM COTTONSEED OIL

	Per cent
Gross	1.445
Less T. F. A. present	0.957
Net protein or phosphatides	0.488
Plus meal	0.090
	0.578

The table shows that the refiner pays for 0.578 per cent of impurity (called "loss not fat") in cottonseed oil which he cannot sell as oil, for phosphatides are removed, not only by boric acid, but also by sodium hydroxide, which removes also free fatty acids in the form of soap, and nonfatty material commonly regarded as "coloring matter." The combined precipitate from the soda treatment of soap, the inevitable emulsified oil, phosphatides, and coloring matter constitute the refining residue known as "soap stock." The following table (Page 396) shows the average analysis of soap stock from 80 tank cars of cottonseed oil, the average analysis of which was as follows:

	Per cent
F. F. A.	1.35
Moisture	0.32
Gasoline insoluble	0.09

BORIC ACID PRECIPITATE FROM COMPOSITE OF 15 TANK CARS OF COTTONSEED OIL

TOTAL PRECIPITATES	Per cent				
A—Boric acid	6.21				
B—Moisture (from boric acid solution)	32.63	*Analysis of C and D—Per cent*			
C—Gasoline-soluble[a] phosphatide + oil	57.94	P_2O_5	3.03[c] (due to meal, 0.0108)		
		N	0.66[d] (due to meal, 0.2900)		
		Analysis of Alcohol-Soluble Portion of C[f]—Per cent		Basis of original oil	
		F. F. A.[h] (oleic)	14.01	0.126	*T. F. A. Constants*
		T. F. A.[i] (by weight)	72.65	0.656	Acid No. 196 (pure cotton oil F. A. 195)
		P_2O_5	2.26	0.0204	Iodine No. 106 (pure cotton oil F. A. 108)
		N	0.26	0.0023	
D—Gasoline insoluble[b] (meal)	3.62	*Analysis of Alcohol-Insoluble Portion of C[g]—Per cent*		Basis of original oil	
		F. F. A. (oleic)	12.33	0.0660	*T. F. A. Constants*
		T. F. A. (by weight)	56.03	0.301	Acid No. 189
		P_2O_5	7.92	0.0424	Iodine No. 100.6
		N	0.43	0.0023	
TOTAL	100.40[e]				

	Per cent
[a] Calculated to original oil	1.45
[b] Calculated to original oil	0.09
[c] Calculated to original oil	0.075
[d] Calculated to original oil	0.016
[e] Calculated to original oil	2.5
[f] Alcohol-soluble portion	36.35
[g] Alcohol-insoluble portion	21.59
[h] Free fatty acid	....
[i] Total fatty acid	....

NOTE: The alcohol-insoluble fatty acids from this treatment were oily, as distinguished from cotton-oil fatty acids, which solidify at room temperature. The alcohol-insoluble portion, which contained 7.92 per cent phosphoric acid, was a transparent, cherry-colored, brittle wax, which did not melt at 100° C.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

Soap-Stock Analysis

(Average from 80 cars of cottonseed oil)

	Per cent
Neutral oil (emulsified in soap stock)	18.70
Fatty anhydrides (combined with Na_2O)	23.50
Ash (Na_2O)	3.25
Water (from NaOH solution)	45.60
Total by analysis	91.05
Foreign matter not fat (by difference)	8.95
Total soap stock (11.8 per cent of original oil)	100.00

The nonfatty matter including meal, calculated to original-oil basis, is 1.05 per cent. The total shrinkage of this oil due to nonfatty impurities is as follows:

	Per cent
Moisture	0.32
Meal	.09
Phosphatides and coloring matter	0.96
	1.37

Sodium hydroxide removes from peanut oil 0.2 to 0.4 per cent nonfatty matter; from coconut oil 0.1 to 0.2 per cent; from soy oil about 0.5 per cent.

The emulsion phenomena during refining are interesting. When the caustic solution is added to the cold oil, a water-in-oil emulsion is first produced, which remains homogeneous even when 10 per cent of caustic solution is used. When heat is applied and the mixture continually stirred, the emulsion undergoes a complete reversal, becoming an oil-in-water emulsion at which point the "break" occurs—i. e., the reversed emulsion, being no longer miscible with oil, coagulates. The flakes of soap stock, consisting of an emulsion of soap, coloring matter, and phosphatides, are then allowed to settle. It is necessary to use sodium salts for this purpose. Lime, for example, produces a permanent water-in-oil emulsion which cannot be reversed by heating. This soap stock may be used by the soap-maker as is, or it may be first "split" by digestion, by means of sulfuric acid, or by Twitchell reagent into free fatty acids, which are then purified by distillation.

Physical Losses in Refining Oil and Reworking Soap Stock

The physical loss or shrinkage incurred in handling soap stock is indirectly a charge against the refinery, and may be divided into five stages:

1—In the case of cottonseed oil, an average of 80 tank cars worked showed that 1.44 per cent of neutral oil was saponified, representing a loss of 0.08 per cent as glycerol. Peanut and soy oils saponify to the extent of about 0.7 per cent, the glycerol equivalent being 0.035 per cent. The treatment of coconut oil with caustic soda is done so rapidly that the amount of saponification is usually negligible, rarely amounting to so much as 0.2 per cent.

2—When soap stock from cottonseed, soy, and peanut oils is acidified with sulfuric acid, a loss occurs by emulsion or adsorption with the carbonized nonfatty matter present, for the recovery of which no means has been found. This amounts to about 0.15 per cent of the oil worked. Coconut oil suffers a loss from this source of 0.85 per cent of the fat acidulated, which is equivalent to 0.075 per cent of the original oil.

3—Solubility losses apply to coconut oil only. These have been found by Gwynn (results hitherto unpublished) to be 0.56 per cent on fat acidulated, representing a loss of 0.049 per cent on original oil.

4—Hydrolysis, or splitting of glycerides on diluting soap stock, due to the presence of combined caustic soda, was found by Gwynn to be 0.028 per cent in the case of coconut oil. (Washing coconut oil with water and salt solution also results in some hydrolysis, the extent of which has not been determined.) No figures are available in the case of the other oils, but there is evidence that the hydrolysis is very much lower than that of coconut oil, and is probably negligible. The hydrolysis on acidulating soap stock probably applies to that of coconut oil only. It has been determined as 0.34 per cent or 0.029 per cent of the oil worked.

5—On acidulating coconut soap stock above 160° F., 0.56 per cent of the fat in the soap stock is volatilized (Gwynn), equivalent to 0.049 per cent of the original oil. In the case of other oils, no loss of this character is known to occur.

Action of Bleaching Agents

After caustic refining the oil is bleached. Chemical bleaches are not used because they injure the flavor of the oil. Benzoyl peroxide has been tried, and while it has no apparent action on the glycerides, its bleaching effect is not stable, the color reverting above 110° C.

On account of the nature of the bleaching process the term "bleaching" is not strictly accurate; what occurs is really a *cleaning* and decolorizing. The agents used are fuller's earth and carbon. They serve as scrubbing agents, and remove soap, moisture, and nonfatty matter, as well as coloring matter. The different kinds of earths used show varying decolorizing effects on vegetable oils, and also a certain degree of oxidation. They absorb a quantity of oil, constituting a loss. The same is true of carbon, with the exception that it does not seem to oxidize the oil. The earths retain, even after steaming and washing, about 24 per cent or more of oil on the dry-weight basis of the earth, and as it is not practicable to recover this, it represents the amount of oil actually lost in bleaching. No data can be given as to whether earths have a selective retentivity for various oils, but from experiments now in process it would seem that peanut oil is retained more tenaciously than other oils.

The loss from bleaching depends on the amount and kind of decolorizing material used. On cottonseed, soy, and corn oils, about 1.5 per cent of bleach is used; and if the retention is 30 per cent on the dry-earth basis, this represents 0.45 per cent loss of the oil treated. Peanut oil requires less earth, and the average loss of oil is about 0.3 per cent. Coconut oil is usually bleached with 0.2 per cent carbon and 0.4 per cent earth. The average loss observed on 60 tank-car lots was 0.24 per cent.

Hydrogenation Losses

If hydrogenation is carried out under the pressure system, where no gases are allowed to escape, there is a gain, increasing directly as the iodine number decreases. This gain, under factory conditions, is 0.04 per cent for coconut oil and 0.78 per cent for cottonseed oil, each oil being completely hydrogenated.

When the open or bubbling system is used, there is a shrinkage due to distillation or entrainment of material by the hydrogen passing through the oil. The distillate is highly colored and of a foul odor, but can be recovered and used as soap stock and therefore does not constitute a physical loss. But the gain in weight due to hydrogenation is not as great in the open system as in the closed type, because at high temperatures noncondensable gases are taken out which constitute a loss.

Losses during Deodorization

The process of deodorization is the final step in the refining of edible oils. Various types of apparatus are used, and the choice of either steam or hydrogen is optional with the operator. In this operation, as in hydrogenation, entrainment and volatilization cause losses due in part to noncondensable products constituting part of the objectionable impurities. Small amounts of free fatty acids and coloring matter are also carried over in the gas current. In the case of coconut oil, there will be a loss due to solubility of the distillate in the condensing water. Assuming that the free fatty acid on coconut oil is 0.03 per cent, this loss amounts to 0.016 per cent, but in the case of the other oils is practically zero. Faulty operation of the deodorizer may at times increase the free-fatty-acid content, in which case this loss is greater. It has been shown that on some poor types of deodorizers the free-fatty-acid content of the distillate may amount to three times as much as could be accounted for by the free-fatty-acid content of the original oil.

VOLATILE MATTER LOST DURING DEODORIZATION

	Per cent
Coconut	0.40
Cottonseed and peanut	0.12–0.35
Soy and corn	0.35–0.75
Beef tallow and oleostearin	1.5 –1.75

The volatile loss is determined by the difference between incoming and outgoing scale weights, after correcting for condensed distillate. Soluble distillate is included as volatile loss, unless determined in the condensing water.

SUMMARY OF LOSSES DUE TO (A) IMPURITIES IN OIL PURCHASED AND (B) REFINING PROCESSES

	Cotton	Corn	Peanut	Soy	Coconut
Moisture	0.27	0.27	0.27	0.27	0.39
Gasoline insoluble[a]	.11	.11	.11	.11	0.037
Phosphatides	0.488	.....	.....	.....	.....
Other nonfatty acid material	0.272	.....	0.30	0.50	0.200
Glycerol loss by saponification	0.080	.....	0.035	0.035	0.000
Loss by emulsion	0.150	.....	0.150	0.150	0.075
Solubility loss	0.000	0.000	0.000	0.000	0.065
Glycerol loss by hydrolysis	.....	.....	.....	.....	0.057
Volatility loss	0.250	0.550	0.250	0.550	0.449
Bleaching loss	0.450	0.450	0.450	0.450	0.240
TOTAL	2.270	1.380	1.565	2.065	1.513

[a] Includes all dirt, solid organic matter (meal), and colloidal meal.

The Catalytic Ammonolysis of Beta-Naphthol and Chlorobenzene in the Vapor State[1]

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β-Naphthol and chlorobenzene mixed with ammonia were passed in the vapor state at definite temperatures over various contact materials. Alumina was the best catalyst found for the ammonolysis of β-naphthol. Good yields of β-naphthylamine (90 to 95 per cent of the naphthol used) were obtained over a range of conditions.

A study of the yield of β-naphthylamine obtained as depending on the catalyst, temperature, ratio of the reactants, and the rate of their flow over the catalyst was made. Curves showing the effect of the temperature and rate of flow of the yield of β-naphthylamine were obtained.

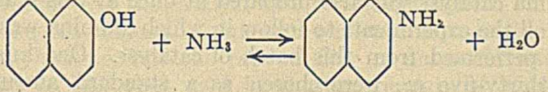
Some conversion of chlorobenzene to aniline was effected. Yields were low (up to 7 per cent) and the catalyst depreciation was rapid. Reduced metals of the iron group were the only contact materials found to catalyze appreciably the ammonolysis of chlorobenzene.

PART I. CONVERSION OF BETA-NAPHTHOL TO BETA-NAPHTHYLAMINE*

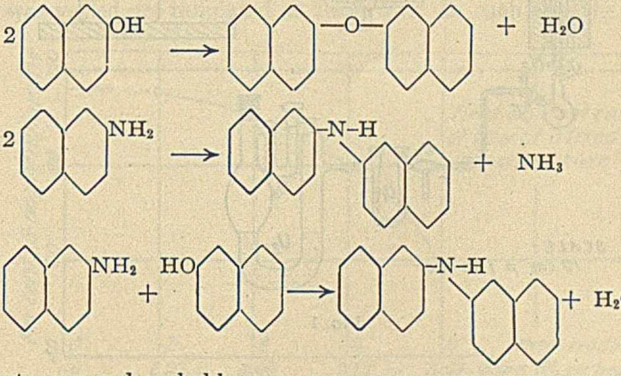
THIS study of the vapor-phase ammonolysis of β-naphthol was undertaken for several reasons. In the first place, while this reaction was tried and found to be successful in the preparation of aliphatic amines[2] from alcohols, yet the action of ammonia on the phenols and naphthols has not been studied. Then too, β-naphthylamine is a valuable dye intermediate and is prepared commercially in quantity. However, the autoclave reaction now in use is necessarily an intermittent one, while a vapor-phase reaction could be made continuous. Also, since the reaction of ammonia on β-naphthol has already been successfully catalyzed by a homogeneous catalyst[3] in liquid systems, a study of it in the gaseous state from the viewpoint of heterogeneous catalysis might help to correlate these two branches of catalytic phenomena.

References to the literature on the preparation of β-naphthylamine by the autoclave process are given below.[4]

Various reactions might be expected to take place when mixtures of β-naphthol vapor and ammonia gas are passed over contact masses. A primary reaction to give β-naphthylamine according to the following equation



as well as some others according to the equations:



etc., seemed probable.

EXPERIMENTAL PART

The experimental apparatus is shown in Fig. 1. It was built with three objects in mind—namely, to get a definite and known mixture of ammonia gas and β-naphthol vapor, to bring this mixture into contact with a catalytic mass at a known temperature, and to collect the products of the reaction.

The general method of conducting experiments, most of which were of 1-hr. duration, was as follows:

The inner tube *t* of the vaporizer V was replaced by a shorter one not reaching to the surface of the β-naphthol B in the vaporizer. Stopcock c_4 was turned off the tubes U_1 and U_2 and to a waste ammonia line and c_1 and c_2 turned in such a manner as either to shunt ammonia from T by or through the wash bottles W_1, W_2, W_3, and W_4, as the experiment required. A slow stream of ammonia was passed through the whole train for about 15 min. thoroughly flushing it out. The furnace F was brought slowly to the required temperature, and the external heating coils H_1 and H_2 turned on. The furnace having reached the required temperature the heating liquid L in the outer jacket of the vaporizer V was made to boil and the flow of ammonia through the flowmeter M

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[1] Received August 21, 1922. Abstract of a thesis presented by A. M. Howald in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1922.

* Patent applied for.

[2] *Compt. rend.*, **148** (1909), 898.

[3] *J. prakt. Chem.*, [2] **69** (1904), 49.

[4] *Ibid.*, [1] **32** (1870), 286; *Ibid.*, [1] **32** (1870), 540; *Ber.*, **13** (1880), 1298; *Ibid.*, **13** (1880), 1850; **14** (1881), 2343; **16** (1883), 19; D. R P. 14,612 (1880); 117,471 (1900); 121,683 (1901); 123,570 (1901); 126,536 (1901); *J. prakt. Chem.*, [2] **69** (1904), 49; **70** (1904), 345; **71** (1905), 433; **75** (1907), 249; **77** (1908), 403.

adjusted by means of the valve v_2 to the rate required by the particular experiment. Next, the short inner tube of the vaporizer was replaced by a long one so that the ammonia would bubble through the molten β-naphthol. After 10 min. more, the reaction tube and catalyst having been flushed with the gaseous mixture of naphthol and ammonia, the bulb C was replaced by a similar clean one and the time recorded. At a definite time 2 to 5 min. later c_4 was turned to pass the ammonia through U_1 into the weighed tubes U_2 and U_3.

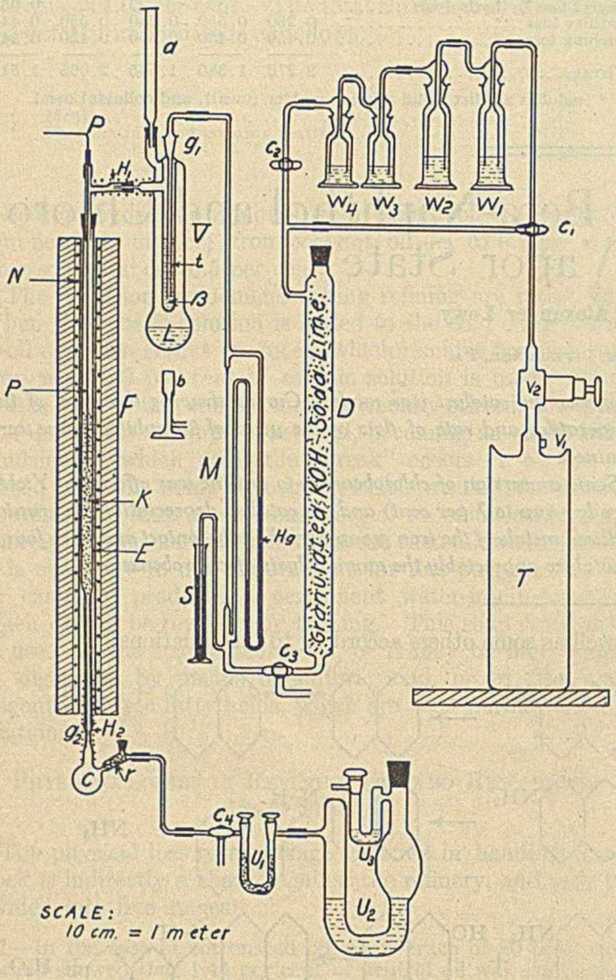

FIG. 1

T, cylinder of anhydrous ammonia.
v_1 and v_2, two valves in series.
c_1, c_3, c_4, 3-way stopcocks.
W_1, W_2, W_3, and W_4, wash bottles for purification of NH_3.
c_2, stopcock.
D, drying tower.
M, glass flowmeter of the capillary and manometer type, calibrated to read grams of ammonia per hour.
S, mercury-seal safety outlet.
V, vaporizer in which the entering ammonia bubbled through a column of molten β-naphthol, B, kept at a constant temperature by the vapors of a liquid, L, kept boiling in an outer jacket. *t* is an inner small bore tube by which the ammonia entered, g_1 a ground joint, and *a* an air condenser to return the boiling liquid L.
H_1 and H_2, two resistance-wire heating coils covered with asbestos cloth by means of which the ammonia and β-naphthol vapor mixture was kept hot between the vaporizer and the furnace F, and between the furnace and the bulb C, in which the reaction products condensed.
P, copper-constantan couple pyrometer extending into the center of the reaction tube.
C, bulb condenser connected to the reaction tube by a ground joint, g_2.
K, catalyst held in the Pyrex reaction tube E.
U_1, U-tube containing granulated KOH for drying the unused ammonia.
U_2 and U_3, two U-tubes in series filled with water and concentrated sulfuric acid, for collecting and weighing the unused ammonia.
F, special 1.2-m. tube furnace of which N is the nichrome heating coil. The furnace was built on a 1.2-m. length of 1.5-in. iron pipe, covered with a thin layer of asbestos cloth and alundum cement, wound with a nichrome coil, then covered with another layer of asbestos cloth and alundum cement, and finally encased in a length of "85 per cent magnesia" 3-in. pipe covering. The furnace temperature was controlled within a 5- to 10-degree range with a sliding rheostat.
r, glass wool.

A series of experiments could then be made by merely replacing the condenser bulb C and the ammonia collecting tubes U_2 and U_3. The solid products were collected in most cases for 1 hr., the ammonia for but 50 min. and calculated to 60 min.

METHOD OF ANALYSIS

The following method of analysis adapted to the determination of β-naphthylamine on small samples in the presence of β-naphthol and β-dinaphthylamine was devised.

A 0.0500 to 0.1000-g. sample was placed in a 25-cc. beaker which had been weighed together with a stirring rod and a 15-cc. Gooch crucible. The sample in the beaker was then dissolved in 10 cc. of dry ether (distilled over fused calcium chloride) and saturated under a desiccated bell-jar with dry hydrochloric acid gas. (Fig. 2) It was then filtered through the Gooch crucible (without suction) and washed five times with a saturated solution of hydrogen chloride in ether. No attempt was made to remove all the precipitate from the beaker, but it was thoroughly washed by decantation. Finally, the outside of the crucible was washed once or twice to remove any soluble deposit left by evaporation of the ether. The precipitate of β-naphthylamine hydrochloride with the crucible stirring rod and beaker was then dried to constant weight at 95° to 100° C. (1 to 2 hrs.) and the weight of hydrochloride was multiplied by the factor 0.797 to give the weight of mononaphthylamine. On distilling off the ether from the filtrate and drying the residue at 50° C., it was weighed as combined naphthol and β-dinaphthylamine.

The analytical method was checked against known amounts of the pure substances, as follows:

TABLE I—CHECK ANALYSIS AGAINST KNOWN AMOUNTS OF PURE SUBSTANCES

β-Naphthylamine Used G.	β-Naphthylamine Found G.	β-Naphthol Used G.	β,β-Dinaphthylamine Used G.	Combined Naphthol and β,β-Dinaphthylamine Used G	Combined Naphthol and β,β-Dinaphthylamine Found G.
0.0614	0.0610	Not weighed	Not weighed	0.0434	0.0437
0.1105	0.1107	Not weighed	Not weighed	0.0485	0.0480
0.2042	0.2045	0.1347	None	0.1347	......
0.1353	0.1337	0.1990	None	0.1990	0.1971

Instead of weighing the β-naphthylamine hydrochloride, it may be determined by titrating its hydrochloric acid content, using phenolphthalein as the indicator.

A preliminary series of experiments was conducted using anhydrous ammonia of coal-tar origin and with aluminium oxide on pumice as the catalytic mass. Poisoning of the catalyst was quite rapid when the ammonia gas was passed only through a soda lime and granulated potassium hydroxide tower. This catalyst depreciation could be, almost if not entirely, overcome by adding to the train wash bottles of alkaline permanganate (W_1 and W_2 of Fig. 1), ammoniacal silver sulfate (W_3), and concentrated potassium hydroxide solution (W_4).

However, in the subsequent experiments, synthetic ammonia requiring no purification was used. A large quantity of alumina catalyst was also prepared at once at this point, so that all the experiments to follow in which alumina was used were performed from this batch of catalyst. One hundred and thirty-five cc. were chosen as a standard amount of catalyst to be used and were taken for all experiments where a different amount is not specifically stated.

Several series of experiments were conducted to determine the effect of the temperature on the yield of β-naphthylamine. Two separate ratios of ammonia to β-naphthol were used by employing dimethylaniline and nitrobenzene of boiling points 191° to 193° C. and 204° to 205° C., respectively, in the outer jacket of the vaporizer. Results for each charge of catalyst are tabulated separately.

For the first series, a meter reading of 4 cm., corresponding to a flow of 5.05 g. of ammonia per hour, was chosen, and dimethylaniline was used as the heating liquid in the vaporizer. The condition and results of the series appear in Table II, and the yields of β-naphthylamine are plotted against temperature as Curve II. (Fig. 3)

TABLE II

Expt.	Temp. °C.	Time in Min.	NH_3 Caught in U_2,U_3 G.	Solids Caught in C. G.	β-Naphthylamine in Solid Condensate %	Naphthol, β,β-Dinaphthylamine, etc. %
1	350	60	5.02	2.36	19.8	....
2	400	60	5.08	2.03	40.6	58.6
3	450	60	....	2.55	91.0	8.0
4	500	60	4.70	1.92	88.1	12.8
5	430	60	4.96	1.55	89.9	10.5
6	450	60	4.52	2.18	90.8	9.2
7	470	60	4.48	2.15	89.0	10.5
8	415	60	4.20	....	79.3	20.4

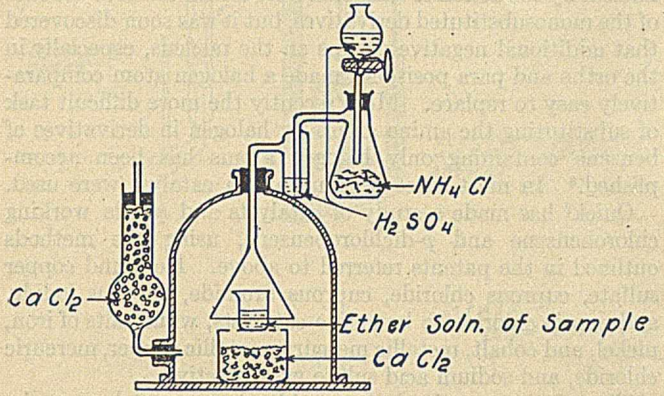

FIG. 2

These results (Curve II) show an optimum yield of β-naphthylamine between 430° and 450° C., which decreases very rapidly between 430° and 400° C. The analyses tabulated are the average of two determinations.

In the next series nitrobenzene was used in the vaporizer and the same temperature range was covered. The duration of each experiment was 1 hr., as before.

TABLE III

Expt.	Temp. °C.	Meter Reading G. NH_3	NH_3 Caught in U_2, U_3 G.	Wt. of Solids Caught G.	β-Naphthylamine in Solid Condensate %	Naphthol, β,β-Dinaphthylamine %
1	350	5.05	5.00	3.39	21.4	78.4
2	400	5.05	5.07	3.31	36.9	63.3
3	450	5.05	4.72	2.40	69.0	30.5
4	500	5.05	4.74	2.38	82.2	20.1

Yields of β-naphthylamine from Table III appear as Curve V. It will be noticed that the yields of β-naphthylamine are everywhere lower than when the vaporizer contained dimethylaniline (Curve II) and that the optimum temperature is higher. That the temperature is higher for a maximum yield when the vaporizer is heated with a higher boiling liquid can be explained by the greater rate of passage of β-naphthol over the catalyst under these conditions.

In the next series the vaporizer was once more heated with dimethylaniline, but the rate of flow of ammonia was decreased to half that used in the experiments of Table II. The conditions and results for this series are given in Table IV, and the yields of β-naphthylamine are plotted as Curve IV.

TABLE IV

Expt.	Temp °C.	Time in Min.	Meter Reading in G. NH_3	NH_3 Caught in U_2, U_3 G.	Solids Caught G.	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	415	60	2.52	2.47	1.06	92.2	7.7
2	450	60	2.52	1.93	.70	95.5	5.0
3	500	60	2.52	1.84	1.07	89.5	9.8
4	400	60	2.52	1.96	.97	88.3	11.8
5	350	60	2.52	2.10	1.06	30.9	67.9

Since decreasing the rate of flow of the vapor mixture (Table IV as compared with Table II) increased the yield of amine, indicating that equilibrium had not been attained, it was decided to conduct a series of experiments in which both the rate of flow of the vapor mixture and the volume of catalyst used should be reduced to one-half their values in the experiments of Table II. In this way was to be determined whether or not the relative yields of amine at a given temperature depended only on the rate of flow per unit volume of the catalyst.

The experiments under these conditions are recorded in Table V.

TABLE V

Expt.	Temp. °C.	Time in Min.	Meter Reading in G. NH_3	NH_3 Caught in U_2,U_3 G.	Solids Caught G.	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	350	60	2.52	2.33	0.91	34.0	....
2	400	60	2.52	2.39	0.93	90.1	9.7
3	450	60	2.52	2.43	1.11	87.8	12.7
4	500	60	2.52	2.39	1.05	88.2	11.7

The percentages of naphthylamine in Table V are plotted as Curve III. It is only at the higher temperatures (range of maximum catalyst efficiency) that this curve coincides, within the experimental error, with Curve II.

TABLE VI

Expt.[a]	Reading of Meter in G. NH_3	NH_3 Caught in U_2, U_3 G.	Solids Caught G.	Ratio by Weight NH_3 Solids	β-Naphthylamine %	Naphthol, β,β-Dinaphthylamine, etc. %
1	2.52	1.93	0.70	2.88	95.5	5.0
2	5.05	4.52	2.18	2.07	90.8	9.2
3	6.30	5.96	2.12	2.91	86.0	14.4
4	10.05	....	4.15	2.43	59.0	40.3

[a] Experiments 3 and 4 were made with one charge of catalyst in the order named. Experiments 1 and 2 are taken from Tables II and IV, respectively.

Some experiments in which the rate of flow of the ammonia was varied are tabulated as Table VI. In each case the va-

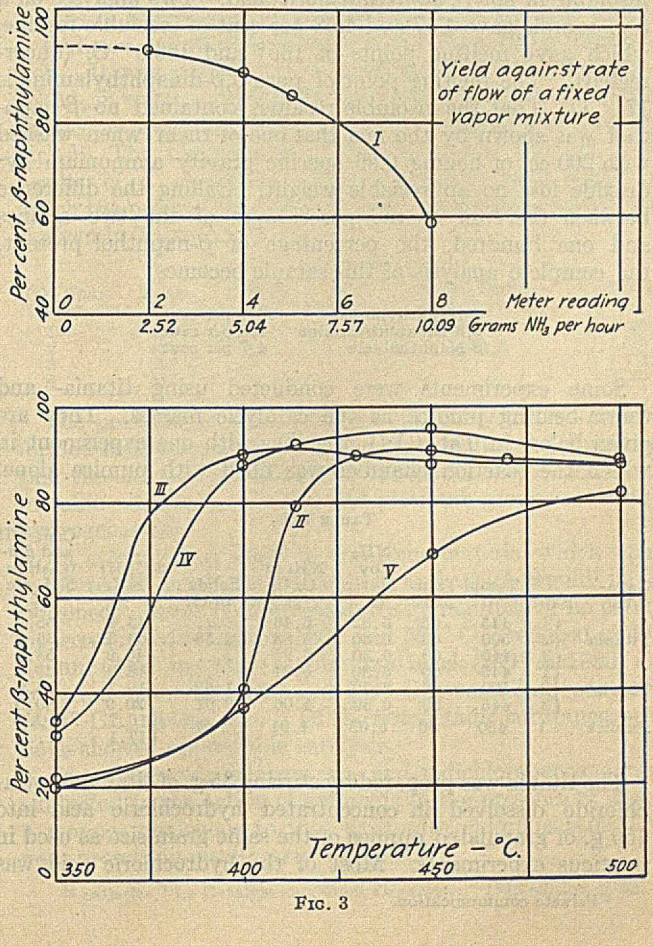

FIG. 3

porizer was heated with boiling dimethylaniline so that approximately a constant ratio of ammonia to naphthol was obtained. The duration of each experiment was 1 hr. and the temperature was kept constant at 450° C.

The results given in Table VI appear as Curve I. The yield of β-naphthylamine increases as the speed of passage over the catalyst decreases. The curve extrapolated to zero speed should give, therefore, the equilibrium concentrations.

A long-period experiment was performed to test the durability of the alumina catalyst. One hundred and thirty-five cc. of catalyst were used with a flow of ammonia of 5.05 g. per hour at the optimum temperature (450° C.) for that rate of flow, as read from Table II and Curve II. It was conducted on two consecutive days for 9 and 7 hrs., respectively. The regular vaporizer was replaced by a 500-cc. flask held in an oil bath kept at 196° to 197° C. by a gas-regulating thermostat. The receiver was also made larger.

Owing to inequalities in the depth of immersion of the tube by which the ammonia bubbled through the β-naphthol, less solid product was obtained per hour on the second than on the first day. The weights were 21.6 and 11.9 g., corresponding to an hourly rate of 2.4 and 1.7 g., respectively. The analysis of the product obtained was as follows:

	β-Naphthylamine %	Naphthol, etc. %
First day (9 hrs.)	85.5	15.4
Second day (7 hrs.)	90.7	9.3
Total product	87.3	13.3

Evidently, the catalyst had not depreciated materially during 16 hrs. The higher yield during the last 7 hrs. is accounted for by the lower hourly rate.

The product from the last 7 hrs. of the long-period experiment was analyzed for β,β-dinaphthylamine by the method of Lee,[5] and Jones, in which it is obtained as a residue insoluble in hot 1 : 30 hydrochloric acid. Two analyses on a 5-g. sample gave 4.57 and 4.58 per cent of insoluble residue, which gave melting points of 165° and 166.5° C. (uncorrected). The melting point of pure β,β-dinaphthylamine is 171° C. That the insoluble residues contained no β-naphthol was shown by the fact that one of them when washed with 200 cc. of boiling 0.96 specific gravity ammonium hydroxide lost no appreciable weight. Calling the difference between the sum of the percentages of the two amines and one hundred, the percentage of β-naphthol present, the complete analysis of this sample becomes:

β-Naphthylamine	90.7 per cent
β,β-Dinaphthylamine	4.6 per cent
β-Naphthol, etc.	4.7 per cent

Some experiments were conducted using titania- and thoria-bearing pumice as the catalytic masses. They are given below in Table VII, together with one experiment in which the reaction chamber was filled with pumice alone.

TABLE VII

CATALYST	Expt.	Temp. ° C.	Time Min.	NH_3 by Meter G.	NH_3 in U_2,U_3 G.	Solids in G.	β-$C_{10}H_7NH_2$ %	$C_{10}H_7OH$ and β,β-$(C_{10}H_7)_2NH$, etc. %
Titania	1	445	65	6.82	6.46	....	43.4	55.7
	2	500	60	6.30	5.88	2.58	63.5	36.4
	3	445	60	6.30	6.25	....	40.9	58.4
Thoria	1	445	60	6.30	5.31	....	18.0	....
	2	500	60	6.30	....	1.62	19.7	78.9
	3	445	60	6.30	4.06	2.01	20.9	80.0
Pumice	1	450	60	5.05	4.91	1.88	16.7 17.1	....

The titania was prepared by stirring 35 g. of titanium tetrachloride dissolved in concentrated hydrochloric acid into 150 g. of granulated pumice of the same grain size as used in previous experiments. Most of the hydrochloric acid was then evaporated, an excess of concentrated aqua ammonia added, the whole evaporated and ignited to dull redness in a muffle furnace.

The thoria was prepared by stirring a solution of 50 g. of hydrated thorium nitrate with 150 g. of pumice, adding an excess of ammonia, evaporating, and igniting to redness.

PART II. AMMONIA ON CHLOROBENZENE

It seemed probable that the halogen atom as well as the hydroxyl group could be replaced by the amino group by the action of ammonia in the vapor phase, if a suitable catalyst could be found. Indeed, chlorobenzene,[6] like β-naphthol, has already been successfully subjected to ammonolysis in an autoclave in the presence of a catalyst.

Earlier[7] attempts to replace halogen atoms on the benzene nucleus by the action of ammonia were unsuccessful in the case of the monosubstituted derivatives, but it was soon discovered that additional negative groups on the nucleus, especially in the ortho and para positions, made a halogen atom comparatively easy to replace. More recently the more difficult task of substituting the amino group for halogen in derivatives of benzene containing only halogen atoms has been accomplished.[8] In most cases pressure and a catalyst were used.

Quick[6] has made a study of catalysts and yields working chlorobenzene and p-dichlorobenzene, using the methods outlined in the patents referred to above. He found copper sulfate, cuprous chloride, cuprous bromide, cuprous iodide, and cupric chloride to be active catalysts, while salts of iron, nickel, and cobalt, metallic mercury, metallic copper, mercuric chloride, and sodium acid sulfite were inactive.

The primary reaction between chlorobenzene and ammonia, if applied above the dissociation temperature of ammonium chloride, can be represented by the equation:

$$C_6H_5Cl + NH_3 = HCl + C_6H_5NH_2$$

However, on cooling, any excess of ammonia would react with the hydrogen chloride formed to give ammonium chloride.

In addition to this primary reaction, other reactions according to the following equations might be expected:

$$3C_6H_5Cl + 2NH_3 \longrightarrow 3C_6H_6 + 3HCl + N_2 \qquad (1)$$

This equation is probable since hydrogen has been shown[9] to reduce chlorobenzene to benzene in the presence of reduced nickel and iron which are also known to decompose ammonia into hydrogen and nitrogen.

$$2C_6H_5Cl \longrightarrow Cl.C_6H_4.C_6H_4.Cl + H_2 \qquad (2)^{10}$$

$$6C_6H_5Cl + 2NH_3 \longrightarrow N_2 + 3C_6H_5.C_6H_5 + 6HCl \qquad (3)^{9}$$

Also an amine, if formed, might react further according to one of the following equations:

$$C_6H_5NH_2 + C_6H_5Cl \longrightarrow C_6H_5.NH.C_6H_5 + HCl \qquad (4)^{11}$$

$$2C_6H_5NH_2 \longrightarrow C_6H_5.NH.C_6H_5 + NH_3 \qquad (5)^{12}$$

EXPERIMENTAL PART

As preliminary experiments indicated the formation of some aniline by the reaction of ammonia upon chlorobenzene in the vapor state, an apparatus was devised to study the course of the reaction. The final form used is shown in Fig. 4. The furnace at F (not shown) was the same as used in

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[5] Private communication.

[6] *J. Am. Chem. Soc.*, **42** (1920), 1033.

[7] *Ann.*, **104** (1857), 225; **121** (1862), 358.

[8] *J. prakt. Chem.*, [2] **48** (1894), 465; D. R. P. 202,170 (1908); 204,848 (1908); Brit. Patent 3847; Fr. Patent 397,443; D. R. P. 204,951 (1908); Fr. Patent 397,495; *Ber.*, **47** (1914), 3165.

[9] Rideal and Taylor, "Catalysis in Theory and Practice," p. 179.

[10] *Ann.*, **189** (1877), 138.

[11] *Ber.*, **36** (1903), 2382; D. R. P. 187,870 (1907).

[12] *Z. Chem.*, **2** (1866), 438.

Part I (Fig. 1), as were the flowmeter and ammonia-washing train, which are not repeated in Fig. 4. The essential differences in the apparatus consisted in the device for obtaining the vapor mixture and in the condenser used in collecting and withdrawing samples of the product.

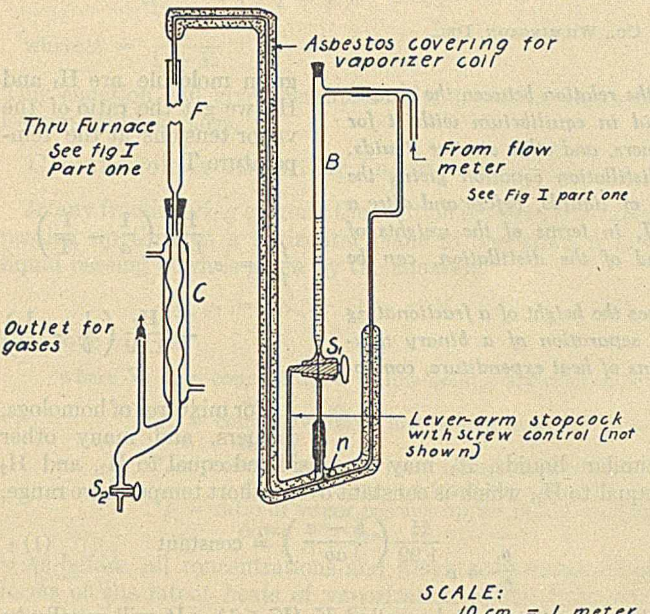

FIG. 4

The chlorobenzene was contained in a buret, B, with a long-armed stopcock, S, fitted with a screw regulator by means of which a constant flow of chlorobenzene could be made to drop into a vaporizer at *n*, where it met the incoming stream of ammonia. The mixture then passed up through the vaporizer which was heated above the boiling point of chlorobenzene by means of a nichrome coil, and passed into the furnace F. By means of a stopcock, S_2, on the condenser C a sample of the liquid product could be withdrawn at any time. A nickel-nichrome couple was used in measuring the temperature.

A method of analysis for aniline was devised based on the fact that the hydrogen chloride contained in its hydrochloride can be titrated with alkali, using phenolphthalein as the indicator.

With the apparatus as described, reduced nickel was tried as the catalyst. In preparing it, 100 g. of pure hydrated nickel nitrate were dissolved in water and the solution poured over 100 g. of granulated pumice screened to pass a 4-mesh standard sieve, but held on an 8-mesh sieve. The mixture was well stirred while evaporating to dryness and then ignited in porcelain over a burner until no more nitric oxide fumes were evolved. A 2-ft. length of it was then charged into the center of the reaction tube and reduced there with hydrogen at 350° C. until no more water was evolved. The hydrogen used was electrolytic hydrogen, as obtained in cylinders, and was purified by passing through wash bottles containing solutions of KOH and Ag_2SO_4, and finally dried by passing over fused $CaCl_2$. When the reduction was complete, the stopcocks were turned so as to replace the flow of hydrogen by ammonia, and the apparatus was then ready for an experiment.

The results and conditions of experiments with the first nickel catalyst are tabulated below. (Table VIII)

Experiment 1 showed promise, but in Experiment 4, conducted under identical conditions, the yield of aniline was only one-sixth as great. This could only be explained by catalyst poisoning.

TABLE VIII

Expt.	Time	Temp. ° C.	C_6H_5Cl Used Cc.	NH_3 Liters	Molar Ratio $C_6H_5Cl : NH_3$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	380	30	21.7	1:2.5	27	5.80
2		480				24	1.30
3		360				32.5	0.51
4		380				32	0.93

A second nickel catalyst prepared as before was used at 380° C., with a greater excess of NH_3 over C_6H_5Cl, and the results with it are given in Table IX.

TABLE IX

Expt.	Time	Temp. ° C.	C_6H_5Cl Cc.	NH_3 Liters	Molar Ratio $NH_3 : C_6H_5Cl$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	380	15	21.7	5 : 1	14	7.35
2						14	5.60

Reduced iron gave results very similar to those obtained with nickel. It was prepared by distributing 100 g. of hydrated ferric nitrate over 100 g. of granulated pumice of the same grain size as used for nickel. It was ignited to ferric oxide, charged into the catalyst tube, and reduced with hydrogen at 550° C. Table X contains the results of experiments conducted with this catalyst.

TABLE X

Expt.	Time	Temp. ° C.	C_6H_5Cl Cc.	NH_3 Liters	Molar Ratio $C_6H_5Cl : NH_3$	Product G.	$C_6H_5NH_2$ %
1	1 Hr.	480	15	21.7	1 : 5	15.5	7.35
2		380				....	.75
3		480				....	3.23

480° C. was evidently a more favorable temperature than 380° C. The same diminishing effectiveness as for the nickel catalyst was apparent.

A new charge of the iron oxide was prepared and reduced as before, and it was then subjected for 5 hrs. to a stream of ammonia gas of the speed used in the experiments of Table X. The idea in this was to determine if the catalyst were being poisoned by an impurity in the ammonia. That this was not the case was shown, as this iron when used according to the conditions of Experiment 1, Table X, gave 7.2 per cent aniline.

Reduced cobalt gave lower results than either nickel or iron. It was prepared by dissolving 100 g. of hydrated $Co(NO_3)_2$ in water, pouring the solution on 100 g. of granulated pumice, evaporating, igniting, and reducing as with iron and nickel. The temperature of reduction was 480° C. The results of a continuous 2-hr. experiment with cobalt, in which the product for each half hour was separately analyzed, is given in Table XI.

TABLE XI

Half-Hour Period	Temp. ° C.	C_6H_5Cl Cc.	NH_3 G.	Molar Ratio $C_6H_5Cl : NH_3$	$C_6H_5NH_2$ %
1	480	15	6.37	1 : 2.5	1.30
2	480				1.05
3	380				1.02
4	480				0.85

The poisoning in each case was probably due to chloride formed in the reaction, as it has been known for some time that the halides[13] are extremely deleterious in their action on metallic catalysts of the iron and platinum groups as used for hydrogenations.

An attempt was made to find some material which would catalyze the production of aniline and which would no be poisoned. Some of the substances giving little or no catalysis were: metallic copper (380° and 580° C.), reduced molybdenum (380° and 480° C.), platinum black (280° and 380° C.), cocoanut charcoal (380° and 580° C.), vanadium pentoxide (480° C.), titania, etc. Of the nonmetallic substances used none showed appreciable catalysis.

Bromobenzene, iodobenzene, and *p*-dichlorobenzene were subjected to the action of ammonia in the presence of iron in a manner analogous to that used with chlorobenzene. No very promising results were obtained.

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[13] Sabatier, "La Catalyse en Chimie Organique," 1913 edition, p. 23.

Calculations on Fractionating Columns from Theoretical Data[1]

By W. A. Peters, Jr.

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An equation is derived giving the relation between the composition of the vapor and of the liquid in equilibrium with it for binary mixtures of homologs, isomers, and other similar liquids. With the aid of this equation the distillation equation giving the compositions of a binary mixture of liquids, before and after a certain portion has been distilled off, in terms of the weights of material at the beginning and end of the distillation, can be integrated.

An equation is derived which gives the height of a fractionating column required to make any given separation of a binary mixture of liquids under given conditions of heat expenditure, composition of distillate, etc.

In an article on the efficiency and capacity of fractionating columns,[2] it was suggested that the efficiency of a column be measured by comparing the performance of a definite unit or length of the given column with the performance calculated for a theoretically perfect plate column under similar conditions. The theoretically perfect plate column is defined as one in which the vapor rising from any plate is in equilibrium with the liquid on the plate, all of the liquid on the plate being of the same composition. The justification of this definition lies in the experimental data, which prove that, for the separation of any given liquid mixture, the height of any column of uniform construction equivalent to a theoretical plate is constant and does not depend on the ratio of heat supplied at the base of the column to distillate withdrawn, to the composition of the liquid in the section of column considered, or to the composition of the distillate or still charge. This ratio varies greatly for different liquids and must be determined separately for each new mixture. The constant will be called the *height of equivalent theoretical plate*, or H. E. T. P. Several values for it are given in the article mentioned above and a method for calculating it from experimental data is also given. A similar method of calculation was developed by W. K. Lewis,[3] but both methods are somewhat tedious. A shorter and more exact method can be used in certain cases where the equation expressing the relation between the composition of the liquid and that of the vapor in equilibrium with it for mixtures of the two liquids under consideration is known. In such cases, an equation expressing the rate of enrichment in the column can be developed and integrated, the resulting equation giving directly the height of column required to make the separation required with the specified heat consumption.

Vapor Composition Equation

The equation for vapor composition in terms of the composition of the liquid in equilibrium with it is derived as follows:

The Clapeyron equation, expressing the vapor pressure of a substance in terms of its latent heat of vaporization and the absolute temperature, is

$$\ln\frac{p}{P} = \frac{H}{1.99}\left(\frac{1}{a} - \frac{1}{T}\right)$$

in which

p = vapor pressure at temperature T
P = vapor pressure at temperature a
H = latent heat of vaporization in calories per gram molecule
1.99 = the gas constant, R

For two materials whose boiling points are a and b at the same pressure, and whose latent heats of vaporization per gram molecule are H_1 and H_2, we get the ratio of the vapor tensions at the temperature T

$$\frac{p_1}{p_2} = e^{\frac{H_1}{1.99}\left(\frac{1}{a} - \frac{1}{T}\right) - \frac{H_2}{1.99}\left(\frac{1}{b} - \frac{1}{T}\right)}$$

For mixtures of homologs, isomers, and many other similar liquids, H_1 may be considered equal to H_2, and H_2 equal to H_1, which is constant over a short temperature range.

$$\frac{p_1}{p_2} = e^{\frac{H}{1.99}\left(\frac{b-a}{ab}\right)} = \text{constant} \qquad (1)$$

$\frac{p_1}{p_2} = e^{\ln K} =$

This constant will be called K (K < 1). It will usually be found more convenient to determine K directly from known data on the vapor tensions of the liquids considered than to use Equation 1, since the vapor tensions are more accurately known than the heats of vaporization.

$K = \alpha$ ([illegible]

From Equation $\frac{p_1}{p_2}$ = K, the vapor-liquid composition relation is derived as follows:

Let X = concentration of low-boiling material in the liquid
Y = concentration of low-boiling material in the vapor
M = total pressure under which the mixture is boiling
A = vapor tension of the low-boiling material at the boiling temperature, all concentrations and ratios being expressed in terms of the latent heats of vaporization of the materials

For mixtures of homologs and isomers, we can write

$$M = AX + AK\,(1 - X) \qquad (2)$$

Now, AX is the partial pressure of the low-boiling material in the vapor. Therefore,

$$Y = \frac{AX}{M} \qquad (3)$$

Eliminating A between Equations 2 and 3, we have

$$Y = \frac{X}{K + X(1 - K)} \qquad (4)$$

If K is chosen as the ratio between the vapor pressures of the two materials at a temperature which is the average between the boiling points of the two at the pressure considered, this equation will give results closer than the results taken from any graph. The equation will first be applied to the case of simple distillation.

Application to Simple Distillation

The equation expressing the weights of a given mixture before and after a portion has been distilled off, in terms of the composition of the vapor and liquid, is

$$\ln\frac{W}{W_o} = \int_{x_o}^{x} \frac{dx}{y-x} \qquad (5)$$

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[1] Received September 15, 1922.

[2] Peters, This Journal, 14 (1922), 476.

[3] *Ibid.*, 14 (1922), 492.

where W_o = weight of original mixture of concentration x_o
W = weight remaining at a time when the concentration of the liquid is x[4]

Substituting in Equation 5 the value of Y given in Equation 4, and integrating, gives

$$\frac{W}{W_o} = \left(\frac{x}{x_o}\ \frac{1-x_o}{1-x}\right)^{A}\frac{1-x_o}{1-x} \qquad (6)$$

where $A = \dfrac{K}{1-K}$

This equation will give accurate results for all mixtures of isomers and homologs.

CALCULATION OF HEIGHT OF FRACTIONATING COLUMN

In any fractionating column, the relation between the vapor passing up through a horizontal plane at the point n and liquid passing down is given by the equation

$$Y_{n+1} = \rho X_n + (1-\rho)\,Y_c \qquad (7)$$

(n above $n+1$)

where Y_{n+1} = concentration of low-boiling material in the vapor
X_n = concentration of low-boiling material in the liquid
Y_c = concentration of low-boiling material in the distillate removed from the column
ρ = ratio of vapor passing up, to liquid coming down

As before, all concentrations and weights are measured in terms of the latent heats of vaporization of the respective materials.

From the definition of the theoretical plate column, it follows that at a point higher than n by a distance equal to the H. E. T. P., the concentration of low-boiling material in the vapor will be Y_n. The difference between the composition at this higher point and at the point n will be $Y_n - Y_{n+1}$, and this difference gives the rate of enrichment in the column. We can write

$$Y_n - Y_{n+1} = \Delta Y \qquad (8)$$

and since it has been proved experimentally that the ratio between the enrichment and the height of the column is constant

$$dY = \frac{dh\,\Delta Y}{\alpha} \qquad (9)$$

where α = H. E. T. P.
dh = an increment in the height of the column measured in theoretical plates

Substituting in (9) the value of ΔY from (8),

$$dY = \frac{dh}{\alpha}\,(Y_n - Y_{n+1}) \qquad (10)$$

Substituting in (10) for (Y_{n+1}) from (7) and (4), solving for dh, and dropping subscripts gives

$$dh = \alpha\,dY\left[\frac{\dfrac{1}{1-K} - y}{-\dfrac{1-\rho}{1-K}Y_c + \left(1-\rho)Y_c + \dfrac{1-\rho K}{1-K}\right)Y - Y^2}\right] \qquad (11)$$

$$\text{Write } A = -\frac{1-\rho}{1-K}\,Y_c$$

$$B = (1-\rho)Y_c + \frac{1-\rho K}{1-K}$$

$$C = \frac{2}{1-K} - B$$

$$q = 4A - B^2$$

Substituting these values in Equation 11 and integrating between the limits Y_1 and Y_2 gives

$$H = \frac{\alpha}{2}\left[\ln(A + BY - Y^2) + \frac{c}{\sqrt{-q}}\ln\frac{-2Y + B - \sqrt{-q}}{-2Y + B + \sqrt{-q}}\right]_{Y_2}^{Y_1} \qquad (12)$$

As an example of the use of this equation, consider the case of the separation of benzene and toluene in a continuously operated plate column.

It has been determined that two standard bubbler cap-type plates are approximately equivalent to one theoretical plate for this separation. If we make $\alpha = 2$, H will be given in actual plates. From data on the vapor tensions of benzene and toluene, average for K is found to be 0.4.

It is desired to obtain a distillate running 99 per cent benzene with a steam consumption of about 1 lb. per lb. of distillate, making

$$Y_c = 0.99$$
$$\rho = 0.8$$

Let it be required to find the number of plates in the column between the top and a point at which the molecular concentration of benzene in the vapor is 0.4. The constants will be

$A = -0.3333 \quad B = 1.3313 \quad C = 2.0 \quad q = -0.439 \quad \sqrt{-q} = 0.663$

$$H = \ln\frac{-0.3333 + 1.3180 - 0.9801}{-0.3333 + 0.5325 - 0.1600} - \frac{2\ln}{0.663}\,\frac{-1.98 + 1.3313 - 0.663}{-1.98 + 1.3313 + 0.663} + \frac{2\ln}{0.663}\,\frac{-0.8 + 1.3313 - 0.663}{-0.8 + 1.3313 + 0.663} = 18.7 \text{ plates}$$

Similar equations can be developed for the exhausting section of the column.

Let R = ratio of liquid down to vapor up (R>1)
X_s = composition of effluent
Y_m = composition of vapor from mth plate
[mth plate above ($m+1$)th plate]

All compositions and ratios in terms of equivalent latent heats of vaporization.

$$\text{Then } \Delta Y = \frac{\dfrac{-X_s(R-1)}{1-K} + \left\{\dfrac{1-RK}{1-K} + (R-1)X_s -\right\}Y - Y^2}{\dfrac{1}{1-K} - Y} \qquad (13)$$

The equation for H for the exhausting section will be similar to (12). In it

$$A = -\frac{X_s(R-1)}{1-K} \qquad B = \frac{1-RK}{1-K} + (R-1)X_s$$

$$C = \frac{2}{1-K} - B$$

$$q = 4AC - B$$

It is desirable to introduce the feed in any continuous column at the plate where the rate of enrichment in the rectifying section is equal to that in the exhausting section. This point is easily found by equating (13) and the value of ΔY from (11). This gives

$$Y = \frac{X_s(R-1) - Y_c(1-\rho)}{K(\rho - R) + (1-K)\left[(R-1)X_s(1-\rho)Y_c\right]} \qquad (14)$$

If, as is usually the case, $X_0 = 0$ or nearly so

$$Y = \frac{-Y_c(1-\rho)}{K(\rho - R) - (1-K)(1-\rho)Y_c} \qquad (15)$$

The minimum height of column which will make a given separation with infinite expenditure of heat is given by making

ρ and R = 1
A then = 0
B = 1
$C = \dfrac{1+K}{1-K}$
$q = -1$

and Equation 12 becomes

$$H = \frac{\alpha}{2}\left[\ln(Y - Y^2) + C\ln\frac{Y}{Y-1}\right]_{Y_2}^{Y_1}$$

The point in a column at which no separation takes place is given by equating (10) to 0. This gives $A + BY - Y^2 = 0$.

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[4] C. S. Robinson, "Elements of Fractional Distillation," p. 45.

Recent Investigations on the Oxidation of Sulfur by Microörganisms[1,2]

By J. G. Lipman

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The following paper is a brief discussion of some investigations on the microörganism Thiobacillus thiooxidans, isolated under the writer's direction at the New Jersey Agricultural Station. The properties and action of this organism and its use as a sulfur-oxidizing agent to solve various soil problems have been described.

THIOBACILLUS THIOÖXIDANS [2,3,8,12,*] is the sulfur-oxidizing organism par excellence. It is one of the autotrophic bacteria that are able to function in mineral media and to derive their carbon from carbon dioxide. Growth readily occurs at 20° to 25° C. in suitable media with a pH of 4.4 to 4.6. Sulfur is oxidized to sulfuric acid, and the organism, because of the energy set free, is able to utilize the carbon of carbon dioxide for the building of its cell substance.

It has been found [3,13] in our investigations that for every 32 parts of sulfur oxidized there is 1 part of carbon assimilated. This would represent a utilization of about 6.5 per cent of the energy liberated in the oxidation of sulfur to sulfuric acid. In case of the bacteria capable of oxidizing ammonia to nitrites the ratio of nitrogen transformation to carbon assimilated is 35 : 1. In case of the organisms capable of oxidizing nitrites to nitrates there is 1 part of carbon assimilated for each 135 parts of nitrogen transformed. In view of the fact, however, that the oxidation of nitrites to nitrates makes available only one-fourth of the amount of energy that is made available in the oxidation of equivalent quantities of ammonia nitrogen to nitrites, the differences are, after all, slight. It is evident, therefore, that in the oxidation of ammonia to nitrites and of nitrites to nitrates about 5 to 6 per cent of the energy available is utilized for the assimilation of carbon by the bacteria. This does not differ very greatly from the amount of energy used for the same purpose by *Thiobacillus thioöxidans*. In the case of higher plants only 1 per cent of the total energy of the sun's radiation is used for the assimilation of carbon from carbon dioxide. It may be added here that aztobacter, representing the most efficient of the nonsymbiotic nitrogen-fixing bacteria, will assimilate, under favorable conditions, as much as 2 parts of nitrogen for every 100 parts of sugar used. In this case, however, the utilization of the carbohydrate is not complete, since organic acids and other organic products appear in the culture medium.

Thiobacillus thioöxidans has a remarkable tolerance for sulfuric acid. In one of our experiments sulfuric acid was added to the medium in varying amounts and the rate of oxidation of sulfur was determined. The increasing concentration of the sulfuric acid did not seriously retard the activities of *Thiobacillus thioöxidans* until the concentration of 5 per cent of acid was reached.

With 0.025 per cent of acid there were oxidized in 100 cc. of the culture medium containing 1 g. of sulfur an equivalent of 249.3 mg. of sulfur. When the concentration of the acid reached 5 per cent there was still oxidized 75.55 mg. With a concentration of 10 per cent of acid in the medium the bacteria could apparently no longer function and no sulfur was oxidized.

Use against Potato Scab

Sulfur oxidation by *Thiobacillus thioöxidans* has been utilized as a means for solving certain problems of agricultural production. It is well known that far-reaching damage is done to our potato crop in certain localities by *Actinomyces scabies*. This organism will grow best in soils that are only very slightly acid or not at all acid. For many years this fact has been recognized by soil investigators and by plant pathologists, and such methods of soil treatment have been recommended as would tend to increase the acidity of the soil. The use of fertilizers tending to increase the hydrogen-ion concentration of the soil solution is advocated. Ammonium sulfate and other ammonium salts are more or less effective for this purpose. Potassium chloride and potassium sulfate, as well as acid phosphate, are helpful in a limited way. Organic acids derived from the decomposition of rye and of other crops used as green manures may also serve to lessen the damage done by the potato-scab organism. Investigations covering a period of more than twenty-five years have indicated the effectiveness of sulfur for the same purpose. The New Jersey Experiment Station was one of the pioneers in the study of sulfur as a means of controlling the damage done by the potato-scab organism. Until recent years, however, consistent results with sulfur were not obtained by different investigators. It was finally shown by the New Jersey Station[9] that sulfur often fails to increase the acidity of the soil promptly and effectively to a point where the activities of the potato-scab organism are more or less effectively suppressed. Two of the important factors that have apparently been overlooked by earlier investigations are the need of uniform distribution of the sulfur and the need of supplying an organism or organisms that would rapidly oxidize sulfur to sulfuric acid. Within the past three years the writer and his associates have compared inoculated with uninoculated sulfur on many different soils and under varying conditions. The results secured in these experiments have been published in part. Other data are to be published in the near future. On the basis of these numerous experiments, covering a period of three years, it is safe to state that sulfur inoculated with *Thiobacillus thioöxidans* is much more effective than equivalent amounts of sulfur not inoculated with these organisms. It appears that 300 lbs. of inoculated sulfur are practically as effective as 600 lbs. of uninoculated sulfur. Methods have been developed for inoculating sulfur with *Thiobacillus thioöxidans* on a commercial scale.

To Produce Soluble Phosphate

The writer suggested some years ago[6,10] that the biological oxidation of sulfur might be employed as a means of producing soluble phosphates. The method as proposed is quite simple. Quantities of ground phosphate rock and

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[1] Presented before the Division of Fertilizer Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Paper No. 113 of the Journal Series, New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

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

ground sulfur were intimately mixed with soil and inoculated with *Thiobacillus thioöxidans*. The sulfuric acid resulting from the oxidation of the sulfur reacted with the tricalcium phosphate and led to the formation of dicalcic and monocalcic phosphate. Our more recent [1, 3, 4, 7, 11] studies have dealt with more effective methods for the production of available phosphates by the process just described. It has been found that when mixtures of sulfur and ground phosphate rock are broadcasted on any soil area conveniently located, and worked into the surface soil by means of ordinary tillage implements, the formation of available phosphates goes on fairly rapidly. If successive additions of mixtures of sulfur and ground phosphate rock are made from time to time and similarly worked into the surface soil, a concentrated material is finally obtained which contains 16 per cent of total phosphoric acid, of which 50 to 60 per cent is citrate-soluble. The time necessary for reaching this result is about 15 to 16 wks. It is expected by the writer and his associates that further improvements in the technic will reduce the time to 12 to 15 wks. Under such conditions it may become practicable to produce any desired quantity of acid phosphate at a very slight cost. This could best be done at points from which supplies of both phosphate rock and sulfur may be readily reached. Portions of Florida, Louisiana, and Texas offer such locations and possess the further advantage of being situated under climatic conditions suitable for the functioning of the sulfur-oxidizing organisms throughout the year.

USE ON LAND DEFICIENT IN SULFUR

The oxidation of sulfur by microörganisms makes this substance suitable for use on land that is deficient in sulfur. It has been demonstrated that in sections of Oregon, Washington, and Idaho much of the land responds to applications of sulfur-carrying materials. Gypsum was at first used by farmers in these localities for increasing the yields of alfalfa. More recently it has been found that sulfur is practically as effective, and, from the standpoint of actual concentration in sulfur, much more satisfactory. Experiments[5] carried on at the writer's suggestion with samples of soil from Oregon show that the addition of *Thiobacillus thioöxidans* intensifies the rate of oxidation of the sulfur and makes the latter much more effective in supplying this element to the crop. Many hundreds of tons of sulfur are already used in the regions referred to and the consumption will materially increase. The greater effectiveness of inoculated sulfur should make the results from its use much more certain.

BLACK ALKALI PROBLEM

Another agricultural problem that may be solved through the oxidation of sulfur by microörganisms is the so-called *black alkali* problem. In certain of the soils on the Pacific Coast an accumulation of soluble salts containing substantial proportions of sodium carbonate and bicarbonate leads to the deterioration of the texture of the soil. The land becomes impervious and ordinary methods of reclamation by the washing out of the excessive salts fail to produce the desired results. The writer was, therefore, led to suggest that the use of sulfur might offer a satisfactory solution. The sulfuric acid formed from the oxidation of sulfur would react with sodium carbonate and bicarbonate and lead to the formation of sodium sulfate. The texture of the soil would improve to a point where the soluble salts could be more or less effectively washed out. Experiments were accordingly initiated with soil derived from black-alkali spots in California. Inoculated sulfur was employed at the rate of 2000 to 6000 lbs. per acre. Two weeks after the inoculated sulfur had been added to the soil it was found that 20 to 25 per cent of the sulfur had been oxidized, all carbonates had disappeared, and the bicarbonates were reduced to about 40 per cent of the original amount. The pH of the soil had changed from 8.8 to 7.9. Where sulfur was added at the rate of 6000 lbs. per acre, the permeability of the soil to water improved to the extent of 30 to 40 per cent. It was evident that the colloids present in the soil had largely been coagulated by the sulfuric acid formed in the oxidation of the sulfur. The experiments are being continued and it is expected that further improvement of the texture of the soil and increased permeability will be brought about.

CONTROL OF OTHER PLANT DISEASES

Among the other soil problems capable of being solved through the biological oxidation of sulfur, there may be noted the control of other plant diseases, such as scurf and soil rot of sweet potatoes, the scab of sugar beets, and certain diseases of flax and of tobacco. It is quite probable that the biological oxidation of sulfur may also serve as an effective means for destroying soil-infesting insects and likewise nematodes. Among the soil-infesting insects wire worms are particularly destructive. Experiments are being undertaken at the New Jersey Station on the control of these and of white grubs by means of sulfur oxidation. Experiments are also being undertaken on the control of nematodes by means of the oxidation of inoculated sulfur. These are one of the most serious and destructive of the known plant parasites. Should these experiments yield the results expected from them we shall have found an economical means for enhancing crop production.

OTHER USES

Other uses of inoculated sulfur have been suggested. At this time mention may be made of the production of potassium sulfate from the mineral glauconite; the control of intestinal parasites of sheep, swine, and poultry; and the eradication of objectionable vegetation. These and other possible uses of inoculated sulfur would seem to indicate a wide usefulness for a material that is both cheap and abundant.

BIBLIOGRAPHY

1—Joffe, "Studies of Sulfur Oxidation in Sulfur-Floats-Soil Mixtures," *Soil Science*, **13** (1922), 107.

2—Joffe, "Preliminary Studies on the Isolation of Sulfur-Oxidizing Bacteria from Sulfur-Floats-Soil Composts," *Soil Science*, **13** (1922), 161.

3—Joffe, "Some Agricultural Relations of Sulfur." Thesis, Rutgers College (soon to appear as a technical bulletin). 1922.

4—Joffe, "Acid Phosphate Production by the Lipman Process," a series of three articles appearing in *Soil Science*, beginning December, 1922.

5—Joffe and McLean, "A Note on the Oxidation of Sulfur in Oregon Soils," *Soil Science*, **14** (1922), 217.

6—Lipman, McLean, and Lint, "Sulfur Oxidation in Soils and Its Effect on the Availability of Mineral Phosphates," *Soil Science*, **2** (1916), 499.

7—Lipman and Joffe, "The Influence of Initial Reaction on the Oxidation of Sulfur and the Formation of Available Phosphates," *Soil Science*, **10** (1920), 327.

8—Lipman, Waksman, and Joffe, "The Oxidation of Sulfur by Soil Microörganisms," *Soil Science*, **12** (1921), 475.

9—Martin, "The Relation of Sulfur to Soil Acidity and the Control of Potato Scab," *Soil Science*, **9** (1920), 393.

10—McLean, "The Oxidation of Sulfur by Microörganisms in Its Relation to the Availability of Phosphates," *Soil Science*, **5** (1918), 251.

11—Rudolfs, "Composting Rock Phosphate with Sulfur in Slightly Alkaline Calcareous Soils," *Soil Science*, **14** (1922), 37.

12—Waksman and Joffe, "Microörganisms Concerned in the Oxidation of Sulfur in Soil," *J. Bact.*, **7** (1922), 239.

13—Waksman and Starkey, "Carbon Assimilation and Respiration of Autotrophic Bacteria," *Proc. Soc. Exp. Biol. Med.*, **20** (1922), 9.

The Determination of Various Monohydric Phenols by the Phenol Reagent of Folin and Denis[1]

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The phosphotungstic-phosphomolybdic acid reagent of Folin and Denis[2] offers a means for the quantitative determination of a number of monohydric phenols in dilute aqueous solutions. The nature of the color produced with these phenols fulfils most of the requirements of a colorimetric method. The intensity of the color produced is dependent upon the concentration of the particular phenol in pure aqueous solutions free from reducing agents. β-Naphthol and isoamyl phenol can be used as satisfactory standards for color comparison, and offer an advantage over the much-used carbolic acid in that they are solids at ordinary temperatures and can be weighed direct with ease.

THE phenol reagent described by Folin and Denis produces a characteristic color with most phenolic as well as a few nonphenolic compounds.[3] It has been proposed as a qualitative reagent for the estimation of phenols in very dilute aqueous solutions[4] and as a basis for the quantitative colorimetric determinations of free and conjugated phenols in body fluids.[2] The three isomeric cresols have been successfully determined by the use of this reagent through the introduction of an empirical factor with carbolic acid as a standard for color comparisons.[5] It was thought that the determination of other monohydric phenols in dilute solutions might be accomplished by this useful color reaction.

The method as first adopted for the determination of phenols in urine consisted primarily of freeing the urine of uric acid and protein, after which an aliquot portion was treated with the phenol reagent and sodium carbonate in a volumetric flask. A standard phenol solution was prepared at the same time and after both solutions had developed the characteristic blue color they were diluted to a convenient volume and compared in a standard colorimeter.

The results of a colorimetric determination are influenced by a large number of factors, and for this reason it is necessary to carry out the details in as nearly a uniform manner as possible. Stock aqueous solutions of pure phenols were prepared and aliquots taken for analysis. The intense blue color produced by even very small amounts of phenols with the reagent limits the final solution to one containing not more than 0.5 mg. per 100 cc. The intensity of the color and the rate at which it is produced by the reagent depends upon the temperature of the reaction and the time allowed between the addition of the alkali and the making of the final colorimeter readings. A temperature of 30° C. for a period of 30 min. produces a deep blue color of sufficient intensity to give sharp readings when the plungers of the instrument are set at a depth of 20 mm. The color obtained is also affected by the quality and concentration of the alkali employed. A 20 per cent solution of C. P. sodium carbonate using pure distilled water and allowing the solution to stand for several weeks before filtering, gives satisfactory results. Aqueous solutions of β-naphthol containing 0.5 mg. per 100 cc. in the final prepared standard gives a very desirable depth of color for comparison in a colorimetric method. It was thought that this compound might be used as a convenient standard. It has the advantage that it can be easily obtained in the pure state and can be weighed directly, whereas carbolic acid solutions must be standardized with iodine.

EXPERIMENTAL

The exact procedure used in this work is as follows:

The standard phenol solutions for color comparison were prepared by introducing 0.5 mg. of β-naphthol, 10 cc. of the phenol reagent, and 50 cc. of water into a 100-cc. volumetric flask. (It is desirable that the β-naphthol be in solution when added to the flask in preparing the standard. A stock solution containing 0.1 mg. per cc. was found to be very convenient for the purpose.) A second flask was prepared in like manner, substituting an aliquot of the unknown phenol for β-naphthol. The flasks were placed in a water bath heated to 30° C. until constant temperature was obtained, and 20 cc. of the 20 per cent sodium carbonate were added. At the end of 30 min. the flasks were filled to the mark with distilled water and, after shaking well to insure uniform distribution of the color, comparisons were made in a colorimeter of the Duboscq type. The results of the determinations of some of the monohydric phenols investigated are given in Table I.

DISCUSSION

The variations in the results are within the reasonable limits of accuracy of a colorimetric method. The indications are that with monohydric phenols in pure aqueous solutions the intensity of the color produced with the phenol reagent is

TABLE I—COLORIMETRIC DETERMINATIONS OF VARIOUS MONOHYDRIC PHENOLS WITH β-NAPHTHOL AS A STANDARD

		Mg. Taken per 100 Cc. Aqueous Solution	Colorimeter Readings Standard Set at 20 Mm.						
			Max. Mm.	Min. Mm.	Average of 4 Readings Mm.	Ratio of Molecular Weights	Mg. Recovered per 100 Cc. Aqueous Solution	Mg. Difference	Per cent Error
β-Naphthol	I	10.0	20.2	20.0	20.07	1.0	9.96	0.04+	0.4
	II	10.0	20.1	19.9	20.0		10.0	0.0	0.0
Meta-cresol	I	10.42	14.4	14.3	14.4[a]	0.75	10.41	0.01−	0.09
	II	10.02	15.1	14.9	15.0[a]		9.99	0.03−	0.29
Thymol	I	10.0	20.5	20.3	20.4	1.041	10.21	0.21+	2.10
	II	10.0	20.6	20.3	20.48		10.18	0.18+	1.80
Isoamyl phenol	I	10.0	22.3	22.1	22.20	1.139	10.26	0.26+	2.6
	II	10.0	22.0	22.4	22.25		10.23	0.23+	2.3
Ethyl phenol	I	10.20	16.6	16.4	16.52[a]	0.847	10.20	0.0	0.0
	II	11.36	14.8	15.0	14.95[a]		11.33	0.06−	0.52
Butyl phenol	I	10.02	20.9	20.7	20.82[a]	1.041	9.99	0.03	0.3
	II	10.42	20.0	20.4	20.25[a]		10.27	0.15−	1.4

[a] Average of 8 readings.

NOTE: The standard contained 0.5 mg. β-naphthol per 100 cc. Temperature of the solution, —30° C. Time allowed for color development at 30° C., —30 mm. Depth of standard solution used for color comparison, —20 mm.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] *J. Biol. Chem.*, **22** (1915), 305.

[3] *Ibid.*, **26** (1916), 507.

[4] Gortner and Holm, *J. Am. Chem. Soc.*, **17** (1920), 1678.

[5] Chapin, *J. Biol. Chem.*, **47** (1921), 309.

proportional to the molecular concentration of the phenol—that is, the factor for these various phenols can be calculated from its molecular weight. In this case any of these monohydric phenols could have been used as a standard. β-Naphthol, because of the ease with which it can be obtained pure and the fact that it is a solid at ordinary temperatures and can be weighed direct, is the most convenient one. Only monohydric phenols were investigated to any extent in this work. An attempt was made to determine resorcinol by this method, with β-naphthol as a standard, but the color obtained by the resorcinol used was of so different a shade that an accurate reading was impossible.

CONCLUSION

The determination of a number of monohydric phenols by the reagent of Folin and Denis can be accomplished with a fair degree of accuracy without the use of an empirical factor by following a uniform procedure.

β-Naphthol, isoamyl phenol, and probably some of the other solid monohydric phenols are good standards for color comparison of phenols.

The Preparation and Separation of Ortho- and Para-Chloroanilines[1,2]

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The purpose of this investigation was a study of the preparation of o- and p-chloroanilines, especially the o-chloroaniline. It seemed possible that o-chloroaniline might be used in the preparation of a large number of azo dyes, replacing aniline, the toluidines, and xylidenes—naturally, with some change in shade. A few such dyes have been prepared, mostly monazo dyes, and a few triphenylmethane and other types of dyes.[3] *There seems to be no reason why the chloroanilines cannot be prepared easily on a large scale and at a reasonable price.*

CHLOROBENZENE was nitrated, and after a part of the *p*-nitrochlorobenzene had been separated, the remaining mixture of *o*- and *p*-nitrochlorobenzenes was reduced. The original mixture of nitro compounds is not easily separated. Therefore, an attempt was made to obtain the pure *o*-chloroaniline after reduction; also to find the best and most economical method for preparing this compound.

PREPARATION OF THE CHLOROANILINES

A mixed acid, consisting of concentrated sulfuric acid and a slight excess over the theoretical amount of nitric acid, was used to nitrate the chlorobenzene. Under the conditions used the nitration was not always complete, and this led to difficulties in the later steps. The mixture of *o*- and *p*-nitrochlorobenzenes was separated from the spent acid and allowed to cool to below 20° C. A large part of the para isomer was thus separated in a very pure state, leaving an oil containing about equal amounts of the isomeric nitro compounds.

The reduction was found to proceed smoothly if chlorobenzene was not present in the oil. Iron filings and hydrochloric acid was found to be the most economical reducing agent. Much less than the theoretical amount of hydrochloric acid was used. Sulfuric acid was tried, but with this acid more than a full equivalent, also more time, was required.

The separation of the chloroanilines may be accomplished in several ways. Beilstein and Kurbatow[4] suggest several different methods. The simplest is steam distillation from a neutral solution, which gives only a partial separation, and the *o*-chloroaniline which distils over first is redistilled from a solution to which an equivalent of sulfuric acid has been added. *p*-Chloroaniline is a stronger base and cannot be distilled out of such a solution with steam. *o*-Chloroaniline is a much weaker base, and its sulfate is sufficiently hydrolyzed to allow it to be distilled from the solution with steam.

The isomers can also be prepared and separated by forming the sulfates in a warm solution and cooling. *p*-Chloroaniline sulfate is nearly insoluble in cold water, while the sulfate of *o*-chloroaniline is much more soluble. *o*-Chloroaniline may be recovered by neutralizing the acid solution with an alkali.

Other methods are known—e. g., the fractional crystallization of the picrates and acetyl derivatives—but these methods were not investigated.

In order to eliminate the two distillations or the necessity of crystallization, direct steam distillation from the completely reduced mixture was tried. When sulfuric acid was used in the reduction the method was not successful, since but little oil came over with the steam. Using somewhat less than an equivalent of hydrochloric acid in the reduction and steam distilling at its completion, a quite pure *o*-chloroaniline was obtained which could be further purified by redistillation.

The presence of unnitrated chlorobenzene led to difficulties in the reduction, since it took much longer to complete the process and also prevented separation by steam distillation. In this case fractional precipitation of the sulfates was used.

p-Chloroaniline was recovered by steam distillation after neutralization of the solution from which the *o*-chloroaniline had been distilled. It may also be prepared by complete reduction, using iron and hydrochloric acid, of the *p*-nitrochlorobenzene separated from the nitration mixture. After neutralization a very pure *p*-chloroaniline is obtained.

NITRATION OF CHLOROBENZENE

For the nitration 1000 g. of chlorobenzene were used. A mixed acid consisting of 1290 g. of 94 per cent sulfuric acid and 900 g. of 70 per cent nitric acid was prepared and run slowly, with constant stirring, into the chlorobenzene. During the addition of the first half of the acid the temperature was kept at about 25° C.; during the addition of the second half of the acid the temperature was allowed to rise, and finally the mixture was heated on the water bath for several hours.

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[1] Presented before the Division of Dye Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Submitted by P. O. Powers in partial fulfilment of the requirement for the degree of Master of Science at the University of Pittsburgh.

[3] *Ber.*, **47** (1914), 1161; *Monatsh.*, **34** (1913), 193; *J. Chem. Soc. (London)*, **97** (1910), 2388; D. R. P. 112,175 (1899); 126,607 (1901); 162,636 (1904); 202,016 (1908); 204,848 (1908); 233,367 (1911); 241,853 (1911); 241,910 (1911); 242,051 (1911); 247,411 (1912); 264,942 (1913); 286,237 (1915).

[4] *Ann.*, **176** (1875), 27.

NITRATIONS

Chlorobenzene	*p*-Nitrochlorobenzene		Mononitrochlorobenzene		Yield
G.	G.	Per cent of Total	G.	Per cent of Total	Per cent of Theory
750	260	34	496	66	72
1000	675	49	686	51	97
1000	478	38	783	62	90

REDUCTIONS

No.	Mononitrochlorobenzene G.	Reducing Agent	Time Hrs.	Steam Distillate G.[a]	Yield as *o*-Chloroaniline	Reduction
2	65	Tin and HCl	5	23	48	Complete
3	130	Iron and H_2SO_4	9	91	87	Incomplete
7	170		12	124	91	
9	110	Iron and HCl	6	31	35	Complete
8	215		7.5	86	49	

[a] In 2, 3, and 7 the steam distillation was made from neutral solution and *p*-chloroaniline is included. In Nos. 8 and 9 only *o*-chloroaniline was in the steam distillate.

The mixture of nitro compounds, a yellow oil consisting of about 70 per cent *p*- and 30 per cent *o*-nitrochlorobenzenes,[5] was cooled to or below 20° C., when the para compound, equal to about 50 per cent of the total mixture, crystallized out. The crystals and oil were separated by centrifugation, and both washed with water and finally with dilute solution of sodium carbonate until free of mineral acid. The oil contained approximately 50 per cent *p*- and 50 per cent *o*-nitrochlorobenzene.

REDUCTION OF THE NITRO COMPOUNDS

The spent acid from the nitration process was first used with iron to effect the reduction. Better results were obtained with increasing dilution of the acid. Iron and hydrochloric acid were also tried with much better results, especially if chlorobenzene was absent. Much less time was required than with sulfuric acid.

Tin and hydrochloric acid were successfully used, but, since a large excess of hydrochloric acid is used, this must be neutralized before steam distillation and another step taken to separate the isomers. Fractional precipitation of the sulfates is satisfactory for this purpose.

The method finally adopted as giving the best results was to add 15 per cent of the weight of the nitro compounds of hydrochloric acid (22° Bé.) and the same amount of water to the nitro compounds in a flask and bring to a boil under a reflux condenser. Then a weight of iron filings equal to the weight of nitro compounds was added in small portions while keeping the mixture at a boiling temperature.

Six hours were found to be sufficient to complete the reduction by this method in the absence of chlorobenzene. (The chlorobenzene may be removed from the mixture of mononitrochlorobenzenes by distillation up to 150° C.) If it were present the reduction might not be complete at the end of 20 hrs. The odor of the nitrochlorobenzenes disappears at the end of the reduction. If the color of the steam distillate is red, the reduction is not complete; if colorless, the reduction is complete.

SEPARATION OF *o*- AND *p*-CHLOROANILINES

Distillation with steam from the completed reduction mixture was found to give a satisfactory separation. When the reduction was finished, the *o*-chloroaniline was distilled off in a fast current of steam. The *p*-chloroaniline, being a stronger base, is held back by the presence of hydrochloric acid used in the reduction, and may be recovered by neutralizing with caustic soda or lime and continuing the steam distillation. The *o*-chloroaniline comes over as a clear, colorless oil, 95 per cent boiling within two degrees of the boiling point of *o*-chloroaniline.

When the reduction could not be completed, the acid was neutralized, and then the chloroanilines and unreduced nitrochlorobenzenes were distilled over with steam. The steam distillate was acidified with sulfuric acid to Congo red and brought to a boil. The unreduced nitro compound was separated while hot, and on cooling the *p*-chloroaniline sulfate separated out. *o*-Chloroaniline as an oil was recovered from the filtrate by neutralizing with sodium hydroxide.

p-CHLOROANILINE

p-Chloroaniline can be made from the separated *p*-nitrochlorobenzene by reducing, as outlined above, with iron and hydrochloric acid, neutralizing the acid, and steam-distilling. A very good grade of *p*-chloroaniline is obtained in this way.

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[5] *Proc. Royal Acad. Sci. Amsterdam*, **7** (1904), 266.

Chemical Equipment Companies Offer Coöperation

The Chemical Equipment Association, comprising manufacturers of the diversified equipment used in the twenty or thirty chemically controlled American industries, which recently began a national work for the advancement both of chemical-equipment interests and those of the industries which its members supply, has now begun some very important industrial work in support of these purposes, according to announcement just made by its board of directors. The announcement is accompanied by an appeal for coöperation in an informational way by the associations in each of the great industries which manufacturers of chemical equipment supply.

The association's committee on standardization, of which E. H. Froman, of the Fuller Lehigh Co., is chairman, is prepared to coöperate with the users of chemical equipment in any of the American industries in working toward the standardization of trade phrases and in the collection of information leading to simplification and standardization in designing and constructing chemical equipment.

The committee on business extension, J. W. Spotten, of the United Lead Co., chairman, in addition to present coöperation with the United States Department of Commerce and with other government departments and agencies in activities leading to the more profitable employment by the country's industries of modern chemical equipment, is prepared to collect information on comparative uses of given types of equipment. According to the Chemical Equipment Association, it is believed that this activity can result in an incalculable benefit to industry as a whole, inasmuch as through it various methods and processes used in connection with chemical equipment in one manufacturing industry but unknown in other industries may be made known elsewhere, and with minor adaptations required, profitably adopted in such other industries.

Another committee, that on ethics, E. C. Alford, Elizabeth, N. J., chairman, is making a survey of commercial and engineering practice among chemical-equipment companies, and also concerning such companies in their relationship with the great American industries purchasing chemical equipment. This committee in due course will recommend a declaration of ethical practice to govern the activities of chemical-equipment manufacturers, not only in their own interests but in the interest of increased business with and improved protection to the users of chemical equipment.

The association's statistical committee, R. Gordon Walker, of the Oliver Continuous Filter Co., chairman, is inaugurating, in connection with various statistical agencies throughout the country and government departments, a compilation of the vital statistics of employment of equipment in the great range of industries using chemical and processing apparatus. The association believes that the collection of these statistics will enable the more economical preparation of equipment for users and its more economical purchase by them.

Other committees, on industrial relations, E. J. Fowler, of the Pacific Foundry Co., chairman; and on membership, T. C. Oliver, Chemical Construction Co., chairman; on legislation and publicity, Irving Fellner, *Chemical & Metallurgical Engineering*, chairman, have also been appointed.

The Chemical Equipment Association welcomes and requests the coöperation of individuals, companies, or associations in a position to assist in the work of its important committees. These may communicate with the association at its executive office, 1328 Broadway, New York City.

The Nickel Industry in 1921-1922[1]

By A. J. Wadhams[2]

The International Nickel Co., New York, N. Y.

The provisions of the Disarmament Conference have caused the shutdown of the great armor-plate plants of this country and the discontinuance of their consumption of nickel, which has always been one of the main features of the world's nickel market. Inasmuch as the nickel-steel business has always consumed about 60 per cent of the world's nickel, of which perhaps half went into armor plate and ordnance forgings, the seriousness of this loss can be realized.

Hitherto the nickel-producing companies have endeavored to produce the nickel required for the ever-increasing uses of government and industry. Now they are turning their attention more actively to the development of new uses for nickel and nickel-bearing alloys and steels. In this effort they are impressed by the fact that not only are there many industrial fields into which standard nickel-bearing products have never assumed their technically correct position, but there are, as well, several potentially valuable nickel products and steels known, which have never been commercially developed beyond the semi-laboratory stage. Development work in the industry is proceeding actively along both lines.

Nickel Steels

Perhaps the most important recent features in this field have been the development of the nickel-bearing type of stainless steels, the increasing use of the 5 per cent nickel, case-hardening steel, and the development of the nickel-molybdenum steels.

The nickel-bearing stainless steels contain from 20 to 40 per cent nickel, 6 to 12 per cent chromium, and from 0.25 to 2 per cent silicon, and are produced in the usual commercial forms under several trade names, by as many different companies. They are characterized by resistance to corrosion by salt water, atmosphere, and many acids, as their name usually indicates, and have unusually good mechanical properties as well. Thus, a 25 per cent nickel, 7 per cent chromium, 0.50 per cent carbon steel will have the following mechanical properties as rolled:

Tensile strength	100,000 lbs. /sq. in.
Yield point	60,000 lbs. /sq. in.
Elongation in 2 in.	20 per cent
Reduction of area	50 per cent

These steels can be machined and fabricated by the usual methods and have a promising commercial future.

The 5 per cent, case-hardening, nickel steel is rapidly gaining favor for automobile gears, by reason of the extremely tough core which can be imparted to it, as well as the freedom from warpage during the process of heat treatment. It has replaced, in many cases, the case-hardening steels of lower nickel content.

Although the nickel-molybdenum steels are perhaps still in the development stage, they have gained some favor both with users and manufacturers, and have commercial promise, particularly for case-hardening. They contain from 1.5 to 2 per cent nickel and from 0.20 to 0.40 per cent molybdenum, in addition often to about 1 per cent chromium.

"Heat Resisting" Alloys

These alloys—chiefly of the nickel-chromium or nickel-chromium-iron type—are not new, but their use for high-temperature service is rapidly increasing, particularly in the form of castings for annealing boxes, carbonizing boxes, etc. These alloys are sold under a variety of trade names, and are often sold under a guarantee to last from ten to twenty times as long as the cast steel or iron for which they are substituted. These alloys contain usually from 60 to 80 per cent nickel, 10 to 20 per cent chromium, and 0 to 25 per cent iron.

Electroplating

Within the past two years a great deal of research work has been done on the subject of electrodeposition of nickel, chiefly in connection with commercial plating and the production of copper-nickel electrotypes. Notable among these researches are those of William Blum[3] of the Bureau of Standards and his associates. They have studied the factors of control of the electrodeposition of nickel, particularly the control of the hydrogen-ion concentration or acidity, and their work has done much to lift the art of plating from its hitherto rather empirical environment.

An ingenious application of nickel-plating has been developed at the Bureau of Printing and Engraving—namely, the alternate deposition of nickel and copper layers in an electrotype in order to secure greater stiffness.

Monel Metal

This alloy has made distinct commercial progress within the past two years. In fact it was the necessity for increasing both the quality and quantity of production of Monel metal that led The International Nickel Company to build its Huntington Mill of 18,000 tons capacity annually.

The recent demand for Monel metal has been chiefly from the power plants, dairy, dyeing, laundry, hotel, and restaurant industries, and for these it is required principally in the form of sheet. The coal-mining industry is also taking up the use of Monel metal.

A recent interesting application of this metal is its use as a filler material in welding cast iron, particularly by the arc-welding process. Its use for this purpose reduces or eliminates the cracking which is so commonly an unwelcome feature of cast-iron welding.

Nickel Seamless Tubes

Within the past year seamless nickel tubes have been produced and made available in pipe sizes for the chemical and allied industries, from which there has come in the past a continual inquiry for nickel in this form. These have been produced by piercing and drawing in the same manner in which seamless steel and copper tubes are produced.

Nickel Cast Iron

Many foundries are now experimenting with the addition of from 2 to 4 per cent of nickel to their iron castings, following the successful practice of a few leading automobile-piston manufacturers and others who have found that its use imparts added hardness, strength, and toughness to the iron. Mayari iron, the natural nickel-chromium bearing product from the Cuban iron mines, is also being developed for iron-foundry use, to harden and toughen castings in much the same manner.

Research Work

A survey of the nickel industry would not be complete without reference to some of the interesting researches which have been recently published.

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[1] Received December 16, 1922.

[2] Manager of Development and Research.

[3] Published by the American Electrochemical Society in 1920–1922.

E. C. Bain[4] has made some very interesting discoveries regarding the crystal structure of nickel alloys by the use of the X-ray diffraction method, emphasizing the heterogeneity of iron-nickel and nickel-chromium alloys.

Burgess and Woodward[5] and Gilett[6] have studied the properties of a large number of new compositions of nickel-bearing steels, principally the nickel-silicon steels. They show that steels having a composition of 3 per cent nickel, 1.50 per cent silicon, 0.50 to 0.60 per cent carbon, and 0.60 to 0.80 per cent manganese, have remarkably high tensile properties and hardness, and conclude that they should have quite a field of industrial application. Such steels have shown the following mechanical properties after heat treatment:

Tensile strength	300,000 lbs. /sq. in.
Yield point	250,000 lbs. /sq. in.
Elongation in 2 in.	10 per cent
Reduction of area	25 per cent
Brinell hardness	550 (3000 kg.)

There has been further research work on the properties and constitution of the iron-nickel alloys by Guillaume,[7] Chevenard,[8] Gumlich,[9] Honda[10] and others, relating chiefly to their interesting thermal, elastic, and magnetic properties. It appears that these properties are to be commercially utilized to an increasing extent in the near future.

[4] *Trans. Am. Inst. Mining Eng.*, February, 1912.

[5] *Bur. Standards, Technologic Paper* **207**.

[6] *Bur. Mines, Bull.* **199**.

[7] *Rev. ind. minèrale*, October 15, 1922.

[8] *C. A.*, **16** (1922), 3297.

[9] *Electrotech. Z.*, November 18, 1920, p. 919.

[10] *Phil. Mag.*, **42** (1921), 115.

Observations of Industrial Conditions in Europe[1]

By W. S. Landis

511 Fifth Ave., New York, N. Y.

FIVE WEEKS spent in Europe in November and December, 1922, is hardly sufficient foundation for building a story of industrial conditions which would adequately convey the very complex situation existent there; and when within this short period three countries had to be rather thoroughly covered, little time was left for three others traversed. Abler individuals have studied in great detail and written at great length on this subject, and, therefore, it is questionable if the writer can add very much value to the sum total of the existing information. Leaving out entirely the purely political situation, only some of the more interesting sidelights, and not details of a purely technical nature, will be considered here.

ENGLAND STILL DEPRESSED

Industry in England had not recovered from the post-war depression. Nearly two and one-half million men were idle. Prices in England seemed very high. Ordinary necessities were more expensive than similar materials in the United States. The English price index confirms this general impression. The most marked industrial improvement seemed to be in the shipbuilding industry, the yards having picked up considerable repair work. The spinning industry was suffering from the shortage and high price of cotton, as well as from serious competition of Germany. The chemical industry was showing improvement, but was far from normal. It must be remembered that England is no longer a free-trade country, and in protecting her key industries she has levied some very high duties on imported products. In a measure this accounts for some of the apparent high prices.

ITALIAN DEVELOPMENT

The most interesting part of the trip was the time spent in Northern Italy. Following the war the extremely weak government of Italy had permitted the socialistic and communistic factions to gain an almost complete control of industrial Northern Italy. Corporations lost control of their factories, and cities of their government. Industry came to a standstill. Even agriculture suffered as a consequence of the destructive raids of the two factions, who, unable to operate the factories, were forced into pillage and robbery for subsistence.

The rapid organization and the perfect functioning of the Nationalist, or Facisti, party had recovered all of Northern Italy and restored the factories to their proper owners and logical directors. They established a strong and stable national government, and as fast as elections could be held were driving the Communists and Socialists out of power in the cities. This probably marks one of the greatest political movements in the history of the world, and, while not carried on without bloodshed, nevertheless there was comparatively slight loss of life in what may be truly styled a revolution. Almost over night the factories opened up and were restored to productivity, agriculture again developed, and the whole complexion of the country completely changed. Railway service improved and capitalists again took an interest in the development of industry. What had been a period of the most extreme depression, suddenly turned into a period of activity and extension. Even in the people on the streets a sign of renewed hope and activity was noticed, and the great industrial towns of Northern Italy seemed like American cities in periods of prosperity. Plans were under way for a much larger development of hydroelectric energy. Railroads were being electrified. Electrochemical industries were not only running full but many extensions were planned and much new work was under construction. Several very important combinations in the chemical industry had recently been completed or were under contemplation during my visit, and, while Italy is not a big factor in this field, the outlook for extensive development was very bright.

SWITZERLAND DEPRESSED

Switzerland was in a very depressed condition. Swiss money has suffered little or no depreciation, and not only have Swiss manufacturers, merchants, and consumers had to compete with surrounding countries having greatly depreciated currencies, which rendered export difficult, but Switzerland has also been forced to compete directly with lower paid labor in Italy, and in particular in Germany and Austria. Many of the factories formerly located in Switzerland have been forced to move across the border to survive, and the outlook for some time to come is not cheerful.

GERMANY'S VARIABLE MARK

The exchange situation in Germany has been dwelt upon by international commissions, prominent bankers, and world-famous economists. During the week and a half the writer was in Germany the official rates of exchange varied between 5500 and 9000 marks to the dollar. It varied irregularly as much as 2000 marks in a single day between ten in the morning and five in the after-

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[1] Received February 17, 1923.

noon, one hour high, another hour low. He traveled from Berlin to Basel first-class, including sleeping car, for approximately 5000 marks, or less than 70 cents in American money. The distance is something over 500 miles. No railroad in the world can afford to transport a person for that distance in that class for that price. All railway trains in Germany are crowded. It means that the government is not only losing money on its railroads but in addition the railroads are drawing enormously upon their capital to continue in operation. A glance at the railway guide showed that considerably less than one-half of the usual number of trains are in operation. It is true that a portion of the railway equipment was transferred under the peace treaty, but it is equally true that much of the remainder is out of service with no funds for replacement or repairs. Comprehensive replacements are out of the question, owing to the enormously increased cost of steel and labor. Upon inquiring of prominent individuals as to why railway fares were so low, the writer was told that they were very high from the standpoint of the internal value of the mark and were in the process of being doubled each month. The traffic would not bear any higher rates. If this is true the German railway system must continue to draw upon its invested capital and will sooner or later find itself in serious difficulties.

German Industrial Problems

The first reaction from an industrial standpoint was the great pressure upon the executives to raise funds for carrying on the current business. Companies whose books showed enormous profits were forced to borrow to the extreme for weekly payrolls. The bank rate was over 10 per cent.

This is a particularly important phase of German industry that has been little discussed in this country—namely, the enormously increased demands for working capital as the mark depreciates and wages and raw materials increase in price. For example, a commission fixes the wage rates for every class of employee in Germany. The rate for common labor in the chemical industry last July was less than 100 marks per day. When the author arrived in Germany in November it was 1600 marks per day, and before departing the next week the commission had fixed it at 1800 marks per day. By the end of December it had gone up to around 2500 marks per day, and is now between 4000 and 5000 marks per day. Can you imagine conducting a business where wage rates increase without control on the part of the management, anywhere from 10 to 50 per cent per week? The cost of raw materials has correspondingly increased. During the month of October the price of copper increased over 400 per cent, the price of coal 60 per cent, the price of coke 100 per cent, and the price of pig iron nearly 200 per cent. The demands for working capital have been so enormous that every industrial manager in Germany has been extremely hard put to keep going. In this country a concern doubling its capital every year would receive considerable publicity, if not investigation. In Germany, if on a sound conservative basis, it would have to double its working capital several times a month. A payroll which amounted to 12,000 marks weekly in January, 1922, would require approximately 3,000,000 marks in December, 1922. In eleven months of 1922 new security issues amounted to sixty billion marks as against two and one-half billion in 1921. No figures are yet available for December, but it would not surprise me if it was nearly double that amount by this time.

Low Fixed Wages Discourage Apprentices

The labor party is in control of the government. Its commission fixes wages. They have adopted the socialistic viewpoint of a standard wage, with very little difference between that of skilled and unskilled labor. There is thus no incentive for apprenticeship, and as a consequence they are developing no skilled workmen in Germany at the present time. Every industrial leader stressed the fact that under the present wage system Germany is not developing the necessary skilled help to enable her to hold her own in the markets of the world, and if the system continues for any length of time she will pay a frightful penalty.

Accounting Methods

The writer was very much interested in the plant accounting. Many of the plants are carried on the books at their old gold-mark basis, and fixed charges and taxes are apportioned accordingly. These are entirely inadequate to take care of present-day replacements and renewals. As an example of this, a plant containing a grinding mill recently broke a gear. The quotations on a replacement gear in the then-existing paper-mark value were higher than the original cost of the whole mill. It is quite evident that the plants as well as the railroads are drawing heavily upon their capital.

The salaries of clerical and managerial employees are not protected by the regulations of the wage-fixing commission. A highly competent stenographer was paid in the early part of November at the rate of 18,000 marks per month, at a maximum not over 200 times the pre-war rate. The shoes she was wearing cost 16,000 marks. With exchange on pre-war ratio of 1200, wages on a pre-war ratio of 500, and cost of living on a pre-war ratio of 700 to 800, here was a salary schedule far behind the cost of living.

A plant manager who before the war received probably some 30,000 marks per year with house, heat, service, and other incidentals, was paid on the first of November at the rate of 110,000 marks per month, or at the prevailing rate of exchange approximately twenty dollars in gold. A new wage schedule went into effect the 15th of November which increased this salary to 140,000 marks per month and at the then-prevailing rate of exchange was something under twenty dollars in gold. Several industrialists frankly admitted that these salaries were entirely inadequate—in fact, any salary was inadequate—and that they were doing all possible to help the situation, but, with the rapid fluctuation in the mark with consequent change in prices and enormous pressure upon them for increased working capital, they were helpless.

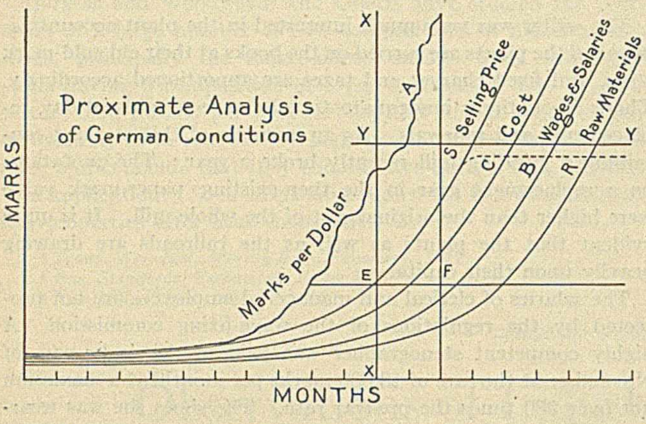
Advance Payment of Wages

Wages are, as far as possible, paid in advance, inasmuch as the purchasing power of the mark drops so rapidly by the end of the salary period that the recipient is unable to purchase the means of subsistence. By paying in advance he can purchase supplies covering the current period at a price more advantageous or at least coincident with the value of his wage. A great many of the industries over there are purchasing foodstuffs at wholesale and permitting their employees to draw upon these stocks as necessary, and in that way help to meet the rapidly increasing cost of living.

Situation Analyzed

The workings of the German industrial situation may be presented with the assistance of a crude chart. While it more particularly applies to those industries whose principal products are used inside of Germany, it also expresses in a quantitative way the workings of industries which had an export trade, although not so directly applicable at the present time under extreme fluctuation of the mark when most of the German export business is done in foreign currency. In this chart, using marks for ordinates and months for abscissas, a curve, A, has been plotted representing the value of the dollar exchange in terms of marks per dollar. It is not necessary to be precise in this analysis, for it would require a logarithmic scale which is complicated to work with here.

Assume the selling price of the manufactured article, and which in turn follows the general direction of the exchange, to be represented by Curve S. Assume the cost of the article to be represented by Curve C, that of wages and salaries by Curve B, and that of raw materials by Curve R. Let us further assume that our manufacturer sells goods at date X. The intersection of the line XX with the various curves gives him the items making up his cost, selling price, and profit. Between the date of manufacture and the time of collection, let us assume an elapsed interval of two months. He collects the value E in marks at a time when his cost of producing goods has reached a point, F.



With the very rapid change in the mark, it is readily understandable that by the time he has collected he may not have sufficient money to operate his factory and pay the then-prevailing costs of raw materials and wages. His existence depends on his ability to increase his working capital sufficiently to meet the new schedules of prices, or else to fix his selling price at such a high point that he has discounted conditions at the time he makes collection. This latter condition represented industry during the early part of the year 1922, when the mark had a slow but fairly regular drop. Since last June, however, the drop has been extremely irregular and at times almost precipitate, and it has been practically impossible to fix in advance a selling price for domestically consumed materials, which is high enough to take care of all possible contingencies. As a result there has been an enormous increase of capitalization in Germany since June, as noted in our previous figures of increases in eleven months of 1922 of twenty-five times the capital increase for twelve months of 1921. Most of these increases took place during the latter part of 1922.

The only hopeful outlook for the manufacturer for domestic consumption is that there is a decided lag between the exchange rate which controls the course of the curves and the actual individual factors of wages, raw materials, etc. In other words, the cost of many raw materials does not increase nearly so rapidly as the selling price, and, therefore, as long as the manufacturer can continue to raise capital enough or borrow from the banks sufficient paper marks, he will continue manufacturing with a potentially increasing profit.

In the case of exports, the manufacturer has a materially greater advantage in this lag of domestic costs of production, for he is selling in values of permanency. In this case the difference between manufacturing costs, which are to a considerable extent controlled by domestic prices, have become so enormously great that the German exporter has lost his sense of proportion and does not seem by any means to be getting all that the foreign market will pay for his products. The exporter has undoubtedly lost sight of the fact that he is drawing heavily upon his domestic capital in order to market at the prevailing low prices.

Probable Effect of Stabilization

The question first asked is "What is going to be the final outcome?" The writer is no economist, he can bring to bear only the peculiar kind of faculties which go to make up a chemist. Turning to the curve again, let us assume that by some means or other the mark is stabilized, at a point we will call Y. The selling price will increase, because wage increases and raw-material costs in Germany have acquired momentum, and this momentum will carry them a considerable distance. The result will be that selling-price levels will turn off at some point, at or below or above world-price levels. The momentum of our costs, however, will carry it along to such a point that business in Germany will be unprofitable on account of the increasing cost of wages and raw materials, and undoubtedly will collapse. The recent history of the Austrian industry bears out this general conclusion. Particular inquiry of German industrialists was made along these lines and it was the one thing which they all feared. As long as exchange declines and the whole fabric is in motion they can continue to profit on the lag, but should the controlling factor stop the machinery would wreck itself. They seem certain that should the mark be stabilized industrial panic would follow.

Acute Coal Shortage

Germany is short of many raw materials. The cutting off of the Saar Basin and the partition of the Upper Silesia coal basin left her with only 60 per cent of her normal coal requirements. With the Ruhr now occupied and more or less interruption of coal supply from this basin—the most important of her sources of supply running somewhere around one hundred million to one hundred and twenty-five million tons per year—industry is going to suffer severely. The brown coals are not coking. They cannot be stored except in briquet form, and except for such plants as are located directly on the brown-coal fields, industry will be seriously handicapped as long as the Ruhr coal is cut off. The dye plants are largely dependent upon the ovens in the Ruhr district for their raw materials. The railroads are largely operated by Ruhr coal. The French occupation has undoubtedly very seriously disturbed industry, but the author has no personal knowledge to what extent. Should the occupation be complete and the coal embargo enforced, a very large part of industry must of necessity come to a standstill. The upper Silesian fields still in German hands are too small and any considerable import is out of the question. The writer does not believe the story of large stocks of coal, because he, personally, came into contact with severe domestic shortage while in the country. Germany is badly hit in a most vital spot. The cutting off of the Ruhr coal will undoubtedly be followed by a decrease in steel production. Her great industrial works—the machine shops, dependent upon the steel industry—must quickly close, and with them will end a considerable export, which in turn means a more rapid precipitation of the mark.

Effect of the Eight-Hour Day

The writer was also firmly convinced that gross misstatements have been made as to German production. In the first place, Germany formerly operated on a two-shift day. Present regulations have forced a three-shift day, which the Germans themselves say has very greatly decreased production. Not only has this reduced the available labor to two-thirds that of pre-war times, but even a less output per man-hour is noted. Of even more importance is the fact that regulations require the operation of factories on a one-shift basis wherever continuous operation is not absolutely necessary. Their great fabricating plants and machine shops are all forced to an eight-hour, one-shift production, which has enormously decreased the output where machine tools and equipment is a limiting factor. An exception has been made in industries doing a large export business. It is quite true that employment is 100 per cent, but at the same time it is not true that production has been anything like the pre-war quantities. We are also apt to compare values of production by merely looking at figures without considering that German statistics are still carried on the gold-mark basis to a very great extent and that all commodities have risen considerably in value since the outbreak of the war. In 1913 Germany exported seventy-five million tons of merchandise, in 1922 (eleven months) less than twenty million tons, and showed a steady decline in the last six months. With the Ruhr occupied a sharp reduction of exports must follow.

Development of the American Arsphenamine Industry[1]

By George W. Raiziss

The Dermatological Research Laboratories, Philadelphia, Pa.

THERE is probably no disease which causes as much suffering and misery in the world as syphilis. In consequence of the more extensive employment of the Wassermann test, it has been found that syphilitic infection is the underlying factor in a large proportion of various chronic diseases, the causes of which had hitherto been either unknown or attributed to various other agents. The economic loss due to the incapacity of those afflicted with this disease amounts to many millions of dollars annually. It has been estimated that about 20 per cent of the male population of Germany and 15 per cent of the adults of Paris are infected with syphilis, while there are probably between seven and ten million syphilitic individuals in the United States.[1,*] According to Sir William Osler, syphilis is the greatest single cause of death in the world. It is estimated that the annual cost in dollars to the United States and its citizens due to syphilis and gonorrhea is hundreds of millions.

It was on account of the alarming proportions which syphilis had assumed that various governments, both during and after the war, began to supervise the treatment of disease. They appropriated large sums of money for research studies in the treatment of syphilis and upon the various therapeutic agents employed, as the latter, after injection into patients, often produced violent reactions and in some cases death. Thus, during the war, there was created in England the Special Committee on the Manufacture, Biological Testing, and Clinical Administration of Salvarsan and Its Substitutes, while in this country the Hygienic Laboratory at Washington was empowered to formulate standards of toxicity for all American-made arsphenamines, as well as to standardize the method of testing the drug upon experimental animals. On July 9, 1918, Congress enacted legislation which established a Division of Venereal Diseases in the United States Public Health Service, created an Interdepartmental Social Hygiene Board, and made appropriations for the activities of the division and the board. The appropriation carried in this legislation, to enable the Division of Venereal Diseases to coöperate with state boards of health, was two million dollars for expenditure during the two-year period ending June 30, 1920. Within the past few years, practically every state in the Union has appropriated funds for the treatment and control of syphilis, as a result of which splendid results were achieved by various state boards of health as well as state and city venereal clinics.

For about four hundred years the chief medicament in the treatment of syphilis was mercury, either in the elemental condition or in the form of inorganic salts, and was administered by intramuscular injections, by mouth, or by inunctions. The results in the main were fairly satisfactory, but a large percentage of patients thus treated remained uncured. The mercurial treatment was not devoid of danger or of unpleasant effects. While a considerable number of deaths have been reported, many were never recorded.

Within the past thirteen years a very marked change in the treatment of syphilis has taken place. The mercurials have been relegated to second place, and primary dependence is placed upon the organic arsenicals, arsphenamine and neoarsphenamine. Prior to the Great War they were known as salvarsan or "606," and neosalvarsan or "914," respectively, but in 1917 the present nomenclature was adopted by the Federal Trade Commission, which licensed the manufacture of these arsenicals.

The wonderful results produced in treating syphilitics with arsphenamine and neoarsphenamine have been definitely established, and the drugs are employed by physicians throughout the world. In many cases, complete cures have been effected by employing intravenous injections of these two arsenicals in the early stages of the infection; severe lesions commonly disappear with magical rapidity after the initial treatment, while patients who have been totally incapacitated have been greatly improved and enabled to return to their normal vocations. The economic and social benefits to the community effected by the use of arsphenamine and neoarsphenamine have been enormous. One of the most important results of the use of these powerful remedies is that the patient soon after treatment is rendered relatively innocuous as far as transmitting the disease to others is concerned. The price of the drugs has within recent years been greatly reduced and the technic of administration rendered comparatively simple.

We can gain some idea of the extent of use of arsphenamine and neoarsphenamine in therapy when we consider that about two million doses of American-made products are employed annually in the United States, about one-half of which is dispensed to indigent patients by the various state boards of health. During the war our Army and Navy alone utilized hundreds of thousands of doses of these arsenicals manufactured in this country, and the results obtained were so striking that patients were again rendered fit for military service within a very short time.

PROBLEM OF DIMINISHING TOXICITY

As is true of most powerful drugs, injections of arsphenamine and neoarsphenamine are sometimes followed by various so-called "reactions," such as nausea, vomiting, headache, chilliness, vertigo, diarrhoea, and rise of temperature, and likewise by other later reactions. In some cases the patient may lose consciousness, and in some rare instances death may occur. These symptoms have been properly ascribed to various factors, but there is much evidence that the quality of the drug is of considerable significance in reducing these disturbing manifestations to a minimum.

The problem of diminishing the toxicity and at the same time retaining or increasing the curative power of these two arsenicals has been of foremost importance both to chemists engaged in chemotherapeutic researches and to the leading health authorities. That this problem is gradually being solved in this country is evidenced by the fact that the American arsphenamine and neoarsphenamine are superior to those manufactured elsewhere. This has been brought about both by the United States Public Health Service in establishing rigid requirements as to toxicity, and also by the increasing efforts of the American manufacturers to continually improve the quality of the drugs.

FIRST USE OF AMERICAN-MADE PRODUCT

Prior to the war all the arsphenamine employed in this country was imported from Germany. Although some of the samples were very toxic, on the whole it was the best medicament for the treatment of syphilis known at the time. In addition, it

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[1] Presented before the Division of Chemistry of Medicinal Products at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[*] The numbers in the text refer to the bibliography at the end of the article

was patented in this country by the German manufacturers, which prevented its production by American concerns. In the latter part of 1915 the Allies had succeeded in effectually blockading Germany so that exportation from Germany to the United States was prevented. The director of the Dermatological Research Institute foresaw the danger of a shortage of arsphenamine in this country, and after considerable experimentation the author succeeded in preparing this drug. Shortly afterward, numerous communications were received from physicians and hospitals from various parts of the country entreating to be supplied with this preparation, as it was practically impossible to secure the German product. Because of the inability of Germany to supply this most valuable therapeutic agent, the Dermatological Research Institute, prompted by humanitarian motives, disregarded the existing German patent rights and began dispensing the drug first to hospitals and then to physicians, thereby rendering invaluable service to the afflicted in time of great stress. Furthermore, during the war the product was not only supplied to the Government in sufficient quantities, but at a price almost one-third of that at which the German product had been sold. The Federal Trade Commission had stated that it would reserve the right to fix the price of the drug, but when it heard of the price established by the American manufacturers, its chairman stated that such a procedure was unnecessary.[2]

A great saving was also effected for the hospitals throughout the country, thus permitting an extension of the use of this valuable remedy for the sick poor. At the present time hospitals are enabled to use four times as much of this valuable drug as before the war, with no greater expense.

During the period of shortage of salvarsan the price of this drug rose to speculative figures. It was not uncommon to hear of quotations of $35 a tube. A physician from the State of Washington had offered $100 for a tube of salvarsan in Tacoma and in Seattle, but was unable to obtain one. He was able to secure the American product at a price about equivalent to fifty tubes for $100.

The fact that we were prepared to furnish salvarsan (arsphenamine) at a time when the supply in this country was inadequate or exhausted, stimulated many physicians throughout the country to petition Congress to abrogate the German patents on this drug. It was the country-wide discussion of the salvarsan situation that brought the question of the utilization of enemy patents to an issue. During the latter part of 1918, two other firms were licensed to manufacture arsphenamine in this country, and at the present time there are altogether five concerns engaged in the production of this drug.

PERFECTION OF QUALITY

Within the last few years great progress has been made in this country in the perfection of the quality of both arsphenamine and neoarsphenamine. According to the government requirements the tolerated dose of arsphenamine in experimental animals should be 100 mg. per kg. of body weight, while that of neoarsphenamine should be 200 mg. per kg. Most of the American manufacturers, however, have been able to obtain products which are borne in larger doses, some samples of arsphenamine passing at 150 mg. and some of neoarsphenamine at 400 mg. per kg. The margin of safety thus created is very large, for, based upon the tolerated dose per kilo of body weight, a man of average weight could tolerate a single dose of 24 g. of neoarsphenamine. The dose of the latter actually employed in practice, however, is only 0.9 g.

As a result of these improvements, fatalities due to arsphenamine and neoarsphenamine have been greatly decreased. In addition, the therapeutic or curative powers of the American-made drug are very high. According to George B. Roth,[3] of the United States Public Health Laboratories, Washington, D. C., "Arsphenamines made in the United States are generally less toxic than those of foreign manufacture, while the neoarsphenamines compare favorably with the foreign neoarsphenamines examined and in certain instances are decidedly less toxic than most of the foreign products."

John H. Stokes, head of the Department of Dermatology and Syphilology of the Mayo Clinic, Rochester, Minn.,[4] stated: "During five thousand injections in which German preparations were used there were considerable periods when scarcely a day passed without a nitritoid crisis, while in seven thousand subsequent injections in which both an American and French product have been employed, the nitritoid crisis has become so rare that we have been compelled to all but abandon the work necessary to confirm the results presented in this paper."

Udo J. Wile, professor of Dermatology and Syphilology, University of Michigan, in a discussion before the American Dermatological Association,[5] said that, after all, the proof as to the efficacy and nontoxicity of the product must be demonstrated on patients, and it was a great pleasure to attest that after some five hundred or six hundred injections of arsenobenzol (American-made arsphenamine) he could say, without hesitancy, that the drug was fully as little or even less toxic in the human being than the German product. According to an article by Oliver S. Ormsby, professor of Dermatology in the Rush Medical College, Chicago,[6] "in its uniform and nontoxic action, the American product commends itself as a remedial agent of great value in the treatment of syphilis and its successful preparation marks an achievement in American chemotherapy."

OTHER USES FOR ORGANIC ARSENICALS

We have seen that the development of the arsphenamine industry led to improvements not only in the treatment of syphilis by means of organic arsenicals, but also in the preparation and quality of these drugs, as well as extensive investigation upon the nature and cause of "reactions" following their use. In addition, a great impetus was given to the elaboration of new chemical compounds for use in the treatment, not only of syphilis, but other diseases, such as pneumonia, tuberculosis, leprosy, etc. As a result, a great number of new chemical compounds have been prepared and described, and many important contributions made to the new science known as *chemotherapy*. Thus, W. A. Jacobs and M. Heidelberger of the Rockefeller Institute prepared a number of arylarsonic acids, diazoamino and azo compounds of *p*-arsanilic acid. Of these the most interesting in the treatment of experimental trypanosome and spirochete infections proved to be the sodium salt of *N*-phenylglycineamide-*p*-arsonic acid, named tryparsamide.[7] W. H. Brown and Louise Pearce, of the same institute, have performed various interesting and important biological experiments upon animals with various arsenicals.[8] Roger Adams, of the University of Illinois, has also synthesized many new organic arsenicals.[9]

For the past eight years, the Dermatological Research Institute of Philadelphia has been engaged in the synthesis and chemotherapeutic studies of organic arsenicals and mercurials, as a result of which there has been elaborated a new and superior mercurial germicide, sodium *p*-hydroxymercuri-*o*-nitrophenolate, called mercurophen.[10] In addition, various serological investigations, studies in connection with the Wassermann reaction, the treatment of syphilis, as well as the toxicity and therapeutic activity of arsphenamine and neoarsphenamine, have been carried out at the same institute. Reid Hunt[11] and W. G. Christiansen[12] have been conducting experiments with reference to the toxicity of arsphenamine under a grant from the United States Interdepartmental Social Hygiene Board, while C. Voegtlin,[13] of the Department of Pharmacology of the Hygienic Laboratory at Washington, has carried out various investigations with arsphenamine and other arsenicals. It is due to this cooperation of the chemist and the physician that such wonderful strides in the struggle against syphilis are being made.

BIBLIOGRAPHY

1—Hazen, *Am. J. Syphilis*, **6** (1922), 17.

2—Report of J. F. Schamberg to the Board of Trustees of the Dermatological Research Institute of Philadelphia, **5** (1921).

3—Roth, *Arch. Dermatology and Syphilology*, **2** (1920), 292.

4—Stokes, *J. Am. Med. Assoc.*, **72** (1919), 241.

5—Wile, *J. Cutaneous Diseases*, May-June, 1917, p. 332.

6—Ormsby, *J. Am. Med. Assoc.*, March 18, 1916, p. 868.

7—Jacobs and Heidelberger, *J. Am. Chem. Soc.*, **40** (1918), 1580; **41** (1919), 1440, 1581, 1809; **43** (1921), 1632.

8—Brown and Pearce, *J. Exp. Med.*, **22** (1915), 517; **30** (1919), 411; **33** (1921), 193; *J. Pharmacol.*, **9** (1917), 354; *Proc. J. Pharmacol.*, **13** (1919), 483, 502; **15** (1920), 242.

9—Adams and Palmer, *J. Am. Chem. Soc.*, **42** (1920), 2375; **44** (1922), 1356; with A. J. Quick, *Ibid.*, **44** (1922), 805.

10—Schamberg, Kolmer and Raiziss, *J. Am. Med. Assoc.*, **68** (1917), 1458; *J. Infectious Diseases*, **24** (1919), 547.

11—Hunt, *J. Am. Med. Assoc.*, **76** (1921), 854.

12—Christiansen, *J. Am. Chem. Soc.*, **42** (1920), 2402; **43** (1921), 370, 2202; **44** (1922), 847, 2334.

13—Voegtlin and Smith, *J. Pharmacol.*, **15** (1920), 475; **16** (1921), 199, 449; **17** (1921), 357; with H. Dyer and J. W. Thompson, *Am. J. Syphilis*, **6** (1922), 526.

The Modern Trend in Fertilizer Plant Operation[1]

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As THE fertilizer industry is based on the production of sulfuric acid, a short review of the development of sulfuric acid manufacture will be given.

We find that in 1746 Dr. Roebuck, of Birmingham, England, built the first lead chambers for the production of sulfuric acid. These chambers were six feet square, the bottom being covered with water. The sulfur and potassium nitrate were introduced into the chamber in small heated pots, and when the charge had burned out another charge was introduced. After a considerable length of time the acid in the chamber bottom reached a specific gravity of 1.25, when it was withdrawn and concentrated in iron pans before being sold.

In 1774, steam was introduced into the chambers, eliminating the necessity of covering the bottom with water, and at about the same time it was found that by allowing a continuous current of air to enter the chambers a considerable amount of nitrate of potash could be saved. By 1815, chambers about twenty-five feet square with two doors for introducing the heated pots containing sulfur were being used.

The next development was a chamber with a small brick furnace having two doors, connected by a flue to the front end of the chamber. In this furnace sulfur was burned, thereby securing a more uniform flow of sulfur gas, and as steam was admitted continuously they were able to secure for the first time a steady production of acid. Later pyrites was substituted for sulfur, and still later several chambers were built and connected by flues.

About 1870, Gay-Lussac installed his first tower for the recovery of the nitrogen compounds, which resulted in a great saving of nitrate of soda, which was being used in the place of nitrate of potash, and also in a considerably greater yield of acid per pound of sulfur. About the same time John Glover, of London, England, introduced the Glover tower for the denitrating and concentration of the acid coming from the Gay-Lussac tower. This brings us up to the present method of making sulfuric acid by the chamber process.

At this time plants were operating on 20 to 22 cu. ft. of chamber space per pound of sulfur burned in 24 hrs. There were no methods used for keeping up with the composition of the gases, etc., but the plants were run by rule-of-thumb methods, and in a majority of cases the results were very poor. About thirty years ago, efforts were made to keep a closer check on the chamber process, the first of which was an apparatus for determining the oxygen content of the exit gases by direct absorption by phosphorus, using the apparatus invented by Professor Lindemann and improved by Winkler. Great difficulty was experienced in getting the operating man to understand and appreciate the necessity for carrying out this step. The next test uniformly introduced was testing the Gay-Lussac acid for nitrogen compounds. This was done by either a 0.2 *N* or some other known strength solution of potassium permanganate. Reich's test for sulfur dioxide in burner gas was also beginning to come into general use, using a 0.1 *N* iodine solution. In many cases this test was given up for Lunge's method, using a 0.1 *N* sodium hydroxide solution, as this test included both the SO_2 and SO_3, whereas Reich's test gave only the SO_2 in the burner gas, and when burning pyrites there is a considerable amount of SO_3 formed owing to the catalyzing action of the ferric oxide.

About this time the subject began to receive the attention of chemical engineers and steps were being taken to increase the efficiency of the plants with regard to the yield per pound of sulfur, the percentage of nitrate of soda used, and the cubic feet of chamber space per pound of sulfur in 24 hrs. At this time a yield of 4.6 lbs. of 50° Bé. acid per lb. of sulfur was considered fairly good work, when using 18 to 20 cu. ft. of chamber space per lb. of sulfur in 24 hrs., but, as there is a theoretical yield of 4.925 lbs. of 50° Bé. acid per lb. of sulfur, the loss between 4.60 and 4.925 lbs. was too great to be sustained. It has been found that by careful training of the operating organization, an average yield of 4.80 to 4.90 lbs. of 50° Bé. acid per lb. of sulfur can be obtained, and it has also been found that the cubic feet of chamber space per pound of sulfur in 24 hrs. can be reduced to as low as 6 by using a Pratt system, and 8 to 10 by using a plain chamber system with intermediate towers—this with a consumption of around 3 per cent of nitrate of soda per pound of sulfur burned.

To obtain the high yields with a small amount of chamber space, it is absolutely necessary to keep a close check on the percentage of SO_2 entering the chambers, the percentage of oxygen in the exit gases, and the percentage of nitrogen compounds recovered in the Gay-Lussac acid. Normally, these tests are made once an hour over the entire 24 hrs., but when anything occurs to cause an abnormal condition it is necessary to make the tests every 30 min., until the process is back to a balanced condition. But this is well worth while, because by using the modern method of operation we are enabled to make twice as much acid in the same chamber space and get a considerably better yield than was formerly possible.

It has also been found necessary in modern practice to use a fan for handling the gases, thereby making the draft conditions in the plant largely immune to atmospheric changes. The fan is placed at any convenient point in the chamber system, depending on what system is being used. In the Pratt system it is placed between the Glover tower and the first chamber, and in a plain chamber system with intermediate towers it is placed between the last chamber and the Gay-Lussac tower.

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[1] Presented before the Division of Fertilizer Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

Production of Acid Phosphate

After the sulfuric acid has been produced, the next step is the manufacture of acid phosphate. In 1842 Lawes took out patents in England covering the acidulation of bones and phosphate rock. So far as we know, this is the beginning of the production of acid phosphate, which in this paper we will call the result of any phosphatic material acidulated with sulfuric acid.

The sulfuric acid was formerly introduced into a lead-lined tank and the ground phosphate rock was emptied into this tank from bags, the resulting mass being agitated with rakes until the reaction was complete, when it was dumped out to dry. The next step was grinding the rock in Burrstone mills, and carrying the dust by elevators to a storage hopper, from which a given amount was weighed and introduced into a mechanical mixer, the acid being introduced into the same. The charge was allowed to mix for a few moments and then dumped into a small tramcar and carried out and dumped on storage. The acid phosphate was allowed to lie undisturbed for several months before using, after which it was dug by hand labor and mixed in varying proportions with materials containing nitrogen and potash, to make a complete fertilizer. At first, this mixing was done by hand and all materials were hand screened; later, small bagging machines were introduced, to which the material was wheeled in wheelbarrows, the machine elevating it to the screens. After screening, the material dropped into a hopper from which it was bagged.

Needless to say, the methods used at this time were very wasteful and inefficient, and a company could exist when using these methods only because of the very large profits that were being made from the business at that time.

The manufacture of acid phosphate has received the attention of some very able minds, and the methods as carried out at the present time are the result of a great amount of experimental and research work which could not have been accomplished without the aid of chemical engineers and analytical chemists. As it has not been many years since a chemical laboratory was considered an unnecessary expense by the fertilizer companies, the scientific men in the business should be proud of the work accomplished, for in many cases they have not had the hearty coöperation of the manufacturers that their work merited.

The first improvements consisted of building a den for receiving the acid phosphate from the mixing machine. Here it was allowed to complete its reaction, after which it was dug by hand from the den and carried to storage, usually by an overhead tramcar. Later, several methods for removing the acid phosphate from the dens were developed, some involving a shaving feature whereby the material is scraped off as a fine shaving and allowed to aerate as the scraping is being done, after which the fine acid phosphate is carried to storage. In others, the acid phosphate is removed by buckets attached to bridge cranes. The mixer in these instances is mounted on a movable car; when the den has been filled the mixer is moved from over it, and after a suitable time has elapsed (usually 12 to 15 hrs.), the acid phosphate is dug from the den with crane buckets and carried to storage, from which it is used in the manufacture of the complete fertilizer.

Vast strides have been made in the methods of grinding phosphate rock, the tendency always being toward a finer product, until now the rock is usually ground to a fineness of from 90 to 95 per cent through a 100-mesh screen. A product of this fineness requires air separation; therefore, there have been developed two types of pulverizers. In one, the rock is finished in the mill and the dust is carried by a fan to a cyclone from which it drops into storage. In the other, the rock passes through the mill and the entire output of the mill is passed over a scalping screen. The product passing through the screen goes to an air separator, the finished dust going by suitable conveyors to the storage, and the coarser material returning to the mill for regrinding. By fine grinding a smaller amount of sulfuric acid is required for acidulating the rock and a dryer and higher-grade product is obtained.

Many factors are involved in the acidulating of the phosphate rock by sulfuric acid, and a proper product can only be produced by maintaining a careful chemical control of the process.

Addition of Other Ingredients

After the acid phosphate is produced and cured, it is mixed with the various fertilizer ingredients. As previously stated, this was originally done by hand and later with small bagging machines, but many plants at the present time are equipped with large bagging machines and also batch mixers, where the entire ton is introduced into the mixer after being screened, and after being thoroughly mixed is discharged into bagging hoppers, from which it is bagged through some rapid, accurate weighing scale, and then conveyed to the cars on electric trucks. It is not unusual for plants to ship 300 tons per day through one of these units. In some cases the material is carried to the machines in load-carrying electric trucks, and in others it is introduced into the machines through a series of hoppers and scales onto a large conveyor belt. These hoppers, in turn, are fed by bridge cranes operating in steel buildings of from 60 to 100 ft. in width. The handling capacity of one crane being about 1000 tons per day, one crane would be able to take care of three shipping units, as built at the present time.

Chemical Control of Process

Under modern operation, the incoming materials are carefully sampled and analyzed by the factory chemist, and then the materials are either made up into complete goods and stored, or into base goods and stored for curing. In either case, the goods should be stored from 2 to 3 mo. if it is expected to ship a fertilizer made from them that will be satisfactory to the purchaser. All complete goods and bases made up and stored in the plant should be analyzed a number of times and these analyses used in formulating when the goods are shipped, as the laws in most states are very strict about any discrepancy in the analysis of the goods. On the other hand, if too great an overage is allowed it means large losses to the manufacturers. A sample from each machine should be analyzed daily, and in large plants these should be posted on a bulletin board, so all the operating men in that department can see what is being done.

Under modern methods of operation, materials are bought on analysis—that is, so much per ton unit for each ingredient contained—and in some cases the sample is referred to a commercial chemist whose certificate controls. In other cases, the mean between the buyer's and seller's chemists' analyses is used as the basis of settlement, provided there is not a greater difference than is agreed upon between buyer and seller. In such a case the sample is referred to some disinterested referee chemist and his certificate controls as to the number of units to be paid for.

It will be seen from the foregoing that the modern fertilizer plant of to-day, instead of operating by the old rule-of-thumb methods, is being run along highly scientific lines, requiring the services of both the chemical engineer and the analytical chemist, and also requiring a decidedly higher grade of operating men than formerly was considered necessary.

The executive board of the American Library Association appeals to American libraries and librarians to solicit books from the public and to send books from their duplicate collections for use in the American Library in Paris and by the American Library Association in meeting the requests for American publications which come from other countries in Europe. The association particularly wishes files of the more important American periodicals, the publications of the more important national societies, other works of reference relating to America, collected editions of the writings of our representative writers and public men, and illustrated books on American art and architecture. Those interested should communicate with the Secretary of the American Library Association, 78 East Washington St., Chicago, Ill., preferably before May 1.

Recent Development in the Chemistry of Organic Mercury Compounds[1]

By Frank C. Whitmore

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During the past two years there has been an unusual increase in the amount of work devoted to organic compounds of mercury. Most of this work has been on theoretical phases of the subject rather than on the practical applications to medicine. This change is encouraging, as too much of the work in the past has been done in the hope of the immediate discovery of pharmacologically useful substances to the exclusion of the development of a suitable basis of pure chemical knowledge of these interesting compounds. The present summary will first take up the reactions of more general interest in the field and then follow this discussion with an enumeration of the special compounds which have been studied.

A PROBLEM which has long interested workers in this field is that of the true nature of the compounds obtained from the mercuric salts and various unsaturated substances. Manchot and his co-workers have long held that the products are mere molecular compounds of the unsaturated substance and a molecule of a basic mercury salt. Other workers believe the products to be true organo-mercuric compounds—that is, compounds containing the C-Hg linkage. Dimroth[1,*] has shown that Manchot's supposed intermediate addition compounds obtained in the mercuration of phenol ethers are really mixtures of mono- and dimercurated compounds. Anisole gives the known acetoxymercuri anisole and also 2,4-diacetoxymercuri anisole. The constitution of the latter substance was proved by conversion to the corresponding di-iodo compounds by means of iodine. Phenetole gives similar results. The methyl ether of *p*-cresol gives only a monoacetoxymercuri compound. All the substances obtained react with sodium chloride to give chloromercuri compounds. The filtrates from these substances are neutral, whereas addition compounds containing basic mercury salts would react with sodium chloride to give alkaline solutions. The structure of the addition compounds obtained from olefins and mercuric salts as true organo-mercury derivatives is practically established by the recent work of Adams and his co-workers.[2] They find that *o*-allyl phenol reacts with mercuric acetate, or even with mercuric chloride, to give a mercurated methyl dihydrobenzofuran, the structure of which has been proved by conversion into the known 2-iodomethyl-2,3-dihydrobenzofuran. This is the first case wherein a mercuric salt which does not hydrolyze has added to an ethylenic linkage.

GENERAL REACTIONS

Of the general reactions of organic mercury compounds, one of the most important is the change of compounds of the type R-Hg-X, to mercuri-bis compounds of the type R_2Hg. Abelmann[3] has found that the Grignard reagent may react to cause this change. It is possible that the first reaction is the formation of a mixed compound, R-Hg-R′. Such compounds are unstable and readily change to the simple compounds R_2Hg and R'_2Hg. Wibaut[4] in repeating the mercuration of nitrobenzene at high temperatures has obtained some mercuri-bis-*o*-nitrophenyl. It is suggested that this was formed from *o*-chloromercuri nitrobenzene during the removal of the excess of nitrobenzene by steam distillation. If this suggestion is correct, it would appear to give a new method of forming mercuri-bis compounds. If it is incorrect, mercuration by mercuric acetate may result in the replacement of both acetoxy groups by organic residues.[5] Steinkopf[6] has found that sodium thiocyanate acts in the same way as sodium iodide in changing thiophene compounds of the type R-Hg-X to the corresponding mercuri-bis compounds.[7] Jenkins[8] has been able to bring about a similar change by means of ammonia. He changed β-chlorovinyl mercuric chloride to the mercuri-bis compound by treating it in dry chloroform with dry ammonia gas. An analogous change may account for the formation of the compound $(C_{12}H_{11}N_4)_2Hg$, obtained by Vecchiotti[9] by adding ammonia to the mercuration product of diaminoazobenzene. In this connection it is interesting to recall that at one time Pesci believed that ammonia could be used for changing his mercurated anilines to the mercuri-bis-anilines.

The reaction of organo-mercuric compounds with various halides has not recently been studied as much as formerly. Challenger[10] has found that α-naphthylbismuth dibromide reacts with mercury diphenyl to give phenylmercuric bromide bismuth triphenyl, bismuth trinaphthyl, mercury dinaphthyl and phenyl bromide. Mercury diphenyl and bismuth tribromide in dry ether give bismuth triphenyl. Zappi[11] has found that mercury diethyl reacts with pentamethylene dichloride to give ethyl chloride and an oil which is presumably cyclomercuripentamethylene. It has recently been found that sulfonyl iodides react smoothly with organic mercury compounds to form sulfones.[12]

INDIVIDUAL RESEARCHES

In turning to a more extensive enumeration of the individual researches on organic mercury compounds, we are impressed by their number and by the fact that so many of them are extensions or corrections of earlier work which was not satisfactorily completed. Maynard,[13] in studying the oldest definite reaction involving organic mercury, has found that the union of methyl iodide and metallic mercury is not speeded up by ultraviolet light, but is by red light from specially cored, carbon arc lights. The reaction is greatly hastened by the use of mercurous iodide instead of metallic mercury—a fact which throws light on the mechanism of the reaction. Using this modification, the reaction can be applied to other iodides, even to benzyl iodide. Sneed and Maynard[37] have shown that methylmercuric acetate has different properties from those recorded in the literature. Maynard and Howard[14] have found that, contrary to the statements in the literature, methylmercuric hydroxide is a very weak base. This conclusion agrees with the results obtained by Evans and Otis[14] working independently on *n*-butylmercuric hydroxide.

Maynard and Howard[18] have prepared mercury dialkyls by the electrolysis of aqueous solutions of the corresponding alkyl mercuric acetates containing pyridine. Goret[15] has prepared propyl and isopropyl mercury compounds using the reaction of Frankland (the interaction of alkyl halides with sodium amalgam in the presence of ethyl acetate as a catalyst). Marvel and Gould[16] have applied the Grignard reagent

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[1] Based on a paper presented at a symposium of the Section of the Chemistry of Medicinal Products at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. The present report is intended to cover the work in this field which has appeared during the past two years and was not included in the monograph on Organic Compounds of Mercury published by the Chemical Catalog Company in 1921.

[*] The numbers in the text refer to the bibliography at the end of the article

in the preparation of mercuri-bis compounds of methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl. Tiffeneau[17] has used Frankland's reaction to make *n*-butylmercury derivatives. Besides the commoner compounds he prepared *n*-butylmercuric fluoride which has properties similar to those of the chloride but melts at a higher temperature. The toxicity of the chloride was found to be about 40 mg. per kg. for dogs. Marvel and Calvery[18] have extended their use of the Grignard reagent to the preparation of mercury compounds of secondary and tertiary alkyl compounds hitherto practically unknown. They have prepared mercury compounds of *sec*-octyl, *ter*-butyl, and *ter*-amyl. In the tertiary compounds the yields are very poor and the products are very unstable to light, heat, and acids.

The action of acetylene with mercuric salts has, as usual, been the object of much investigation.[19] Nieuwland[20] has contributed an important paper on the role of mercury salts in the catalytic preparation of acetaldehyde from acetylene. Besides a consideration of the catalytic complexes formed, he takes up at some length details of the process of commercial significance. He also considers the possibility of utilizing the acetaldehyde in the reaction mixture for further preparations, such as those of paraldehyde and quinaldine. Jenkins[8] has improved the method of preparing β-chlorovinyl mercuric chloride from acetylene. The former substance, treated with ammonia in dry chloroform, gives mercuri-bis-β-chlorovinyl, a well-defined crystalline substance, soluble in ether, chloroform, or benzene, and melting at 60° C.[21]

Biilmann[22] has studied the action of allyl alcohol with mercuric salts and has devised a method for determining the double bond in olefins based on this action. Schoeller[23] has confirmed his work on the formation of acetoxymercuriformic esters from carbon monoxide.

Maynard[18] has prepared benzylmercuric iodide directly from benzyl iodide and mercurous iodide. Tiffeneau[24] has used Frankland's reaction to prepare mercury compounds of cyclohexyl and *p*-methyl-cyclohexyl. Hanke[19] has prepared the mercurated phenyl halides both by direct mercuration and by the method of Peters (the reaction of sulfinic acids with mercuric salts). These substances are being used in a study of the electronic structure of benzene. Vecchiotti[25] has continued his study of the mercuration of *p*-toluidine. He is extending his work to derivatives of phenol and of naphthalene. Paolini[26] has isolated acetoxymercuri derivatives of phenols by mercuration in glacial acetic acid. He has prepared diacetoxymercuri thymol, diacetoxymercuri phenol, acetoxymercuri-β-naphthol, and acetoxymercuri vanillin. Mameli[27] has also studied the mercuration of phenol in some detail. As has been mentioned, Dimroth[1] has mercurated anisole and phenetole, obtaining both mono- and dimercurated products.

Raiziss and his co-workers have mercurated *p*-nitrosophenol,[18] *o*-nitrophenol (obtaining "mercurophen"),[28] and *p*-nitrophenol. They have also prepared mercury compounds from *o*-aminophenol and *o*-acetaminophenol,[18] obtaining products containing three atoms of mercury, one being supposedly attached to nitrogen. *p*-Acetaminophenol, mercurated in alcohol, gives a product containing five atoms of mercury for two molecules of the phenol, one of the mercury atoms being attached to the two nitrogen atoms. The substance gives metallic mercury when treated with alkali. Mercuration of *p*-acetaminophenol in water, on the other hand, gives a dimercury compound which dissolves undecomposed in alkali. Nitrosothymol and nitroresorcinol yield monomercury compounds.

Goddard[29] in studying the action of various organometallic compounds with thallic chloride finds that 1-acetoxymercuri-β-naphthol gives thallous chloride and mercurous chloride, the naphthyl ring being completely disrupted. Whitmore and Middleton[30] have shown that mercurated aromatic acids may be changed to their acid chlorides by means of phosphorus pentachloride without breaking the C-Hg linkage. Esters of mercurated *p*-nitrobenzoic acid have been prepared by this means.

One of the few new "mercurials" or mercury drugs which have been put on the market recently is "mercurosal," the disodium salt of hydroxymercuri-salicyloxyacetic acid. Another modification of the much-used salicylic mercurials is a cyanomercuri compound which is water-soluble.[31] Raiziss[28] has prepared 3-chloromercuri-5-nitrosalicylic acid. Besides this compound, which would be expected, he has obtained dimercury derivatives from 5-nitrosalicylic acid. From 3,5-bromonitrosalicylic acid and from 3,5-dinitrosalicylic acid he has obtained mixtures of mono- and dimercury derivatives of undetermined constitutions. Whitmore and Middleton[14] have mercurated salicylaldehyde and 5-nitrosalicylaldehyde. The former gives chiefly a dimercury compound. The latter gives a monomercury derivative from which have been prepared a number of mercurated Sciff's bases. Henry and Sharp[32] have studied the mercuration of the three hydroxybenzaldehydes, obtaining dimercurated products from the ortho and para compounds and a monomercury derivative from the meta compound.

White,[33] in continuing his work on the mercurated phthaleins and related compounds, has developed "flumerin," a disodium compound of hydroxymercurifluorescein. Abelmann[3] has treated phenacylmercuric chloride with methylmagnesium iodide, obtaining methylmercuric iodide and mercuri-bis-(methylenemethylphenylcarbinol), Hg(CH$_2$MePhCOH)$_2$. Chloromercuribenzophenone in a similar way gives mercuri-bis-(phenylenemethylphenylcarbinol). Hartmann[34] has patented organomercury derivatives of glucosides, using as examples amygdalin, salicin, and arbutin.

Oliveri-Mandala[35] has prepared mercury derivatives of antipyrine. Vecchiotti[9] has mercurated aminoazobenzene and diaminoazobenzene. The former gives a monoacetoxymercuri compound. The latter gives a mono- and a diacetoxymercuri compound and a crystalline substance of the formula (C$_{12}$H$_{11}$N$_4$)$_2$-Hg. Raiziss[18] has prepared mercury derivatives of Orange II, of chrysoine, and of alizarin yellow.

A number of papers have appeared on the analysis of organic compounds of mercury.[36] Raiziss[18] has developed a modification of the Dennstedt method for carbon and hydrogen analysis in which the mercury is retained by weighed silverized asbestos.

Mercury Derivatives of Thiophenes

Among the few generalizations which have ever been made in the field of organic mercury compounds are three generalizations by Steinkopf on mercury derivatives of thiophenes. His more recent work shows that these must be discarded.[6] The statement that all thiophenes having a free alpha position react readily to give organo-mercury derivatives must be modified, since it is found that 3,4-diphenyl-thiophene does not react with mercuric chloride and sodium acetate. This is in sharp contrast to the behavior of the presumably less reactive 2,5-diphenylthiophene, which contains no free alpha position and yet reacts readily to give a chloromercuri compound. The generalization that a chloromercuri group enters an alpha position but not a beta position *directly* must be discarded, as 2,4-thioxene behaves in the same way as 2,5-thioxene, forming an intermediate addition compound which gives the chloromercuri compound only on boiling. The converse of this statement, that mercury enters the beta position only *indirectly* through the formation of an intermediate addition product, is nullified by the fact that 2,5-diphenylthiophene forms no addition product, but gives a chloromercuri derivative directly. On the other hand, the formation of intermediate addition compounds in the beta as well as in the alpha series seems to strengthen Steinkopf's original hypothesis that the mercuration of thiophene always takes place by way of a preliminary addition. The third generalization suffers the same fate as the others—that an alpha-mercurated thiophene reacts readily with two mols of sodium iodide to give a mercuri-bis compound, while a beta-mercurated compound cannot be changed to the mercuri-bis compound except by vigorous treatment with metallic sodium. This statement must be discarded because the β-chloromercuri-2,5-diphenylthiophene reacts with sodium iodide to form the mercuri-bis compound and because the α-chloromercuri-2-ethylthiophene gives only the corresponding iodide and no mercuri-bis compound.

Bibliography

1—Dimroth, *Ber.*, **54B** (1921), 1505; *C. A.*, **16** (1922), 1223. Cf. *Ber.*, **54B** (1921), 571; *C. A.*, **15** (1915), 2627; *Ber.*, **53B** (1920), 2144; *C. A.*, **15** (1921), 1310; Manchot, *Ann.*, **421** (1920), 334.

2—Adams, Sperry, and Roman, *J. Am. Chem. Soc.*, **44** (1922), 1781.

3—Abelmann, *Ber. pharm. Ges.*, **31** (1921), 240; *C. A.*, **16** (1922), 2491.

4—Wibaut and Jürgens, *Verslag. Akad. Wetenschappen Amsterdam*, **29** (1922), 1074; *C. A.*, **16** (1922), 1571.

5—"Organic Compounds of Mercury," p. 274.

6—Steinkopf, *Ann.*, **424** (1921), 23; *C. A.*, **15** (1921), 2872. Cf. *Ann.*, **428** (1922), 123; *C. A.*, **16** (1922), 3653.

7—"Organic Compounds of Mercury," p. 61.

8—Jenkins, *J. Chem. Soc.* (*London*), **119** (1921), 747; *C. A.*, **15** (1921), 2416.

9—Vecchiotti, *Gazz. chim. ital.*, **52** (1922), I, 137; *C. A.*, **16** (1922), 2126.

10—Challenger and Allpress, *J. Chem. Soc.* (*London*), **119** (1921), 913; *C. A.*, **15** (1921), 2846.

11—Zappi, *Anales soc. quim. Argentina*, **8** (1920), 55; *C. A.*, **15** (1921), 3283.

12—Unpublished results, Whitmore and Thurman.

13—Paper presented before the Division of Organic Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

14—Paper presented before the Division of Organic Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

15—Goret, *Bull. sci. pharmacol.*, **29** (1922), 297; *C. A.*, **16** (1922), 3062.

16—Marvel and Gould, *J. Am. Chem. Soc.*, **44** (1922), 153.

17—Tiffeneau, *Bull. sci. pharmacol.*, **28** (1921), 65; *C. A.*, **15** (1921), 2273.

18—Private communication.

19—*C. A.*, **15** (1921), 1029, 3271; **16** (1922), 566, 2150, 2518, 2868, 3665.

20—Vogt and Nieuwland, *J. Am. Chem. Soc.*, **43** (1921), 2071; *C. A.*, **16** (1922), 235.

21—Note errors in *C. A.*

22—Biilmann, *Meddel. Vetenskapsakad. Nobelinst.*, **5**, No. 12, 2; *C. A.*, **14** (1920), 2489.

23—Schoeller, *Ber.*, **53B** (1920), 2144; *C. A.*, **15** (1921), 1310. Cf. *Ber.*, **53B** (1920), 62; *C. A.*, **14** (1920), 2203.

24—Tiffeneau, *Bull. sci. pharmacol.*, **28** (1921), 7; *C. A.*, **15** (1921), 2432.

25—Vecchiotti, *Gazz. chim. ital.*, **51** (1921), II, 208; *C. A.*, **16** (1922), 556.

26—Paolini, *Gazz. chim. ital.*, **51** (1921), II, 188; *C. A.*, **16** (1922), 557.

27—Mameli, *Gazz. chim. ital.*, **52** (1922), I, 352; *C. A.*, **16** (1922), 2681.

28—Raiziss and Prouskouriakoff, *J. Am. Chem. Soc.*, **44** (1922), 787; *C. A.*, **16** (1922), 1571. Cf. *C. A.*, **16** (1922), 315.

29—Goddard and Goddard, *J. Chem. Soc.* (*London*), **121** (1922), 482; *C. A.*, **16** (1922), 1937.

30—Whitmore and Middleton, *J. Am. Chem. Soc.*, **44** (1922), 1546; *C. A.*, **16** (1922), 2856.

31—*C. A.*, **15** (1921), 2529.

32—Henry and Sharp, *J. Chem. Soc.* (*London*), **121** (1922), 1055; *C. A.*, **16** (1922), 2856.

33—Private communication. Cf. *C. A.*, **16** (1922), 1487.

34—Hartman, *C. A.*, **15** (1921), 148.

35—Oliveri-Mandala, *Gazz. chim. ital.*, **51** (1921), I, 125; *C. A.*, **15** (1921), 3086.

36—*C. A.*, **15** (1921), 488, 541, 2808, 2872, 3428; **16**, (1922), 789, 884.

37—Sneed and Maynard, *J. Am. Chem. Soc.*, **44** (1922), 2942.

Alsatian Potash[1]

By John E. Teeple

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On invitation of the director of the "Société commerciale des Potasses d'Alsace," the writer visited the French potash mines and refineries at the end of January. He went there with a feeling, which is probably prevalent among Americans, that the French potash mines were under French government control, and therefore in all probability, being governmental, poorly and wastefully managed, and serving as a resting place for broken-down politicians and lame ducks. He spent about a week in visiting the different shafts, going down some of the mines, visiting the different levels, inspecting the underground methods of mining and filling, their hoisting equipment, muriate refineries, and aboveground works. They also opened their records to him, such as daily report sheets over long periods, from the different shafts, showing all tonnage produced, per cent K_2O, workmen per shift above and below ground, electric-power consumption, coal consumption, scales of wages, etc. In fact, everything was frankly placed at his disposal to enable him to determine what they were doing and what they could do in the way of producing potash.

The writer left Alsace with the picture of a potash industry well managed by competent business and technical men, whose equipment for production has been very rapidly and thoroughly improved, and whose improvement is still continuing; an industry which produced 228,000 tons of K_2O in 1922, which is producing at the annual rate of over 300,000 tons now, and which at any time on two months' notice could be producing at the rate of 500,000 tons K_2O per year, provided they have a market for so much; an industry which hereafter must always be reckoned with as an important factor in the world's potash production. How important a factor this is will be realized when we remember that the total consumption of potash in the world, outside of Germany, has probably never materially exceeded 500,000 tons per year, and very likely has never reached that figure, with the possible exception of the two years 1913 and 1922. These figures mean that the German potash monopoly which existed since about 1860 no longer exists, and, as far as quantity is concerned, if Germany were again shut off from the world, the world would not necessarily be lacking its full quota of potash.

The two beds of potash salts in Alsace near Mulhouse—their extent, thickness, richness, etc.—have so often been described that further description is unnecessary here. There is a sufficient quantity of potash to last several hundred years at the present rate of consumption, at a depth of only about 700 meters. The beds are thick enough to be mined economically, there is no trouble from accumulating water in the mines, and the product is richer than the German product—averaging 16 per cent or more of K_2O, while the German average is only about 12 per cent. There are seventeen shafts at present in these potash beds. With the existing carriages and hoisting machinery their capacity is limited to from 700 to 1200 tons of salt per day at the different shafts, with an average of close to 1000 tons per day capacity per shaft. It will be seen that for the seventeen shafts this represents a possible shaft capacity of over 2500 tons of K_2O per day. As the shaft capacity is the limiting factor—the neck of the bottle—an estimate of a possible 500,000 tons per

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[1] Received March 20, 1923.

year is very conservative. Given the market and the need for producing that quantity or more, the mines, with their present organization but with the necessary additional workmen, can do it with ease.

Assuming, then, that France has the necessary quantity of potash and has the machinery and the ability to produce it as fast as needed, the next question is—can she compete in price? It is difficult to-day to compare costs of German, French, and American potash on account of the fluctuations in exchange. With German potash this is particularly true. During all this period that the mark has been falling there is no doubt that Germany could undersell any other country and still make a profit, but in looking ahead we must assume that conditions will some day stabilize. When this happens, as it must, then the play of real competitive forces will come into effect. To-day these competitive forces are overshadowed by exchange fluctuations, but in the long run the determining factors of competition will be, for example, the number of man shifts of labor, the kilowatt-hours of electricity, the tons of coal, and the ton-miles of haul by rail or steamer that will be necessary, in the French mines, the German mines, and the American potash works, to produce 1000 tons of K_2O and get it to a definite market. Figured on this basis, which is the one that is bound to prevail in the long run, it becomes obvious that France can very definitely compete with Germany. As a matter of fact, it costs no more in man shifts and kilowatt-hours to get a ton of potash salts above ground in France than it does in Germany, and when this ton is above ground it contains more K_2O on the average in France than it does in Germany. This in the long run gives France an advantage, which is only partially offset by her longer haul to sea. Buyers of potash should definitely convince themselves that both French and American production of potash are here, and here permanently. That there is no longer a German monopoly, that Germany can be entirely shut off and the world can be supplied from other sources, and that the German boast of her ability to starve any part of the world or feed any part of the world she chooses, is now only an empty boast, as the world can now entirely feed itself without the help of her potash.

The New Element "Hafnium"

In the January 20, 1923, issue of *Nature*, Coster and Hevesy, of the University of Copenhagen, announced the discovery, through the use of the X-ray spectrum, of a new element which they called "hafnium," and which they stated was found in certain zirconium minerals and had properties similar to those of zirconium. They claimed that it represented the missing element of atomic number 72. In a further communication they stated that continued experiments enabled them to confirm all their previous statements. By the addition of a known quantity of tantalum to their samples, and by a comparison of the intensity of the tantalum lines with the hafnium lines, a closer estimate of the amount of hafnium present had been obtained, and they stated that a great number of zirconium minerals from different parts of the world all contained from 5 to 10 per cent of hafnium. They had also by means of chemical methods separated zirconium and hafnium so that some preparations contained about 50 per cent of hafnium, and on the other hand had obtained zirconium preparations which showed no hafnium lines.

This announcement was followed up by a paper on February 1 before The Chemical Society by Dr. Alexander Scott, on "The Isolation of the Oxide of the New Element," which he claimed was the new element, hafnium, and that his discovery pre-dated that of Coster and Hevesy. He stated that in 1913 he received for analysis samples of a black sand from New Zealand, from which he extracted a cream-colored sand containing about 75 per cent of titanium dioxide. In further treatment of this titanium dioxide he always obtained a highly refractory residue of which he collected a considerable amount and labeled it a "new oxide," but until the announcement of the discovery of hafnium by Coster and Hevesy he did not do any further work. Thinking that there might be some connection between the two, he took his old material and found that the atomic weight was approximately 180 and the chemical characteristics those which X-ray spectroscopy would assign to hafnium. He then sent some of the material to Coster and Hevesy, giving them the opportunity to apply the X-ray method to his oxide.

In a letter to *Nature* under date of February 24, Coster and Hevesy stated that "an investigation of certain preparations extracted from a titanium mineral from New Zealand and kindly sent to us by Dr. Scott did not reveal any hafnium line. Taking the sensitiveness of the method into account, this mineral cannot contain appreciable amounts of hafnium." Whatever Dr. Scott's residue oxide may be, this seems to dispose of his claim that it contains the same material as that which gives the lines found by Coster and Hevesy, and on which they base their claim to the discovery of a new element.

The claim of Dr. Scott was followed by a letter under date of February 17, written by Urbain and Dauvillier, stating that the element hafnium was undoubtedly identical with the "celtium" of these chemists, announcement of the discovery of which had been made eight months previous to the discovery of hafnium. Indeed, as long ago as 1911 Urbain had indicated the possible existence of this element, but had been able to get only extremely small concentrations. Urbain and Dauvillier examined not only the optical spectrum of celtium, but also the X-ray spectrum and obtained two unknown lines in the latter which they stated were identical with two of the lines assigned to hafnium by the Danish chemists. Urbain and Dauvillier found that celtium was associated with the rare earths and apparently had none of the properties of zirconium.

Coster and Hevesy have come back with a rather definite reply to the claims of Urbain and his co-worker. They state that celtium and hafnium show great differences in chemical properties. Whereas they have been able to purify hafnium and obtain high concentrations of the element, Urbain and Dauvillier have not succeeded in doing this in connection with celtium. In addition, with hafnium salts of high concentration they have been unable to reproduce the characteristic optical spectrum ascribed by Urbain to celtium. They also claim that the two X-ray lines obtained by Urbain do not coincide within the limit of experimental error with their own measurements on the hafnium X-ray lines, which were supposed to be identical with those obtained by Urbain.

This letter has been confirmed by a more recent one by Hansen and Werner, of Copenhagen, giving the optical spectrum of hafnium. They give wave lengths for fifty-two characteristic hafnium lines. They also state that they have examined the hafnium preparations of high concentration for the presence of the lines belonging to the characteristic spectrum ascribed by Urbain to celtium, and have not been able to find the slightest trace of these lines from any of their preparations, although the minerals used as a starting point for the work of Coster and Hevesy contain rare-earths limits in considerable amount.

NICHOLS MEDAL AWARD

The Nichols Medal was awarded to Thomas Midgley, Jr., of the General Motors Research Corp., Dayton, Ohio, at the meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY, held at the Chemists' Club, New York City, on March 9, 1923, in recognition of his researches on detonation in internal-combustion engines. Dr. C. A. Browne, chairman of the Section, presided and opened the meeting with appropriate remarks on the history of the medal. Previous to 1913 it was given for the best address before the New York Section, but at that time its scope was broadened to cover all papers representing original research and published in either of the two journals of the SOCIETY.

Dr. Wilder D. Bancroft followed with remarks of a personal nature about Mr. Midgley and his work. Mr. Midgley, who is only thirty-four years old, was a student at Cornell and came under Dr. Bancroft's tutelage.

The presentation of the medal was made by Dr. Chas. H. Herty in the absence of Dr. Nichols, donor of the medal. Dr. Herty pointed to the notable men who had previously received it and the fact that it has been a truly representative group of men from every field of chemistry.

Previous awards of the Nichols Medal have been made to

1903	E. B. VOORHEES
1905	C. L. PARSONS
1906	M. T. BOGERT
1907	H. B. BISHOP
1908	W. H. WALKER
1908	W. A. NOYES AND H. C. P. WEBER
1909	L. H. BAEKELAND
1911	M. A. ROSANOFF AND C. W. EASLEY
1912	CHARLES JAMES
1914	MOSES GOMBERG
1915	IRVING LANGMUIR
1916	C. S. HUDSON
1918	T. B. JOHNSON
1920	IRVING LANGMUIR
1921	G. N. LEWIS

In accepting the medal, Mr. Midgley said that his part in the work for which the medal was given was merely that of a collector of the results of others, and after all the credit was due to his organization to a far greater degree than to himself. An abstract of Mr. Midgley's address follows.

Some Fundamental Relations among the Elements and Compounds as Regards the Suppression of Gaseous Detonation


THOMAS MIDGLEY, JR.

UNDER certain conditions the combustion of gases is characterized by detonation. In the case of the combustion of a mixture of any given fuel in the internal-combustion engine the development of detonation is controlled primarily by the pressure to which the unburned portion of the mixture is subjected during combustion. In view of the fact that both the power output and the efficiency of the internal-combustion engine are functions of its compression, this factor has a large significance. Economical utilization of fuel demands that engine compressions shall be as high as is compatible with proper performance from a mechanical standpoint. Since the motor fuel available is practically of fixed composition, the factor that now limits the compression of automotive engines is the tendency of this fuel to detonate.

It has been found that the presence of very small amounts of certain materials in a fuel-air mixture influences its combustion in such a way that detonation is prevented. This detonation-influencing property is a function of certain compounds of a considerable number of the elements.

RECENT RESULTS OBTAINED IN THE STUDY OF GASEOUS DETONATION

Two things have recently been added to our knowledge of the mechanism of gaseous detonation. First, it has been demonstrated that even in nondetonating, or normal, combustion a higher pressure must exist ahead of the flame front than behind it. It has been shown, further, that the pressure immediately in advance of the flame front is controlled by the reaction velocity of combustion. If the reaction velocity is expressed by the equation $W = KD^nT^m$, a mathematical expression can be derived for the pressure differences existing in the flame front at different total pressures. In this equation W is the reaction velocity expressed in pounds of gas entering the reaction per second, K is a constant whose value must be determined experimentally, T is the absolute temperature immediately in front of the flame, D is the density or concentration, and n and m are exponents whose values must be determined experimentally.

The expression derived on this basis predicts a critical pressure above which the combustion reaction proceeding through the gas must travel at the velocity of sound. When the transmission of chemical activity reaches this velocity, a condition that we call "detonation" is produced.[1]

These developments may be considered as being based upon the physical chemistry involved in gaseous detonation. But they shed no light on the ultimate nature or mechanism of the chemical reactions involved. They merely apply the known laws of physics and chemistry to the analysis of the progressive combustion of a gaseous mixture.

WHAT ANTIKNOCK MATERIALS DO

Those compounds which, when present in combustible mixtures in very small amounts, have the effect of entirely removing the disturbances that characterize detonating combustion are called for convenience "antiknock" materials. Their effect appears to be that of increasing the critical pressure at which detonation occurs. Thus, if a mixture of acetylene and air of proper proportions contained in an open tube is ignited at one end, a detonation wave is set up after the flame has traveled a short distance along the tube, as is shown by the high luminosity and by the loud and sharp "crack" that is produced. If the experiment is conducted in a strong glass tube, the intensity of

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[1] Midgley, *J. Soc. Automotive Eng.*, **10** (1922), 357; Midgley and Janeway, "Laws Governing Gaseous Detonation," to be published in an early issue of *J. Soc. Automotive Eng.*

the pressure wave resulting from the detonation is often such that a few inches of the tube at the end opposite the point of ignition are shattered into small pieces. But when a very small percentage of an antiknock material such as diethyl selenide is present in the acetylene-air mixture, the burn is very quiet and it lacks the high degree of luminosity that characterizes detonating combustion.[2]

The effect of antiknock materials upon internal combustion is even more striking. If, for example, an airplane engine, which has a compression ratio of about 5.3:1, is run on the commercial motor gasoline of to-day, a violent detonation or knock is produced. Even in the absence of instrumentation for detecting and measuring it, the detonation manifests itself by a loud hammering sound of a metallic quality and by a reduction in power from what should be the normal output of the engine. When a small amount of the vapor of diethyl selenide is admitted with the intake air, the detonation is entirely eliminated and a noticeable increase in the power of the engine is apparent. In a similar way, if a very small amount of tetraethyl lead, about 0.1 per cent by volume, is added to the fuel, the detonation entirely disappears, the engine runs with perfect smoothness, and its power rises to normal or to the value that it should have in the absence of detonation. Computation shows that quantitatively this result is produced by virtue of the presence of only 1 molecule of tetraethyl lead in over 80,000 molecules of fuel-air mixture.

In distinction from these materials whose effect is to eliminate detonation, there is another class of substances that induce detonation. This is in addition to those materials that are neutral as far as effect on detonation is concerned. The knock-inducing property characterizes to a small degree the ethyl compounds of bromine, oxygen, and sulfur. These elements also show this negative characteristic in the elemental form.

But the simple alkyl compounds of these elements exhibit a relatively small detonation-inducing effect. When oxygen is bonded into compounds such as alkyl nitrates or nitrites and phenyl nitro compounds, its effect for inducing detonation becomes very marked. Thus, if an engine is run on a fuel such as a benzene-gasoline mixture that does not produce any knock, a violent detonation can be produced by the admission of a very small amount of some volatile organic nitrate or nitrite along with the fuel-air mixture. This detonation-inducing material is equally effective whether it is admitted as a vapor with the intake air or whether it is dissolved in the fuel. Quantitatively 1 gram molecule of isopropyl nitrite has a detonation-inducing effect that is equal to the inverse of about 0.1 gram molecule of tetraethyl lead.[2,3] (The detonation-inducing elements are considered as possessing the negative of the antiknock property.)

The mechanism by which these materials control the reaction velocity of combustion is not understood. It is inconceivable that their effect can be due to a simple thermal effect, such as an absorption of heat with a consequent cooling of the flame. The amount of the antiknock material present in the burning gas is too minute for such to be the case. As has previously been shown,[2] the presence of as little as 1 molecule of tetraethyl lead in over 200,000 molecules of a combustible mixture of kerosene and air exerts an effect in the suppression of detonation that is equivalent to the blending of 25 per cent of benzene by volume with the kerosene. Benzene is a fuel that does not detonate even when burned at compressions in excess of 200 lbs. per sq. in.; and, when it is blended with kerosene, the resulting mixture partakes of the nondetonating property of benzene to the extent to which benzene is present.[4] It has previously been suggested that, in view of the small amounts of some of these materials needed to exert a large effect on the character of combustion, their action bears some analogy to that of catalytic agents.

An adaptation of the Perrin radiation theory has been proposed as an explanation for the behavior of knock-suppressing and knock-inducing materials. The presence of a small amount of one of these materials during the combustion of a highly compressed mixture of gases is conceived as presenting a screen which absorbs some radiation and thereby controls the velocity of flame movement. The application of the principles of this theory to the explanation of the behavior of such materials would appear to be profitable field for research on this subject. With the exception of this one suggestion, which is not as yet borne out by any experimental evidence, no adequate explanation of the action of these materials has been advanced.

PHYSICAL CHEMISTRY OF THE DETONATION-INFLUENCING PROPERTY

But whatever the mechanism by which these materials influence combustion, quantitative measurements of their effects may be obtained by the application of proper instrumentation to the internal-combustion engine. Thus, in a given motor, when operating on a given kerosene, the constants in the equation $W = KV^nT^m$ (see above) were found to have the following values:[5]

$$K = 3.25 \times 10^{-7}$$
$$n = 0.9$$
$$m = 3.22$$

After 2 cc. of tetraethyl lead per gallon had been added to the kerosene, the values obtained in the same way were

$$K = 3.075 \times 10^{-7}$$
$$n = 0.9$$
$$m = 3.22$$

The following data show how K varies with a number of concentrations of tetraethyl lead in the kerosene used as fuel:

Concentration $PbEt_4$ Cc./Gal.	K
0	3.25×10^{-7}
1	3.17×10^{-7}
2	3.075×10^{-7}
4	2.97×10^{-7}
8	2.86×10^{-7}
16	2.76×10^{-7}

From these figures it is obvious that the effect of the presence of tetraethyl lead in a detonating fuel is to change the value of K in the equation. The results of a number of determinations show the relationship between the concentration of tetraethyl lead and the constant K to be as follows:

$$K = K_0 - 0.173 \times 10^{-7} \log_e (C + 1)$$

where K_0 is the reaction-velocity constant of the original fuel, C is the concentration of tetraethyl lead in cubic centimeters per gallon, and 0.173×10^{-7} is a constant.

The form of this equation is suggestive of a selective radiation absorption, but by itself it must, of course, be considered as inconclusive. Nevertheless, it does make a material addition to the data tending to substantiate the applicability of the Perrin radiation theory to these cases.

These figures should not be considered as expressing the relationship of all antiknock materials to the constant K, because the values for aromatic amines are known to differ from those of tetraethyl lead. It will be some time before complete data of this character on the different types of antiknock materials can be obtained and the true relationships existing between them definitely ascertained.

The amount of work necessary to determine the values of antiknock materials in a comparative way may be materially reduced by determining simply the concentration of any given compound required to produce an effect on detonation that is equal to some standard. Thus, 1 per cent of aniline by volume may be used as the standard. The values so obtained are only relative, because in some cases the relationship changes with concentration. This should, therefore, be considered as an

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[2] Midgley and Boyd, THIS JOURNAL, 14 (1922), 894.

[3] *Ibid.*, 14 (1922), 849.

[4] *Ibid.*, 14 (1922), 589.

[5] See Footnote 1, Midgley and Janeway.

approximate rather than an absolute method of comparison. However, for comparing the antiknock effect of one compound with that of another this method is a satisfactory one.

Detonation-Influencing Property Primarily in the Atom

The magnitude of the detonation-influencing effect is primarily a function of one atom in the molecule, but it is modified to a great extent by the radicals or groups attached to that atom. The relative antiknock effects of the ethyl and phenyl compounds of four elements are given in Table I. By comparing the values for the ethyl compounds of iodine, selenium, and tellurium with those for their corresponding phenyl compounds, it is observed that they are of the same order of magnitude for each element, the alkyl compounds being somewhat more effective than the aryl compounds. The reverse is true with oxygen, diethyl ether being a slight inducer of detonation, while diphenyl ether is a weak antiknock material. From the table it may be observed further that the antiknock value changes enormously with the element, while it is merely modified by the change in grouping. Thus, diethyl telluride is about twenty-five times as effective molecularly as ethyl iodide, and the same relation holds for the phenyl compounds of these elements. It seems reasonable to conclude, therefore, that the antiknock property is primarily a function of the element rather than of the groups attached to it.

Table I—Comparison of Relative Effects Exerted upon Detonation by Ethyl and Phenyl Compounds of Four Elements

Element	Reciprocal of Number of Gram Molecules Required to Give Anti-knock Effect Equivalent to One Gram Molecule of Aniline[a]	
	Ethyl Compound	Phenyl Compound
Iodine	1.09	0.88
Selenium	6.9	5.2
Tellurium	26.8	22.0
Oxygen	−0.036[b]	0.122

[a] Based on concentrations of aniline up to 3 per cent by volume in kerosene.

[b] Induces detonation.

Personals

With great regret we announce the death at Munich, at the age of 78, of **Prof. W. K. von Röntgen**, the discoverer of X-rays.

Mr. J. Emil Frank, owner and publisher of the *Textile Colorist*, died of pneumonia at his home in New York on March 1, in his forty-eighth year. Mr. Frank had been connected with the *Textile Colorist* throughout his life. The journal was founded by his father, Dr. Morris Frank, in 1879. Upon the death of the father, his widow controlled it until her death in 1921, when it descended to the son.

Dr. J. R. Turner, dean of the Washington Square College of New York University, has been appointed chief economist of the Tariff Commission, and **Dr. A. L. Faubell**, also of the Washington Square College, has been appointed assistant chief economist.

Mr. Ralph Hayward has resigned as treasurer of the Newton Falls Paper Company to accept an assistant professorship in chemical engineering at the University of Michigan. Mr. Hayward will give courses in mechanical handling and preparing of bulk materials, in plant design, particularly of the sulfite mill, and will aid in the development of the industrial research department among the paper mills of Michigan.

Mr. R. C. Bardwell, who for the past thirteen years has been connected with the development and operation of water-softening plants on the Missouri Pacific Railroad, has been appointed superintendent of water supply of the Chesapeake & Ohio Railroad, with headquarters at Huntington, W. Va., to organize a similar department for that railroad.

Mr. H. H. Richardson, formerly assistant sanitary engineer for the St. Louis & Southwestern Railway, with headquarters at Pine Bluff, Ark., has been appointed engineer of water service for the Missouri Pacific Railroad with headquarters at St. Louis, Mo., to have charge of the laboratories and Water Service Department.

Secretary Hoover has appointed the board of visitors of the United States Bureau of Standards for a period of three years as follows: President F. W. McNair, of the Michigan College of Mines; Dr. Ambrose Swasey, of Cleveland, Ohio; Dr. John R. Freeman, of Providence, R. I.; Prof. Wilder D. Bancroft, of Cornell University, and Dr. Samuel W. Stratton, of Massachusetts Institute of Technology.

Dr. Marston T. Bogert, professor of organic chemistry at Columbia University, has been appointed referee in chemistry for the American Field Service Fellowships for French universities.

Mr. Irving B. Morgan has resigned his position as chemist in the Illinois State Highway Testing Laboratory at Springfield, Ill., to take charge of the Missouri State Highway Commission, Jefferson City, Mo.

Mr. John Morris Weiss, consulting chemical engineer of Weiss & Downs, 50 East 41st St., New York, N. Y., has been selected by the Manufacturing Chemists' Association to serve as their representative on the recently formed Subcommittee on Benzol Poisoning of the Chemical Section of the National Safety Council.

Dr. C. K. Francis has resigned his position with Cosden & Co., to accept the vice presidency, in charge of refining, of the Producers & Refiners Corp., Chicago, Ill.

Mr. A. W. Ambrose, assistant director of the Bureau of Mines, has been placed in charge of the newly created leasing branch of that bureau.

Mr. J. H. Hall has resigned his position as assistant professor of chemistry at Illinois State Normal University, Normal, Ill., to become research chemist for the California Fruit Growers' Exchange Laboratory, near Los Angeles, Calif.

Mr. E. H. Manahan, formerly with Innis, Speiden & Co., is now in charge of the heavy chemical business of Eugene Suter & Co., Inc., 160 Broadway, New York, N. Y.

R. T. Vanderbilt Co., Inc., 50 East 42nd St., New York, N. Y., announces an addition to its personnel in the appointment of **Mr. W. H. Cope** as technical secretary and assistant to Dr. A. A. Somerville. Mr. Cope has been connected during the last seven years with the Lee Tire & Rubber Co., Conshohocken, Pa.

Mr. Alfred I. Phillips, formerly service engineer of the American Gas Association, has accepted a position as gas engineer with Arthur D. Little, Inc., Cambridge, Mass.

Mr. James G. Vail, chairman of the Philadelphia Section of the American Chemical Society, sailed on March 17, for an eight-weeks' trip in England, Belgium, Holland, and Germany in the business interests of his firm, the Philadelphia Quartz Company.

Dr. E. S. Merriam has resigned as chief chemist of the Safe-Cabinet Co., in order to resume his consulting work in connection with natural gas, casinghead gasoline, and carbon black, at Marietta, Ohio.

Mr. Charles Duvoisin, superintendent in the Powers-Weightman-Rosengarten Company's chemical plant at Philadelphia, who suffered serious injuries on February 14, when the motor car in which he was driving plunged from a bridge over the Schuylkill River and was shattered on the lower deck of the bridge, a sheer drop of nearly forty feet, is making very favorable progress toward recovery at the Medico-Chirurgical Hospital. Mr. Duvoisin sustained a severe fracture of the pelvis bone and one arm, together with numerous lacerations of the face and head, and for some little time his recovery was regarded as highly precarious.

Mr. George Wolf, deputy appraiser of the Port of New York, has been appointed to take charge of the Dye Division of the U. S. Appraisers' Stores, New York City.

AMERICAN CONTEMPORARIES

William H. Nichols

What is here said of Dr. Nichols is said behind his back, for he is at the moment far away on one of the occasional vacations which he permits himself.

This vacation, following close upon the celebration of his golden wedding, may be regarded as a sort of golden honeymoon. No man deserves one more and few can point back to fifty years of happy married life as one of the main inspirations to their achievement.

Dr. Nichols' achievements have been important and varied. He has touched life at many points. His career has been based both on science and on business; but the science has been applied science devoted to turning scientific knowledge to practical uses, and the business has been of the kind to exploit science for the general good.

His scientific attainments found their crowning expression when he, an American for generations back, after having been president of the British Society of Chemical Industry, was made, in succession to Sir William Ramsay, president of the International Congress of Applied Chemistry. This organization, which the war disrupted, had been the most distinguished body of international chemists and workers in applied chemistry in the world. In his own country he has been president of the American Chemical Society.

Pirie MacDonald

William H. Nichols

His business attainments have lately found their crowning expression—or so he would think—in the formation of the Allied Chemical & Dye Corporation, of which he is chairman of the board.

The steps by which these distinctions have been won may be of interest. They came as the reward of a life of hard work—guided by that highest form of self-interest which finds one's own interests in the things that benefit others.

Dr. Nichols commenced his career in the chemical business in 1870 in association with a friend named Walter, under the firm name of Walter & Nichols, subsequently incorporated as Nichols Chemical Company. As he was then but eighteen years of age, he borrowed his father's name for the firm, pending his minority.

Sulfuric acid, then as now, was the foundation stone of the business, and oil of vitriol standardized as 66° Bé. was its most important strength. The young Nichols soon learned that many makers produced under this name acid of only 65° Bé., but he made his of standard strength and was soon rewarded by a great demand for his high-quality acid for the newly discovered business of refining oil.

In those days, too, the acid was made from Sicily brimstone, containing 97 to 99 per cent pure sulfur, but this young concern learned how to use pyrites containing only 35 to 45 per cent sulfur —a far cheaper source of supply. Ultimately, a copper pyrites mine was acquired and the smelting business undertaken, and the concern thus controlled its own raw material both for acid and for copper matte. One thing led to another and later a refining plant was built and the concern refined its copper and sold refined ingots.

About 1898 Dr. Nichols conceived the advantages of a merger in the chemical trade. This was accomplished in 1899 by the consolidation of twelve chemical businesses under the name of the General Chemical Company. The Nichols copper business was kept separate. This new merger was large enough to realize the advantages of large-scale production, but not extensive enough to unduly restrict competition. It is significant that the legality of this merger under the trust laws has never been questioned by any public authority.

The contact or catalytic method of making sulfuric acid next attracted Dr. Nichols' attention. In 1905 certain foreign basic patents were acquired, and since then all the plants of the company have been equipped with contact units, which alone are capable of making oleum, so essential for munitions in war and for colors and heavy oil refining in peace.

As catalysis was the new slogan in chemistry, the next thought was how through catalysis to reach that unlimited supply of raw material—the refractory nitrogen of the air. That a large commercial plant at Syracuse is now making anhydrous ammonia from the nitrogen of the air is due to Dr. Nichols' original impulse.

To coal-tar colors he had given much thought, but all the conditions in America seemed against this industry. However, he succeeded in forming, with two other concerns, the Solvay and the Barrett companies, a little company to make aniline oil out of coal-tar crudes. This was prior to 1914. This company achieved success technically, but German "unfair methods" kept it down until the war broke out. It then came into its own and it formed the basis for the new National Aniline & Chemical Company.

It is not too much to say that just as the contact method of making oleum assured to the country its war munitions, so this little aniline company assured to the country and its textile interests during the war the coal-tar intermediates necessary to the making of colors and high explosives.

Dr. Nichols' next important and, so far, his latest work, was the merger which resulted in the Allied Chemical & Dye Corporation. Coöperation in aniline and subsequently in colors had led those concerned to perceive the essential unity of their interests and the advantage of integrating the industry by merging complementary processes.

Naturally, Dr. Nichols has not been alone in accomplishing all these results. He would be the last person to make such a claim. The truth is, he is a born leader of men and has known how to surround himself with the best. His was often the vision where others did the work. It has been his boast that he would never himself do what he could find some one else to do better.

It was both by good luck and by good judgment that early in life he found as an associate such a man as J. B. F. Herreshoff, an accomplished chemical engineer and an inventor of great merit. And so it was with the late Sanford H. Steele, with whom he enjoyed an almost life-long association. Dr. Nichols was often heard to declare how much of his success he owed to Steele's rare judgment and acumen as a lawyer and a business man.

But Dr. Nichols is not merely a chemist and a manufacturer;

he is a banker as well, for years connected, as vice president or otherwise, with the upbuilding of the Corn Exchange Bank and its new and original system of branch banking—now being imitated by other banking institutions.

Has such a varied and useful career led on to wealth? Most assuredly it has, but his has been a wealth created in the service of the community, in which the community gained more than he.

As we are talking behind Dr. Nichols' back, we might ask ourselves—have all these successes been unmarred by the making of mistakes? I think not; Dr. Nichols is too broadminded a man not to admit his occasional mistakes. But an associate once said of him, "I would rather follow Nichols *right and wrong* than any other man always right." The reason is obvious. His sum of successful accomplishment was far greater than that of the man lacking in vision, always taking the safe, inglorious, and unprogressive course, who could make no mistakes.

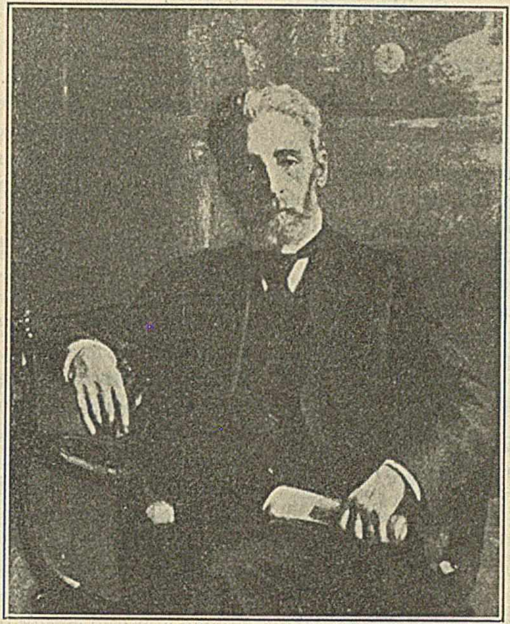
Finally, it may be asked—after so much accomplishment what has Dr. Nichols done to perpetuate his work and carry it forward? He has two able sons who are guiding two of the important branches of it; and it was he who picked out the very remarkable man chosen as president of the Allied Chemical & Dye Corporation.

Should any ask what may be the other faults of a man so gifted, I would answer, "They shall not be written down here." I love the man too well to publish his faults if I knew them—and I am not the one to know them.

Charles Robinson Smith

Obituary

Walter Stanley Haines



Walter Stanley Haines

Walter Stanley Haines, professor (beloved teacher of students) at Rush Medical College since 1876, died on January 27, 1923, at the Presbyterian Hospital, from bronchiectasis complicated with chronic nephritis.

Dr. Haines was born September 27, 1850, in Chicago. His father, John G. Haines, was for two terms mayor of the city. Dr. Haines attended the Chicago High School, graduating first in his class, and then attended the Massachusetts Institute of Technology from 1869 to 1871. While there he fell ill with pleurisy and was compelled to give up his work; since then he suffered constantly with a lung disturbance. In 1871 Dr. Haines entered the Chicago Medical College, from which he graduated in 1873. Even before his graduation he showed great promise in his chosen field, and was offered the chair of chemistry in his Alma Mater while still a student, holding the position from 1872 to 1876. During this period, having completed his medical education, he served an interneship in Mercy Hospital and spent several months in Europe in study. In 1876 he was called to the chair of chemistry in Rush Medical College, where he taught for forty-six years. This made fifty years of teaching in medical colleges. It was his great ambition to round out fifty years of teaching at Rush Medical College.

Twenty years ago, when Rush Medical College became affiliated with the University of Chicago, the entrance requirements of medical students were raised to include general chemistry. From that time on Dr. Haines was director of materia medica and toxicology and devoted all his time to the teaching of these subjects. Dr. Haines was known nationally by the medical profession as a chemist and toxicologist. He was the expert witness for the state in many of the famous murder cases where poison was the instrument of death. As a witness he was admired and respected by court and counsel wherever he was heard.

Last summer the alumni of Rush Medical College presented Dr. Haines with a gold watch in testimony of his fifty years of teaching. To further show the high esteem in which Dr. Haines was held, they started an endowment fund for the library at Rush Medical College, to be known as the "Walter S. Haines Fund." An oil painting of him hangs in the college where he taught. His whole life was spent in assisting others, which is exemplified in the following:

> It is for my students, however, that is reserved the warmest place in my heart and the largest measure of my thought. I have seen more than six thousand five hundred of them go forth to every state of this nation, to nearly every town of this land and in almost every country of the globe, to give comfort to the sick and to stay the hand of the fell destroyer—to teach, to investigate, and to make great discoveries. My one fondest hope is that perhaps I have done a little to prepare them for that work and that possibly I have helped them, even though slightly, in their splendid careers.

An able teacher, he kept in close contact with his students, showing a keen and sympathethic interest in all that concerned them. Both faculty and students have lost a valuable adviser and ardent friend. His politeness and refinement in speech and manner should be emulated by more of us. Each time one came in contact with him one carried away some useful information.

His influence for good over the student body was far-reaching. There is no one who can fill in the hearts of the students and alumni the place left vacant by "Daddy Haines," as he was familiarly known to thousands of alumni.

Dr. Haines was a member of the Committee of Revision of the United States Pharmacopeia from 1900 to 1920, has been professorial lecturer of toxicology, University of Chicago, since 1901, member of the Illinois State Food Commission since 1909, member of the American Medical Society, Chemical Society of London, American Medical Association, and Chicago Medical Society and American Chemical Society. He was the author of a "Text Book of Legal Medicine and Toxicology," chapters on alkaloidal poison in Hamilton's "System of Legal Medicine," 1894; reviser of Purdy's "Practical Urinalysis and Urinary Diagnosis," 1901.

Wm. D. McNally

NOTES AND CORRESPONDENCE

The Mechanism of the Corrosion of Iron

Editor of Industrial and Engineering Chemistry:

Iron implements have been used from prehistoric times, one of these found in a pyramid of Egypt being probably five thousand years old. Possibly, even as long ago as that people were interested in the corrosion of iron, although a study of the literature of the last twenty years would almost make one believe that the problem is a new one. Recently, hundreds of papers and several books have been written on this subject. Most of these papers are concerned either with the description of some personal experiences with corrosion or with work done in attempting to clear up the understanding of the mechanism of corrosion in the light of modern chemical theory. Perfect agreement with regard to any theory is hardly to be expected, and it is not surprising that there should be marked disagreement with respect to the theory of corrosion.

According to J. W. Mellor,[1] "Rusting is a complex process and workers are by no means agreed on the simple facts. Dry iron in dry air does not rust; moisture must be present before rusting can occur. Some deny and others affirm that the presence of an acid is necessary." It is interesting to note that Mellor then proceeds to outline the so-called "carbonic acid" theory, and refuses to say a word about the "electrolytic theory" beyond stating that "several other hypotheses have been suggested and the subject is still *sub judice*." Just as this prominent English author utterly ignores the large amount of literature that has been published, especially in the United States, in support of the electrolytic theory suggested by Whitney,[2] so in many recent articles it has been assumed here that this theory of Whitney has been adopted quite generally, and but little attention is paid to the conflicting testimony of some very capable English observers. Thus, in a recent article R. E. Wilson[3] writes, "There can be no real doubt but that the fundamental reaction in the corrosion of iron is essentially $Fe + 2H^+ \longrightarrow Fe^{++} + 2H$." Expressed in this form, the first stage of iron corrosion is the action of hydrogen ions upon the metal. This corresponds just as well to the carbonic acid theory of Moody as to the views of Whitney, Walker, Cushman, and others. These latter, however, have assumed that water itself furnishes enough hydrogen ions to start the process. Wilson's assumption that all chemists unite in agreeing that this is the fundamental reaction of iron corrosion is not quite true. Probably the only thing that has not been contradicted by different writers is that iron rust contains ferric oxide, so both iron and oxygen must have something to do with its formation.

Everybody knows that iron under certain conditions can decompose water with liberation of hydrogen. Walker and Cushman have undertaken to show that this decomposition takes place to an appreciable extent at room temperatures, but English observers have doubted whether all traces of carbon dioxide and dissolved oxygen were removed from the water. Walker and Cushman admitted that the water itself could not account for the formation of rust, because if iron does dissolve at room temperature in pure water there is not enough ferrous hydroxide formed to give a precipitate, and no hydrated ferric oxide is formed until the solution is brought into contact with air.

The rusting of iron is unquestionably an *oxidation* process. A study of rusting, therefore, suggests a study of the oxidation potentials involved. Few chemists appear to realize that the solution tension of a metal is merely another name for the tendency of the element to be oxidized. Just as we can measure the relative tendencies of the different metals to be oxidized, in the same way we can measure the relative readiness with which all reactions of oxidation or reduction take place, and a complete potential series will show, not only the relative activities of the metals and nonmetals, but also the tendencies of reactions such as the reduction of permanganate or dichromate and the oxidation of stannous, ferrous, or titanous iron.

When iron dissolves in an acid the reaction emphasized by Wilson undoubtedly takes place. Interpreted in terms of the modern theory, metallic iron is oxidized and hydrogen ions are reduced. Chemists are so used to thinking of hydrogen as a reducing agent that they hesitate to think of this reaction as expressing an *oxidation* of iron and a *reduction* of hydrogen ions, but this is exactly true. In the potential series, the oxidation of metallic iron to the ferrous condition when measured against a molal solution of ferrous ions is about 0.43 volt above the potential of hydrogen in a normal solution of hydrogen ions. Consequently, at room temperature metallic iron is oxidized, or dissolved, by any appreciable concentration of hydrogen ions. As to whether enough hydrogen ions are present in pure water to cause an appreciable oxidation of iron, is not worth arguing about. Everyone will agree that theoretically there is a slight reaction, and practice shows that at room temperature the action proceeds only to a slight extent just as the theory demands. In this respect we fully agree with the conclusions drawn by Wilson.

The oxidation of ferrous iron to the ferric condition is an entirely different matter. It is harder to oxidize ferrous iron than it is to dissolve copper. The oxidation potential of copper against a molal solution of cupric ions is about 0.34 volt below that of hydrogen, but that of ferrous iron to ferric iron is 0.75 volt below hydrogen or 1.28 volts below the oxidation potential of metallic iron. It requires a much stronger oxidizing agent, therefore, to oxidize ferrous ions, and at room temperature hydrogen ions and certainly water are incapable of exerting such an oxidizing effect. Such an oxidation can be accomplished by dissolved oxygen, as Cushman, Walker, and many others have shown.

The astonishing thing about this whole matter is the fact that few investigators have realized that if dissolved oxygen is capable of oxidizing ferrous ions it will be even more effective in oxidizing iron from the metallic to the ferrous condition. It is just as absurd to assume that the fundamental reaction in the corrosion of iron is always the oxidation of the metal by hydrogen ions as it is to assume that the electric current decomposes a solution of sodium chloride setting sodium free at the cathode, which then reacts with water to form sodium hydroxide. LeBlanc pointed out the absurdity of such an assumption about thirty years ago.

In the presence of dissolved oxygen it seems reasonable to express the stages in the oxidation or rusting of iron as follows:

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{++} + 4OH^- \quad (1)$$

$$4Fe^{++} + O_2 + 2H_2O \longrightarrow 4Fe^{+++} + 4OH^- \quad (2)$$

and then

$$2Fe^{+++} + 6OH^- \longrightarrow Fe_2O_3 + 3H_2O \quad (3)$$

It is clear that such an explanation of the corrosion of iron is just as plausible as that given by Wilson. It agrees with his observation that at concentrations of hydrogen ion corresponding

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[1] "Modern Inorganic Chemistry," **1919**, p. 486.

[2] *J. Am. Chem. Soc.*, **25** (1903), 394.

[3] This Journal, **15** (1923), 127.

to pH = 11 the reaction between iron and the hydrogen of water is extremely slow and that at higher acidities it becomes appreciable. It agrees perfectly well with the observations which he cites that were made at the laboratories of the National Tube Company, and it agrees with the observations of Walker[4] and others, that "the rate of corrosion is directly proportional to the oxygen content of natural waters." This explanation does away with all hypothetical deductions with regard to films of hydrogen, etc.

If the hydrogen-ion concentration becomes higher, eventually there will be so many more hydrogen ions available that the reaction $Fe + 2H^+ \longrightarrow Fe^{++} + H_2$ will take place, but this is no argument for assuming it to be the *fundamental* reaction of corrosion. Hydrogen ions may cause the first stage of corrosion, but only when the reduction potential of the hydrogen ions due to increased concentration becomes greater than that of dissolved oxygen.

This view nearly, if not quite, reconciles the differences between the interpretations of corrosion by American and English chemists.

WM. T. HALL

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
February 6, 1923

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Editor of Industrial and Engineering Chemistry:

The writer is in substantial agreement with the views of Professor Hall regarding the corrosion of iron, with the exception of the theory advanced in his closing paragraphs. Here he states:

> The astonishing thing about this whole matter is the fact that few investigators have realized that if dissolved oxygen is capable of oxidizing ferrous ions it *will* [italics are mine] be even more effective in oxidizing iron from the metallic to the ferrous condition.

It would be strange if no one had realized that this *might* be the mechanism of corrosion, but any electrochemist can testify that to reason from data on oxidation potentials that any given reaction *will* take place in a given manner is a distinctly dangerous proceeding. In this case many chemists have unquestionably considered the possibility of a direct reaction between dissolved oxygen and metallic iron, and promptly rejected it because it entirely failed to account for many of the *established facts* regarding the rate of corrosion of iron—for example, that:

1—While the rate of corrosion in natural waters is proportional to the total area of iron exposed, all the corrosion may be localized in a comparatively small area.

2—When corrosion is thus localized there is a net decrease in H^+ ions (or increase in OH^- ions) at points where the iron is not going into solution (but where hydrogen is being oxidized).

3—Corrosion is accelerated by contact with any less positive electrical conductor, and roughly in proportion to the area thereof within reasonable distance.

4—Iron in a solution *containing no oxygen* will corrode if connected in an electrolytic circuit with a metal, such as copper, in a solution which does contain oxygen.

5—Any localization of corrosion is accompanied by the flow of electricity through the conductors in the direction predicted by the electrolytic theory.

6—Corrosion practically stops in strongly alkaline solutions.

None of the foregoing facts seem to be explainable on the basis of the direct reaction between dissolved oxygen and iron postulated by Professor Hall, but they would all be predicted on the basis of the fundamental reactions emphasized by the writer:

$$Fe + 2H^+ \longrightarrow Fe^{++} + 2H \text{ (polarizing film)} \qquad (1)$$

$$2H + {}^1/_2O_2 \longrightarrow H_2O \qquad (2)$$

since the two parts of Reaction 1 ($Fe \longrightarrow Fe^{++}$ and $2H^+ \longrightarrow 2H$) can obviously take place at separate points if provision is made for the accompanying flow of electricity.

Furthermore, the deductions regarding the presence of polarizing films of hydrogen are far from being "hypothetical," as claimed, for their actual existence has been proved by a variety of methods.

Professor Hall cites the following statement of the writer (including the first part of the sentence from the original article) as evidence that he paid little attention to the testimony of some English observers who do not subscribe to the electrolytic theory:

> Regardless of the school of corrosion theory to which we may give our personal allegiance, there can be no real doubt but that the fundamental reaction in the corrosion of iron is essentially $Fe + 2H^+ \longrightarrow Fe^{++} + 2H$.

This inference appears inconsistent in view of Professor Hall's admission, in the second sentence following, that "This (reaction) corresponds just as well to the carbonic acid theory of Moody as to the views of Whitney, Walker, Cushman, and others." Within the scope of his journal article the writer could obviously not outline even a tithe of the voluminous literature on corrosion, but after a careful study of most of the recent work in both America and England he is more than willing to stand back of the foregoing statement regarding the fundamental reaction of corrosion.

ROBERT E. WILSON

CHICAGO, ILL.
March 7, 1923

"America First"

Editor of Industrial and Engineering Chemistry:

When I first read Dr. Noyes's article under the above caption I was so impressed with his attitude of scientific fraternity, which every right-thinking scientific man desires, that I failed to grasp his major premise that " 'America First' is so like 'Deutschland über Alles' that it is hard to distinguish the spirit of the two slogans." The increasing elements of unrest in Europe which give promise of renewed war led me to reread the article. Dr. Noyes ascribes the similarity of the two slogans to nationalistic and capitalistic tendencies. I admit that there is a large body of our chemists engaged in the coal-tar industries who are not particularly happy over the suggestion that Germany pay us for the upkeep of our army on the Rhine by sending us $350,000,000 worth of coal-tar dyes. My own impressions of "America First" are not those entertained by Dr. Noyes. I think it is not only the duty but the privilege of the citizens of every country to love their own country first. In the light of recent events I think there is a distinct feeling in this country, even among chemists, that Germany would not be second in our choice of nations. I, for one, would much prefer France or England as my second choice. I fear I shall have to reëducated, if not reborn, before I can have equal regard for the land of Washington, Lincoln, and Emerson, and the land of Bismarck, Emperor William II, and Nietzsche. If Dr. Noyes will read the memoirs of Bismarck and Moltke he will no longer believe that France is just as culpable as Germany in initiating the Great War. I cannot accede, moreover, to Dr. Noyes's idea that the "so-called reparations," now the base of the disturbance in the Ruhr, are intended to provide pensions in France. Anyone acquainted with the terrible devastation of the German occupation of France fully realizes that if France could receive the total amount of reparations awarded her by the Versailles treaty it would fall far short of the payment of the damage done.

There are other reasons which lead me to object to the equality of "America First" and "Deutschland über Alles." One of our national anthems at least is not based upon the idea of military

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[4] Walker, Cederholm, and Bent, *J. Am. Chem. Soc.*, **29** (1907), 1251.

supremacy. "My Country 'Tis of Thee" suggests no paeon of triumph over enemies; nor can I find in the history of our country that a noble woman engaged in deeds of mercy has been stood up against a wall and shot to death. I cannot find in the annals of my country that passenger ships, carrying no cargoes of munitions, but loaded with women and children, have been ruthlessly destroyed. I have not noticed thousands of my fellow-countrymen wearing medals commemorative of such an inhuman event. I have never seen any round robin signed by the scientific men and professors in our colleges commending such an action on the part of our Government. I have never known the United States to deliberately and contemptuously disregard its own sacred agreement not to violate the territory of a helpless neighbor. I have never read any account of the United States military authorities breaking up the homes of an occupied enemy territory, sending the able-bodied men to military prisons and deporting children to our own country, never again to see their parents.

There is a deep-spread impression among the unbiased economists and bankers of this country that Germany has deliberately made her currency worthless, as a basis for pleading the "baby act" to excuse her from repaying the damages assessed against her. If German science has deteriorated to the extent of the German political economy, there is no use shedding tears for our lack of fraternity. As I read my ancient history, especially that part of it written by Caesar, I learn that "Omnis Gallia" extended to the Rhine. The Rhine is, moreover, a natural barrier. Nature never intended that Gaul should be dismembered. Probably a lasting peace will not be restored in Europe until the plan of nature and the dream of Napoleon Bonaparte are again realized. By the time this millennium appears we will have forgotten the inhumanity of our scientific brothers beyond the Rhine and will be ready to admit them to complete fraternity.

HARVEY W. WILEY

WASHINGTON, D. C.
March 11, 1923

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Editor of Industrial and Engineering Chemistry:

With much that Dr. Wiley writes I am in hearty accord. He seems to have overlooked the statement in my article, that "*both* slogans are also used in the sense of a patriotic international rivalry with no thought of injury to others."

In saying that every European nation was responsible, in part, for the militarism which has cursed Europe for fifty years or more, I did not say *equally* responsible. I am inclined to agree that Germany was more responsible than others, especially in the policy following the Franco-Prussian war, but the roots of the difficulty go back to the Napoleonic wars and further.

If Dr. Wiley will read the treaty of Versailles again he will find there pensions for British and French soldiers. In the supplement to *Le Temps* for October, 1922, page 6, is given a summary of "reparations" due France which includes 15 billion francs already paid for pensions and an estimate of 47 billion francs to be paid from now till 1990.

I make no apology for German brutalities during the war nor for the violation of the neutrality of Belgium, and I agree with Dr. Wiley that ruthless German profiteers are partly responsible for the economic ruin which is coming over Germany, but I cannot agree that that is a sufficient reason why France should refuse to accept Secretary Hughes's plan of a commission of experts who should determine how much Germany can and should pay.

W. A. NOYES

URBANA, ILL.
March 12, 1923

Bricklayers and Chemists

Editor of Industrial and Engineering Chemistry:

In a recent number of THIS JOURNAL are advertisements for six chemists wanted and twenty chemists wanting positions.

In to-day's *Chicago News* are advertisements of 33 men wanting positions and 801 men wanted, or twenty-four times as many vacancies as men. Among these men wanted are eight laborers at $27 per week, sixteen bricklayers at $72 per week, and one chemist at $30 per week.

What has H. W. Jordan to say about this?

D. DAVIDSON

4309 ELLIS AVE.
CHICAGO, Ill.
March 5, 1923

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Editor of Industrial and Engineering Chemistry:

The advertisement described by Dr. Davidson confirms my frequent prediction that creative, research chemistry and engineering would slow down. Also the flattering "It is a chemists' war" brought a flood of young graduates who, added to the torrent of near and pseudo chemists trained during 1918 to read burets to 0.1 cc., have inflated the profession numerically and punctured it financially. The main processes of chemistry have become static and require only routine. The financial executives of many large plants have dropped their older chemists of twenty or thirty years' experience, under the excuse of economy, and have demoted the younger ones to routine plant-control analysis. Research is tolerated rather than sought. Promotion prospects suffer from low visibility, and ambitious, restless chemists shift to other positions at lower salary in the hope of better chances.

The colleges with swollen registration of three or four thousand turn out far more white-collar workers than industry can absorb. There is a glut in the brain-working professions.

In contrast, organized labor restricts apprentices and few employees attempt to train them. Building contractors say that in ten years there will be scarcely any masons or carpenters, because so few youths are undertaking those trades. Eighty per cent of the Brotherhood of Locomotive Engineers are reported to have sent children to college. Thousands of Greeks, Slavs, and similar foreigners of the labor type are bootlegging, shining shoes, delivering telegrams, carrying ice water, and doing other luxury work and boys' tasks.

Organized labor has about two hundred schools with twenty thousand ambitious young folks studying economics, civics, and oratory, preparatory to promoting the rights of labor. The duties are not so interesting. They are neglected options. Meanwhile, chemists and engineers remain in civic coma, except for the little group of forward-looking men who center in the Federated American Engineering Societies.

Another labor factor is the host of parasites who receive doles of coal, food, and rent from community chests and associated charities. This army, numbering about 15 per cent of our city populations, is recruited from those industrial workers who are incapacitated by preventable disease, bad housing, inherited physical inferiority, and coddled shiftlessness. They cost more than $500,000 a year in Syracuse. Science and sense applied to elimination of the causes of their troubles would cut that figure in half and add regiments to our working force.

Proper psychological tests would eliminate 10 to 25 per cent of freshmen before they get fresh, and steer them back to plow, trowel, and hammer, instead of letting them clutter up college. These worthy but misguided boys of C and −C grade would earn bigger wages and be better citizens in vocations that fit their capacity. They need education like that given at Tuskegee to prepare them for constructive, creative life.

Churches and Masonic lodges could do a work of sublime Christianity by helping able-bodied English mechanics and craftsmen to come over and settle in America. Two hundred dollars judiciously spent would bring a man here and establish him so that he could pay back the money or use it to bring over others. We have lost our immigration contacts with the northern people of our own blood. We should start the stream westward again and fill our quota with our sort of folks. Pastors and masters abroad would coöperate with us in selecting sturdy young men from the three million unemployed of England.

These are some of the reasons why bricklayers and chemists are at the ratio of 16 to 1 and $72 to $30 per week.

H. W. Jordan

133 Stolp Ave.
Syracuse, N. Y.
March 14, 1923

A Letter from Germany

Editor of Industrial and Engineering Chemistry:

Germany is still suffering from the lack of necessities of life, foods and raw materials, which a land as rich in these materials as America can hardly comprehend. Even the outlook for the future still is very gloomy, chiefly because the prices of the raw materials and the products made from them have already practically reached the world's market price. For several months Germany, which in former years exported chemicals all over the world, has had to import from other countries such important products as sulfuric acid and chromium salts. Considered purely superficially—that is, according to their dividends and business budgets—certain industries appear to be in excellent condition; but if these are changed to a gold basis, they amount, in most instances, to a very small percentage. For example, a big company recently distributed a dividend of half a gold mark. The only outlook for improvement offered to Germany is through eastern and southeastern Europe, to which the whole German economic life will have to turn gradually. In the meantime, German chemical industry is trying to continue in the same way in which it has made its greatest progress—namely, to carry on manufacturing processes in a scientific spirit. Recently, therefore, the interest of chemical research and science has turned to the textile industry.

The textile industry of Germany was, until lately, somewhat inferior to that of other countries, although in the field of dyes Germany was able to compete with other nations in the world's production. For about ten years there has been in existence the "Kaiser Wilhelm Gesellschaft zur Förderung der Wissenschaften," and by this was founded in December of last year the "Kaiser Wilhelm Institut für Gaserstoffchemie," which will make a thorough study of the structure of textile fibers and from this draw conclusions regarding the handling of such fibers. Glycylalanine anhydride, which has been found in proteins, seems to be an important constituent of silk. Several methods have also been worked out which make possible a factory control in the textile industry; up to this time it was thought that this problem could not be solved.

Germany is a poor country in raw materials. This was shown especially during the war, when efforts were made to obtain sulfur and sulfuric acid from gypsum and other sulfates. In this connection the sulfur patents of the Badische Anilin und Soda Fabrik and of other firms may be mentioned, in which, for example, barium sulfate is mixed with coal and heated in the electric furnace; the primarily formed barium sulfide, reacting with the excess of barium sulfate, forms sulfur dioxide. Recently F. Martin and O. Fuchs made the very important observation that if iron, instead of coal, is used as a reducing agent, the alkali-earth sulfates can be readily reduced to the sulfides with the formation of sulfuric acid. The highest yields are obtained from calcium sulfate using the mixture $CaSO_4 + 16/15$ Fe, giving theoretically 80 per cent sulfur dioxide, and from strontium sulfate using the mixture $SrSO_4 + 8/9$ Fe, giving theoretically 88.9 per cent of sulfur dioxide. In practice pyrites is used for the reduction of gypsum. Besides the production of sulfur dioxide the formation of small amounts of sulfur was observed, and without doubt the development of this process will be important for the industry.

A certain sensation was created in chemical and medical circles by the new preparation, "Bayer 205," which forms a new class of trypanosome medicines. It does not contain mercury, arsenic, antimony, or other ordinary therapeutic agents, but belongs to a new class of highly complicated, organic synthetic compounds. After the medicine was tested with good results in the laboratories of the dye factories formerly belonging to Friedrich Bayer & Company in Leverkusen, the English government permitted a German expedition under Professor Kleine to test the medicine in Rhodesia on monkeys, other animals, and men. According to the experimental data published a short time ago, the medicine has proved a success in sleeping sickness and nagana, and this has been confirmed recently by the English physicians.

The endeavors in the medico-chemical field to combat cancer are also worth mentioning. Research has been turned to the study of selenium compounds and has been carried out especially by Professor Wassermann. Bismuth compounds also have been applied by Wassermann and his collaborators to combat syphilis.

Walter Roth

Göthen, Germany
February 1, 1923

The Rapid Determination of Potash in Acid-Insoluble Silicates—Addendum

Editor of Industrial and Engineering Chemistry:

In a recent article in This Journal, **15** (1923), 163, under the above title, I failed to make any reference to a publication in This Journal, **13** (1921), 225, by Prof. Jerome J. Morgan, entitled "A New Method for the Determination of Potassium in Silicates," in which he also used perchloric acid as a substitute for sulfuric acid in silicate analysis.

My work was completed and published in ignorance of Professor Morgan's article. He has called my attention to it in a private communication, however, and was evidently the first to decide on perchloric acid as a substitute for sulfuric acid in the determination of potash in silicates.

Manuel M. Green

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Mass.
February 26, 1923

A New Bottle for Carbon Dioxide and Moisture—Correction

In the article under the title above [This Journal, **15** (1923), 266], in the second table, under date of December 14, the figure for grams of carbon dioxide should read 0.4357.

William E. Morgan

Columbia University
New York, N. Y.
March 8, 1923

WASHINGTON NOTES

TREASURY DEPARTMENT PROMULGATES DYE RULES

Regulations for the administration of Paragraphs 27 and 28 of the new Tariff Act, relative to dyes and chemicals, were officially issued by the Treasury Department on March 2 in the form of a treasury decision. Practically every section of the tentative regulations, issued two weeks previous, was rewritten. Some of the changes are in phraseology only, but others are important.

TEXT OF OFFICIAL REGULATIONS

Regulation 1—Taking samples prior to entry. An importer may be permitted under proper supervision to take samples from his own importations prior to entry of articles dutiable under Paragraphs 27 and 28, and appraising officers may take samples of such articles prior to entry when deemed necessary by them.

Regulation 2—Information required prior to entry. When an importer seeks information from the appraising officer prior to entry or for the importer's convenience, formal entry is withheld as hereinafter provided; in return therefor the importer shall furnish to the appraising officer such relevant information as he may request

Regulation 3—Determination of similar competitive articles. (*a*) A domestic article shall be considered a similar competitive article if, in the use or uses which require a major portion of the total consumption in the United States of the imported and the domestic article, the imported article accomplishes results substantially equal to those accomplished by the domestic article when used in substantially the same manner.

(*b*) An imported article which is or may be used for the same purpose as a domestic article not freely offered for sale but used in the manufacture of another domestic article freely offered for sale, shall be considered a similar competitive article.

Regulation 4—Lists of competitive and noncompetitive articles. (*a*) The appraiser at New York shall issue at once lists of articles which he believes to be competitive and noncompetitive, and shall from time to time add articles thereto or remove articles therefrom as investigation shall justify. Such lists shall be advisory only, and at the top of each list shall appear the following statement:

> This list is advisory only and in no manner relieves appraising officers from the duty of independent appraisement required by law.

The appraiser shall furnish copies of such lists and amendments thereof to the Customs Information Exchange for circularization to other appraising officers and to the public upon request.

(*b*) In the case of an actual importation of a similar competitive article, the appraising officer may furnish to the importer upon application in writing information of the American selling price, provided the appraising officer shall be satisfied that the importer after exercising due diligence has not himself been able to obtain such information and that he has submitted to the appraising officer all relevant information in his possession. All information furnished by the appraising officer shall be advisory only. In communicating such American selling price, however, the appraising officer shall not disclose the source of his information.

(*c*) In the case of noncompetitive articles, appraising officers shall not advise importers prior to entry concerning values.

Regulation 5—Entry of articles on neither the competitive nor the noncompetitive list. The appraiser at New York, upon application of an importer having an invoice of an article not named on either the competitive or the noncompetitive list, shall proceed immediately to ascertain to which list the article belongs, and upon such ascertainment shall add the article to such list, pending which the importer may withhold formal entry. The appraiser shall inform the importer of his action.

Regulation 6—Difference in strength of imported and domestic articles. When an imported article is of different strength from a similar competitive article manufactured or produced in the United States, the value of the imported article shall be adjusted in relation to the selling price of the domestic article in the proportion which the strength of the imported article bears to that of the domestic.

Regulation 7—Determination of American selling price of articles not freely offered for sale, but used in the manufacture of other articles. When an article is a similar competitive article, as defined in Regulation 3 (*b*), the value of the imported article shall be the American selling price of the domestic article freely offered for sale adjusted in the relation that it bears to the domestic article not freely offered for sale.

Regulation 8—Ascertainment of American selling price when an article is offered for sale at arbitrary prices. When the appraising officer shall be satisfied, after investigation, that a similar competitive domestic article is offered for sale at an arbitrary and unreasonable price not intended to secure bona fide sales and which does not secure bona fide sales, such price shall not be considered as the American selling price, and such office shall use all reasonable ways and means to ascertain the price that the manufacturer, producer, or owner would have received, within the meaning of Section 402 (*f*) of the Tariff Act of 1922.

Regulation 9—Where there are two or more similar competitive domestic articles. Where two or more domestic articles are considered similar competitive articles as compared with an imported article, the American selling price of the domestic article which accomplishes results most nearly equal to those of the imported article shall be taken as the basis for the assessment of the ad valorem rate.

Regulation 10—Articles which are not coal-tar products. The words "similar competitive articles" in Paragraphs 27 and 28 shall not be construed as relating exclusively to coal-tar products. An imported coal-tar product may be compared with a domestic noncoal-tar product, or an imported noncoal-tar product dutiable under Paragraphs 27 or 28 with a domestic coal-tar product, for the purpose of determining whether they are similar competitive articles. The rule provided in Paragraphs 27 and 28 for the determination of similar competitive articles and the regulations herein provided shall be applied in such cases.

Regulation 11—Ascertainment of United States value. The following instructions for the ascertainment of United States value are reproduced from Treasury Decision No. 39,297 of October 31, 1922:

Appraising officers instructed how to ascertain "the United States value of imported merchandise" as defined in Title IV, Section 402, Subdivision (*d*) of the Tariff Act of 1922.

Treasury Department
October 31, 1922

To Appraising Officers:

Attention is invited to the definition in Title IV, Section 402, Subdivision (*d*), Tariff Act of 1922, of the term "the United States value of imported merchandise."

Certain questions having arisen in connection with the application of this definition to imports classifiable under Paragraphs 27 and 28 of Title I of the Act, the department offers the following concrete example as best illustrating its views on the procedure and computations necessary in arriving at the United States value of such merchandise:

Assume that certain dyes classifiable under Paragraph 28 were exported from Germany on September 15, 1922, and imported at New York on October 1, 1922; and that the "such or similar imported merchandise" which Subdivision (*d*), Section 402, Title IV, contemplates shall be taken as the standard of comparison, was selling at New York on September 15, 1922, in the usual wholesale quantities, etc., at $1.45 per pound. This price includes the various items for which Subdivision (*d*) provides that allowance shall be made. Assume a maximum allowance of 8 per cent for profit; dividing $1.45 by 1.08 gives $1.34 and subtracting this from $1.45 leaves 11 cents as the amount of the profit included in the $1.45. Assume a maximum allowance of 8 per cent for general expenses; dividing $1.34 by 1.08 gives $1.24 and subtracting this from $1.34 leaves 10 cents as the amount of the general expenses, included in the $1.45. Assume that the cost of transportation, insurance, and other necessary expenses from the place of shipment in Germany to New York was 3 cents, and deducting this from $1.24 leaves $1.21, which includes the dutiable value and the duty. Assume that such merchandise was an article which on September 15 was dutiable under Section 500 of the Act of September 8, 1916, at 30 per cent ad valorem. Dividing $1.21 by 1.30 gives 93 cents as the value upon which duty was assessed, and which is the United States value of the merchandise imported on October 1, and subject to the 60 per cent ad valorem rate provided for in the proviso of Paragraph 28. When the article is subject to both a specific and ad valorem rate, the specific duty will be deducted before making the division.

The amount to be deducted as duty in each case will be governed by the amount of duty actually paid on the article used as the basis for computation.

The foregoing applies to purchased goods. In the case of consigned goods the appraiser will ascertain the amount of commission paid or contracted to be paid and allow not to exceed 6 per cent of the gross selling price, in lieu of the 8 per cent profit and 8 per cent general expense. The transportation costs and duty will be ascertained in the same manner as on purchased goods.

Appraising officers will ascertain in the usual way through the special agency service or otherwise, as provided by law and regulations, the facts necessary to be used in such computations.

EDWARD CLIFFORD,
Assistant Secretary

Regulation 12—Tests. Tests which are necessary in the appraisement of imported articles shall be made under conditions approximating as closely as practicable the conditions in which the articles will be actually used in trade or manufacture.

Regulation 13—Trade papers as sources of information. Appraising officers may consult the trade papers, but the weight to be given to the quotations and other information therein is for the determination of the officers themselves.

Regulation 14—Obtaining information on doubtful questions. Appraising officers at ports other than New York, when in doubt on any question arising under Paragraphs 27 and 28, shall take the question up direct with the appraiser at New York, who shall give his advice as promptly as possible. If the appraising officer shall be dissatisfied with the advice of the appraiser at New York, or the latter shall be in doubt on the inquiry, the question shall be submitted to the Department for an expression of its views.

COMMITTEE TO PLAN WORK FOR COLOR LABORATORY

A committee of dye chemists has been appointed by the Secretary of Agriculture to formulate plans of work for the Color Laboratory.

The committee consists of R. Norris Shreve, secretary of the Dye Division of the American Chemical Society; Willard H. Watkins, of the National Aniline & Chemical Co., Buffalo, N. Y.; Louis A. Olney, of Massachusetts, president of the American Association of Textile Chemists and Colorists; William J. Hale, of Michigan, chairman of the Dye Division of the American Chemical Society; and Clarence G. Derick, of Buffalo, N. Y.

The Bureau of Chemistry has for some time felt the need of a more intimate knowledge of those problems of a fundamental nature which are of interest to the dye industry. Innumerable questions of an interesting scientific character come to this laboratory for solution, and it is hoped that by bringing dye chemists from different sections of the country into frequent consultation with representatives of the Bureau of Chemistry only those problems will be attacked which are for the promotion of the dye industry as a whole, rather than those which will be of consequence to the individual or a few firms.

NEW HELIUM PLANT

As a further development of the Bureau of Mines' work on helium, that bureau has been requested by the Navy Department to design and construct at Lakehurst flying field a plant which will be used for the repurification of helium after it has become contaminated when used in lighter-than-air craft. The plant is to have a capacity of 10,000 cu. ft. of impure helium per hour. There are two general methods of repurifying the helium—one being liquefaction of the impurities, consisting of oxygen and nitrogen, under high pressure and at low temperatures; and the other being absorption of the impurities by activated charcoal at low temperatures. In the Lakehurst plant use will be made of a combination of these two processes. The first step of the process will be that using the liquefaction scheme whereby the helium will be raised in purity from 85 to 94 per cent. This 94 per cent helium will then be passed through the charcoal units, which will take out the remaining impurities, giving 100 per cent helium. It is expected that the plant will be completed in the fall of 1923.

NAVY TO FILL DIRIGIBLE WITH HELIUM

Helium will be used for the inflation of the Navy's first rigid dirigible ZR-1, which is being built at Lakehurst, N. J. This dirigible will require 2,000,000 cubic feet of the gas and will draw heavily upon the supply available. Nevertheless, the Navy Department has directed that helium be used regardless of cost, in order to reduce the explosive risk to a minimum.

The recent Navy Appropriation Act increased the amount allowed for the production of helium, permitting the continuous operation of the plant at Fort Worth.

REPORT ON COÖPERATIVE SCIENTIFIC WORK

In view of the growing interest in coöperation as a means of advancing scientific work for the public benefit, the National Research Council in 1921 appointed a committee to study the nature and extent of coöperative scientific work carried on by the Federal Government and outside agencies, as well as the principles which should guide in such work. This committee consisted of E. W. Allen, chief, Office of Experiment Stations, United States Department of Agriculture, *chairman;* Edwin F. Gay, president, New York Evening Post, Inc.; M. W. Glover, Bureau of Chemistry, United States Department of Agriculture; N. C. Grover, Geological Survey, United States Department of the Interior; Vernon Kellogg, permanent secretary, National Research Council; and E. B. Mathews, state geologist for Maryland and professor of geology, Johns Hopkins University.

The committee's report shows a great diversity as to types of work, agencies coöperating, nature of the coöperation, terms of agreement, and extent of participation of the parties to it. The inquiry revealed 553 separate coöperative projects, involving more than 1100 coöperative undertakings. Of the 553 separate projects, 360 fall under the head of research, the acquisition of new knowledge by the method of systematic scientific investigation; others deal with routine testing and technical service, gathering of statistics, enforcement of regulatory laws or measures, and the like.

The federal agencies engaged in the coöperative work included about 23 bureaus and independent establishments of the Government, and the outside coöperating agencies included various branches of the state governments, municipalities, chambers of commerce, state and endowed universities, agricultural colleges and experiment stations, botanical gardens and similar institutions, as well as associations and societies of various kinds and numerous industrial concerns and private individuals.

MUSEUM FOR ENGINEERS

The joint committee appointed by the American Society of Mechanical Engineers has decided to accept the offer of the Smithsonian Institution to establish at Washington, D. C., a central historical museum of engineering with local branches in other sections.

The museum will be a storehouse for records of American engineering achievements, and will afford opportunities for research and investigation. The plan has the approval of the Federated American Engineering Societies, from which body the joint committee was selected by the American Society of Mechanical Engineers.

The Smithsonian Institution, in offering to act as custodian of collections, urged that the movement be broadened from an engineering-society standpoint to that of a national museum. This idea was acceptable to the engineers and the museum will be founded on the broadest possible basis.

CORROSION INVESTIGATIONS COÖRDINATED

To avoid any duplication of work, a coöperative arrangement has been completed between the Bureau of Mines and the Bureau of Standards for handling corrosion investigations. The work is confined mainly to the corrosion problem as it affects metals and alloys exposed to mine waters.

Despite the fact that corrosion has been one of the most active deteriorating agents throughout the entire history of the use of metals, the factors underlying the phenomena of corrosion are little understood. Considerable progress already has been made, particularly in devising methods whereby corrosion can be brought about quickly in the laboratory to an extent which would require years of exposure under ordinary conditions.

SALARIES OF SCIENTIFIC EMPLOYEES

In the 1924 Appropriation Act of the Department of Agriculture the maximum salary provision affecting scientific employees of the Department is continued for the fiscal year 1924, so amended as to increase from eight to twelve the number of persons who may be paid salaries in excess of $5000 and up to $5500, and from three to five the number who may receive in excess of $5500 up to the limit of $6500.

NAVAL STORES STANDARDS

In the closing hours of Congress, a bill to establish standard grades of naval stores was passed. This bill is a substitute for previous measures which have been pending before the Senate Committee on Agriculture and Forestry, but embodies the essential points agreed upon between the Department of Agriculture and a committee representing producers and large consumers of naval stores.

TARIFF COMMISSION ORDERS INVESTIGATIONS

The Tariff Commission has ordered investigations on a number of articles affected by the Tariff Act of 1922, concerning which applications have been made. These investigations will be conducted under the provisions of Section 315 of Title III of the Act, and are designed to aid the President in exercising the power given him to modify any particular existing rate of duty where the findings with respect to the differences between foreign and domestic costs of production warrant it. In each case the authority of the President is predicated upon the finding, after an investigation by the United States Tariff Commission, that the rate of duty upon a particular article as fixed by the law does not equalize the cost of production of competing articles produced in the United States and in foreign countries. The purpose of the Tariff Commission in the investigations now ordered will be to determine whether any such difference exists in the case of the articles in question and, if so, precisely what it is.

Some of the investigations ordered are based upon applications for increases, and others upon applications for decreases in the present rates of duty. But a finding either way can be made upon any application, as the facts developed may warrant.

Under the Commission's rules of procedure formal notice of investigation into each article will be published, and opportunity afforded to all persons interested to appear, present evidence, and be heard in person or by a representative. Applications relative to other articles are still pending before the Commission and will be acted upon in due order.

The articles upon which investigations of interest to our readers have been ordered are: oxalic acid (Para. 1); diethyl barbituric acid and derivatives thereof (Para. 5); barium dioxide (Para. 12); casein (Para. 19); logwood extract (Para. 39); potassium chlorate (Para. 80); sodium nitrite (Para. 83).

January 19, 1923

LONDON LETTER

By Hugh Griffiths, 15 New Bridge Street, London, E. C. 4., England

The Institute of Chemical Engineers

After a considerable period of delay which has been spent in overcoming difficulties, the Institute of Chemical Engineers has now been established, and a number of members and associate members have been elected. This institute has been modeled substantially along the lines of the American Institute of Chemical Engineers, and at present admission to membership is controlled by a selection committee. It is believed, however, that at a later date the institute will endeavor to set up a definite standard of professional qualification, and the candidates will have to be prepared to pass an examination.

In England the profession of chemical engineer is comparatively new, and, while the institute is very favorably received, the difficulties leading up to its formation have been created on the one hand by engineers, and on the other hand by chemists. This has been due to the circumstance that a very considerable number of individuals have described themselves as chemical engineers who were neither chemists, engineers, nor chemical engineers, but it is now fully realized that with the formation of the institute the profession of the chemical engineer has received a definite status.

Patent Law

The peculiarities of the patent law in this country and its bearings upon chemical processes were recently discussed in a paper by E. F. Erhardt at a meeting of the Society of Chemical Industry in Manchester. This subject is certainly not sufficiently understood by chemists, and it was pointed out by Dr. Erhardt that there has been considerable confusion as to whether a chemical patent could cover a product so far as to preclude the use of any new method of manufacture. Various leading cases were discussed, and it was shown that at present a patent could only satisfactorily protect a process as distinct from a product.

Dr. Erhardt, whose experience and knowledge of patent law are of the very highest order, considered that this position, which was based upon a decision given in the case of Heath *vs.* Unwin, was bad; and he pointed out that as the processes involved in the production of azo dyestuffs—namely, the formation of a diazonium compound and coupling—are not "special" operations, it might be held that no patent claim for a new azo dyestuff could be sound. Dr. Levinstein, on the other hand, stated that any alteration in the law would result in a decided unfairness, and gave as an example a hypothetical case. If, after the first synthesis of indigo, a patent had been obtained, and this sufficed to cover the product as distinct from the process, the first inventor would have been able to prevent the production of indigo by any other process, no matter how superior to that originally discovered.

It is rather difficult to find a satisfactory basis or criterion on which claims should be based, but if it is remembered that patent law is based essentially on public interest and advantage, it may perhaps be possible to find some satisfactory middle course between the above-mentioned extremes.

Jet Apparatus

It is rather interesting to notice that, while the old-fashioned steam-jet pump has long since disappeared from regular use in the chemical works, there is a significant increase in the application of more modern devices working on the same principle but constructed more carefully.

For the purpose of moving corrosive gases, this principle has again been revived. During the war it was found to be difficult to secure an adequate supply of stoneware fans for drafting nitric acid absorption towers, and ejectors operated by air from an ordinary cupola fan were employed. By using a stoneware ejector system similar in shape and design to an Evasé stack, it was found to be a simple matter to produce a suction of 6 or 8 in., water gage, on the towers, and at the same time avoid all troubles attendant on the use of stoneware fans. Evidently, this system has come to stay, and, in spite of the somewhat higher power consumption, the cost of running is probably not much greater than in the direct system.

The Evasé stack method of producing induced draft on boiler plants has been installed in a number of works in England, and is evidently becoming more popular.

The substitution of multijet condensers for vacuum pumps is also becoming more general, and a number of different types, both with and without intercondensers, are now being regularly used. It is to be realized, however, that these devices consume a large proportion of steam, and unless the exhaust can be used for feed-water heating the system is not attractive.

A suggestion has been made to use such devices on vacuum drying plants, but this is hardly a suitable application, since the whole of the air exhausted has to be passed through the heating spaces, and causes diminution in heat transmission; furthermore, the cost of operation under such conditions would be unquestionably higher than the ordinary vacuum pump.

Stainless Steel

A very interesting treatise has been published by the firm of Thomas Firth & Sons, of Sheffield, giving in collected form the results of investigations on the resistance to corrosion of stainless steel. A large number of different corrosive agents have been tried in contact with this steel, and the results are extremely interesting.

A further paper by W. H. Hatfield, director of the research laboratories of this firm, has been published, giving the results of comparative tests of twenty-one metals and alloys in contact with various materials. This paper contains information of great value to the chemical worker.

While the search for ideal constructional materials continues, it is interesting to note that in Germany some wonderful things are now being made of stoneware. It is now possible to purchase vacuum evaporators constructed entirely in stoneware, and these can be used for evaporating solutions of the most troublesome character—for example, those containing hydrochloric acid and ferric chloride. Ebonite is also rapidly gaining ground in this country, whereas the so-called "acid-resisting" irons are being used less and less. There is, however, considerable prospect that stainless steel will occupy a very favorable place in chemical-engineering work, but most of us are still anxious to learn more about this material, so as to be in a position to judge whether its high first cost will be justifiable and whether it will be possible to construct easily in this material.

Tar Distillation

While a number of different types of plants specially designed for the distillation of tar are available, continuous systems are not extensively adopted in England, apart from plants of medium and small size constructed according to the Hird system.

While in Germany the Raschig system, in which the distillation is effected in a series of vessels at different pressures, has been adopted to some extent, in this country most firms are using the ordinary intermittent system with vertical stills, and employing tar preheaters.

During recent years, however, a number of firms have introduced into this type of plant a very simple modification, which consists in coupling up four or five stills so that the tar may be passed continuously through the series. This simple modification gives very satisfactory results, and has a higher thermal efficiency than the intermittent system. It has the advantage that no special vessels or elaborate equipment are necessary, and the firms employing this method claim to secure not only economies in fuel, but also better control over the distilled fractions than in some of the plants which are much more elaborate.

February 10, 1923

Meeting of American Leather Chemists' Association

The 20th Annual Convention of the American Leather Chemists' Association is to be held at White Sulphur Springs, W. Va., June 7 to 9, 1923.

White Sulphur Springs is an ideal vacation spot, and the manager of The Greenbrier, the convention headquarters, has kindly extended the special rates for one week, beginning June 7, so that all those who wish to can remain and get the full benefit of the change. All who are even remotely interested in leather are cordially invited to be present and help make this meeting the biggest success that this society has ever had. All inquiries will be gladly answered by the secretary, H. C. Reed, 22 East 16th St., New York, N. Y.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Potash Competition

The rivalry in the world market between French and German potash is still acute. Our exports of potash, which in 1921 were 163,800 tons, were about 346,500 tons in 1922. During the same period the German industry produced 1,300,000 tons, a figure which has never been equaled before. The world consumption of potash is estimated at 1,500,000 tons, of which Germany can furnish about two-thirds.

The French agriculturists fear that the struggle for the world market will work to their detriment. In fact, Alsace is being criticized, especially in the United States, for entering into competition with German potash. The low price, agreed on because of the low value of the mark, should have been compensated by a rise in price in our domestic market.

Alcohol as a Fuel

The various reports and meetings on the use of alcohol as a fuel have resulted in the presentation of a project to the Chamber of Deputies, following a meeting composed of parliamentarians, manufacturers, and chemists. This project would compel all importers of oil (gasoline or other motor fuels) to incorporate in the oil, upon arrival in French ports, a certain amount of alcohol. The project has been approved by the Commission of Mines of the Chamber, by M. Mallet for the Petroleum Syndicate, and by M. Patard, inspector-general of explosives, who has described the experiments carried out with the national fuel. M. Berthelot, chairman of the scientific committee of "l'Carburant national," has likewise pointed out the technical results obtained in the different laboratories of the committee, and the finally accepted formula proposes a 40 to 50 per cent content of alcohol in the oil.

This bill, however attractive it is, will be vigorously discussed. The present political situation is causing us to pass through an economic crisis, and the French public points out that we are obliged to import sugar for our consumption for which we are subject to the fluctuations of exchange, and that the agricultural distilleries that make alcohol from beets would be more profitably employed in manufacturing the sugar which we are compelled to import. This is true, so that the French government has recently put an exemption on sugar, molasses, and glucose used by these industries.

I have previously described some of the results obtained by the dehydration of alcohol. New researches, concerned not only with alcohol, but with the carburetor, have resulted in establishing a type of carburetor which will distil a mixture of gasoline and alcohol, even if the mixture contains water. The alcohol and gasoline are not mixed in the container, but go through two separate tubes to the carburetor where the two liquids are volatilized at the same time and are also mixed in the proper proportion. At the same time as this volatilization takes place the high temperature decomposes the water of the alcohol into oxygen and hydrogen.

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National Fuel

The Chamber has adopted the project placing on all importers of combustible liquids (oil, benzene, benzine, toluene, lignite, etc.) whether pure or mixed, the obligation, before obtaining their importers' license, to obtain each month a quantity of alcohol (measured in absolute alcohol) corresponding to 10 per cent by volume of the quantity of oil imported the preceding month. However, when these products are to be used for the manufacture of dyestuffs and chemicals, importers will be exempt from the obligation of buying the alcohol. The alcohol is to be sold by the French government, at a price to be fixed by ministerial decree.

The technical committee of "l'Carburant national" has, moreover, estimated that this quantity of 10 per cent of alcohol was a minimum, and M. Berthelot, chairman of the committee, stated that he preferred a mixture of oil and alcohol containing 40 to 50 per cent alcohol. This mixture should be of uniform formula throughout France. Such a formula, according to M. Berthelot, would protect France from the fluctuations which we have recently seen of the price of oil, which are necessarily functions of the variations of the rate of exchange.

This point of view has already been strongly opposed. In absolute value, alcohol costs more than the oil and has a lower calorific value, and nevertheless the oil is encumbered in France with large customs and transportation taxes.

When one considers using alcohol as a fuel, he encounters economic difficulties, especially in the South (overproduction and dullness of sale of wine). A more general use of alcohol would absorb this excess, and even necessitate the production of additional quantities of alcohol, which would make an increased demand for the beet, and this is the cause, the criticism made of the fuel project.

In 1921 we imported oil valued at more than 350,000,000 francs. If we were to decrease this importation by the use of alcohol with it, it would necessitate the production of alcohol from the beet, and consequently lessen our production of sugar. Last year we produced 270,000 tons of sugar, and we consumed 670,000 tons. The difference, 400,000 tons, had to be imported.

Evidently, attempts will be made to extend the culture of the beet, but they will only be successful by limiting the production of cereals, especially wheat, for which we still depend upon imports. It seems, then, that on the whole the problem cannot be solved to our advantage. The government, which has a monopoly on the sale of alcohol, pays industry 150 francs per hectoliter for it, and sells it at an average of 120 francs—a net loss of 30 francs per hectoliter. This loss may even reach a higher amount, and it is calculated that, per hectare of beet converted into alcohol, the loss would reach 1890 francs—that is, a loss higher than the value of the wheat harvest per hectare which is about 1600 francs.

These arguments will be placed before the Senate when the project comes up and may prevent it from being passed. It will then be necessary to hunt for another solution of the national fuel problem—in wood alcohol, distillation of lignites and peat, etc.

M. Kling, along the same line, has recently explained to the Society of Industrial Chemistry the actual status of the lignite problem and of its transformation into combustible liquids. Lignite does not come from the cellulose, for the furfuran nucleus is not found there. MM. Kling and Florentin have modified the genealogical tree of lignite established by Fischer. Cellulose is extremely resistant, and only bacteria in the presence of oxygen are able to dissociate it; it is found absolutley intact in the charcoal, which preserves it from the action of air and bacteria.

The large number of more or less hydrocarbonaceous constituents of the oil permits a large number of products to be derived from it. It is known that pulverized lignite, in alkaline suspension, can be treated with oxygen or ozone at temperatures varying between 120° and 200° C., under a pressure of 50 kg. Fifty per cent of the lignite is thus dissolved, and in this soluble product are found the aromatic acids—benzoic, phthalic, etc. These substances could be thus prepared directly by decomposition of the lignite, which would greatly simplify the dye industry. On the other hand, it is known that hydrogenation at a temperature of 430° C., under a pressure of 230 atmospheres, permits the transformation of the lignite (less the ashes) in a mixture of oil, taking 30 per cent of light oils for automobile motors, 30 per cent of oil for Diesel motors, 30 per cent of heavy oil (mazout, tar), and finally, 10 per cent gaseous hydrocarbons. Tests on these methods are now under way in France.

"Hafnium" Not a New Element

Two Danish chemists, MM. Coster and Hevesy, thought that they had discovered a new element, with atomic weight 72, to which they gave the name of *hafnium*.

M. Urbain has just shown that this element has already been described by him in 1911, under the name of *celtium*. MM. Coster and Hevesy have only found an abundant source of this celtium in the minerals of zirconium, and have not discovered a new element.

March 2, 1923

BOOK REVIEWS

The Petroleum and Allied Industries. By JAMES KEWLEY. 302 pp. D. Van Nostrand Co., New York, 1922. Price, $3.50.

In the preface the author states:

> This great industry employs a multitude of men, a large proportion of whom are necessarily engaged in nontechnical work. Among these men there exists a very commendable desire to know something of the great industry with which they are associated, a desire which is shared by many others whose connection with the industry is indirect. This book has been written in the hope that it will appeal to such, and to many university graduates to whom a knowledge of the outlines of an industry may be of assistance in determining their choice of a career.

The author has carried out his intentions in a very acceptable manner.

The book covers not only the petroleum industry itself, but has chapters on the related industries of natural gas and crude oils produced by the distillation of shales, coals, etc.

While the book is obviously not intended as a reference book for the technical man, it is written in technical style and is remarkably accurate and up to date in its statements.

It is recommended to those who, without wishing to go into technical details, would obtain an accurate general survey of the petroleum industry.

RAYMOND F. BACON

Die Fabrikation von Leim und Gelatine. By LUDWIG THIELE. 2nd edition. 189 pp. Verlagsbuchhandlung Max Jänecke, Leipzig, 1922. Price, 80 cents.

After discussing the constitution and properties of glue and gelatin, and the various raw materials, the author devotes a chapter each to the manufacture of bone glue, hide glue, and gelatin. Then follow chapters on fish glue and isinglass, commercial grades of glue and gelatin, and glue testing. The ninth and last chapter includes the plan of a glue factory, an abstract of patents, chemical and physical tables, and an index.

The book is a big improvement over the first edition, published in 1907 before the author's coming to this country, and it reflects to some extent the great progress that has been made in the glue and gelatin industry since then. Especial attention has been given to some recent American work on testing glue, and to some new types of manufacturing apparatus. In common with many other technical books, complete descriptions are given of processes patented but not operated, and elaborate details are recorded of the working of values, etc., in well-known types of apparatus. Since continual modifications and improvements are being made in evaporators, extractors, etc., any intending user must go to the manufacturers for the latest types, book descriptions being often obsolete.

Although the technical aspect is treated at length, the theoretical part of the book is weak. Thus, there is no adequate discussion of colloidal phenomena, hydrogen-ion concentration, etc. The author's method for valuing gelatin, is as follows: Gelatins are given an arbitrary group number determined by rating them between −20 and +70, by comparison with a 0.2 per cent solution of potassium bichromate. The group number, plus the Engler viscosity of a 5 per cent solution at 350° C. plus the Cambon fusiometer value in degrees centigrade, gives a figure which when multiplied by two equals the value of the gelatin in German marks per 100 kilos (p. 148). How the author figures foreign exchange is not stated This method is fanciful and valueless to others, but fortunately the author gives a good résumé of more generally accepted methods of testing.

The book is the best German publication on the subject that the reviewer has yet seen.

JEROME ALEXANDER

Modern Gasworks Chemistry. By GEOFFREY WEYMAN, D.Sc., F.I.C. $7^{3}/_{8} \times 9^{5}/_{8}$ in. x + 184 pp. Benn Brothers, Ltd., London, 1922. Price, £1 5s.

The author states in the preface, "This volume has not been written with the intention of discussing the chemical and physical theories which form the basis of the various processes carried out and the relative merits of various types of plant. Rather is it intended to describe the methods of controlling plant processes in everyday use, in the hope that those who are endeavoring to introduce scientific control may be saved much time and trouble."

The book carries out the author's promise and presents to the gas chemist a compact outline of the tests and methods of analysis for coal, coke, tar, ammonia, oxides, gas, lubricants, refractory, and insulating materials, and other chemical and physical tests used in carbonization, maintenance of heats, oxide purification, steam raising, and water supply. Theory and processes are touched upon sufficiently to show the application of chemical and physical control tests. In the 184 pages of the book it is impossible to describe methods completely in the style of the "Gas Chemists' Handbook," published by the American Gas Association. Inexperienced chemists will, therefore, need to refer to the larger handbooks and special articles on the particular subject in hand. The author gives a list of references at the end of each chapter.

The chapters on coal and coke discuss briefly the theory of coking, and outline the methods for sampling, analyzing, and determining the gas yields of coal. The author describes many of the newest tests, such as resistance of coal during carbonization, Lessing's coking test, Sinnatt's modification of agglutinating power, arsenic in coke, etc. He should have made some reference to the standard methods of sampling and analysis of the American Chemical Society and the American Society for Testing Materials.

Disregard of American literature has led the author to state that the Dumas method for determining nitrogen gives results 0.5 per cent higher than obtained by the Kjeldahl method. Fieldner and Taylor[1] have shown that the use of ordinary copper oxide ignited in air gives high results in the Dumas method, owing to occluded nitrogen, to the extent of 2 or 3 cc. in the fine copper oxide. When suitable methods were applied for removing this nitrogen, excellent checks were obtained between the Dumas and Kjeldahl methods.

Gas, tar, and ammonia tests are also described according to English practice, and the relation of such tests to the control of carbonization, cooling, and condensing is shown.

The appendix contains fourteen tables of physical and chemical constants.

In "Modern Gasworks Chemistry" the author has filled a real need in providing the busy gasworks chemist with a brief and concise picture of the chemical and physical control of gasworks operation. It points the way in which the control chemist can apply himself to the many operating problems in gas-making processes.

A. C. FIELDNER

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[1] *Bur. Mines, Tech. Paper* **64** (1915).

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.*

February

There is a lively market for **copper** in Austria. (P. 339)

Another **substitute for gasoline** has been discovered in France. The use of a certain mixture of alcohol and benzene appears, however, to have proved an acceptable fuel and one which offers a way of utilizing cheap surplus alcohol in France. The use of this mixture is being promoted by the French government.

Petroleum production in Japan during the first nine months of 1922 amounted to 1,436,462 bbls., as compared with 1,652,255 bbls. during the first nine months of 1921. (P. 358)

A translation of a recent decree of the Congress of the Republic of Ecuador, amending the existing law relative to **beds or deposits of hydrocarbons**, is on file in the Department of Commerce and may be consulted in the Petroleum Division of that Department. (P. 358)

The Petroleum Division has on file a publication which gives a history of Argentine **petroleum legislation**, and methods of obtaining exploration and exploitation rights in the various fields of the Republic. (P. 359)

Results of considerable industrial importance have already been achieved by the Australian Institute of Science and Industry in the discovery of new sources of **tanning materials**. It is thought that the kino or gum from the West Australian red gum trees contains a considerable percentage of tannin. (P. 362)

Swedish production of **cellulose** during 1922 is estimated at 745,000 tons, or about 68 per cent of the normal production; **sulfate cellulose**, approximately 240,000 tons, or 86 per cent of normal capacity of mills; and **mechanical wood pulp**, 334,000 tons, or 90 per cent of normal. (P. 366)

The following articles have been added to the list of goods which may be imported into Ecuador free of duty; all **fertilizers**; **acetate of copper**; **oxide of iron for purifying gas**; **metallic oxide** for enameling pottery; **preservatives for rubber**; **carbon sulfide**; and **formaldehyde**. (P. 376)

The new Argentine regulations for the **chemical analysis of imports** are described. (P. 378)

The Rumanian industries are reviewed, among them the **chemical industry** including petroleum. (Pp. 383–5)

Only three groups of American exports showed an increase in 1922, **chemicals and allied products** being one of the three, with a gain of 1.4 per cent. Decreases ranging from 8 to 31 per cent occurred in other groups. (Pp. 421–3)

The foreign demand for American **naval stores**, **gums**, and **resins** expanded 62 per cent last year, exports rising from an aggregate value of $11,449,253 in 1921 to $18,510,331 in 1922. Shipments of wood tar, wood turpentine, and pitch reflect the most rapid growth of this group, having increased 133 per cent. Shipments of turpentine advanced 68 per cent and of resin 44 per cent. (P. 423)

A distiller of essential oils of various kinds in Mysore, India, is desirous of getting in touch with American importers and manufacturers using these oils, particularly **eugenol** and **thymol**. Further information may be obtained upon application to the Chemical Division of the Department of Commerce. (P. 423)

A rich **quicksilver vein**, said to extend for over 7 miles on the surface and to vary in width from 2 to 6 ft., has been discovered in Japan. Assays show the ore to contain 18 per cent of quicksilver, and preliminary excavations indicate that the vein increases in thickness the deeper it is followed. (P. 434)

The **tin** market of British Malaya is slowly reviving, present prices being at a level that was considered a fair return in pre-war years. (P. 434)

Japan **cement** trade is brisk. Demand is increasing and stocks are short. (P. 434)

The value of the output of **metallic minerals** in Canada during 1922 was $61,731,000 (1921, $49,343,232) and **nonmetallic minerals** $83,891,000 (1921, $87,833,161). (P. 435)

Recent tests made by the Imperial Institute indicate that the talipot palm or fan palm of South India may prove a promising **paper-making material**. The leaf stalks give a fairly good yield of pulp. which furnishes a strong brown paper suitable for wrapping. (P. 438)

An important series of tests on the possibilities of using certain Tasmanian timbers for the manufacture of **paper pulp** has been completed by the Institute of Science and Industry, and favorable results are reported. (P. 438)

Brazil has decreed changes in individual duties, mostly upward, on the following: **oxides of lead**, **gypsum**, and **cream of tartar**. (P. 449)

The Rumanian government has decided to prohibit the exportation of **oilseeds** with the exception of poppy seeds. (P. 450)

The importation of **amorphous phosphorus** and **sesquisulfide** into Spain is reserved exclusively to the Spanish government. (P. 450)

A new **artificial-silk mill** will be constructed shortly in the outskirts of Strassburg. The plant will start operations with a capital of 10,000,000 francs and will give employment to 2000 workers. (P. 490)

The very low price of **tin** caused a depression in Nigerian tin mining during 1921. (P. 499)

The **mineral resources** of New Caledonia are very great. Chromium, cobalt, nickel, iron, and manganese abound. (P. 499)

The **petroleum trade** of the Dutch East Indies is reviewed. (P. 500)

The production of **oil** in Japan for the 10 months ended October, 1922, showed a loss when compared with the same period in 1921. (P. 501)

The total production of **petroleum** in India in 1921 showed a gain of 342,857 bbls. over 1920. (P. 501)

Production of **vegetable oils** in the Netherlands is reviewed. (P. 502)

British Guiana has increased her **customs duty** on petrol, including gasoline, mineral naphtha, benzine, and petroleum spirit. (P. 514)

The Chinese are cornering the German stocks of **indigo** in anticipation of a great advance, the price having risen 10 per cent already. (P. 534)

A measure is before the Philippine legislature to permit a 20-year use of about 50,000 acres under the forestry bureau for the cultivation of **rubber**, **camphor**, and **quinine**. (P. 535)

The Kaiser Wilhelm Institute for the Advancement of Science has recently added to the scheme of its activities an "Institut für Faserstoffchemie" which will devote its energies to investigating the possibilities for producing in Germany **textile fibers** suitable for use in cloth manufacture. (P. 547)

The British **petroleum trade** during 1922 is reviewed. (Pp. 562–3)

Freely translated extracts are given of a report on **petroleum operations** in Mexico during the year 1922. (P. 563)

Italy has made changes in her customs valuations of **essential oils** not specially mentioned, **terpeneless essential oils**, **synthetic perfumes** and constituent essences, and **alkaloids** not specially mentioned, and salts thereof. (P. 571)

The Eastern European Division of the Bureau of Foreign and Domestic Commerce has on file the details of the Soviet decree regarding **mining** in Siberia which will be furnished to interested parties. (P. 576)

The Chilean **nitrate market** showed greater activity during December than during any month since the crisis of 1920. The firm tone of the American **copper market** has also been reflected in Chile, where prices have stiffened considerably. (P. 579)

Wood chemical plants in the United States produced about twice as much **acetate of lime** and **wood alcohol** in December as a year ago. Price index numbers of **crude drugs**, **essential oils**, and **chemicals** advanced in January, while **drugs** and **pharmaceuticals** declined. Receipts of **turpentine** and **resin** were higher than in January, 1922. Receipts and shipments of **flaxseed** were less than in December, but greater than a year ago. (P. 583)

Production of **zinc** in the United States in January rose to 92,634,000 lbs., the highest since March, 1920, while stocks declined to 33,148,000 lbs., the lowest since the armistice. Stocks of **tin** declined slightly. (P. 583)

SPECIAL SUPPLEMENTS ISSUED

DUTCH EAST INDIES—Petroleum Trade and Industry of the United Kingdom. *Trade Information* **80.**

CURRENT PUBLICATIONS

NEW BOOKS

American Petroleum Refining. H. S. Bell. 456 pp. Price, $5.00. D. Van Nostrand Co., New York.

Atoms: The Structure of Atoms. Alfred Stock. 88 pp. Price, 6s. Methuen & Co., Ltd., London.

Atomic Constitution: The Theory of Spectra and Atomic Constitution. Niels Bohr. 126 pp. Price, $3.00. The Macmillan Co., New York.

Cements, Limes, and Plasters. Edwin C. Eckel. 2nd edition, revised and enlarged. 655 pp. Price, 32s. 6d. Chapman & Hall, Ltd., London.

Chemistry: Outlines of Theoretical Chemistry. F. H. Getman. 625 pp. Price, 18s. 6d. Chapman & Hall, Ltd., London.

Cleaning and Restoration of Museum Exhibits. Second Report upon Investigations Conducted at the British Museum. Department of Scientific and Industrial Research. 11 pp. Price, 2s. net. H. M. Stationery Office, London.

Clinical Laboratory Methods. Russell L. Haden. 295 pp. Illustrated. Price, $3.75. C. V. Mosby Co., St. Louis.

Electrical Handling of Materials. Vol. III. Electric Cranes. H. H. Broughton. 352 pp. Illustrated. Price, $12.50. D. Van Nostrand Co., New York.

Fabrics and How to Know Them. Grace Goldena Denny. 146 pp. Illustrated. Price, $1.50. The J. B. Lippincott Co., Philadelphia.

Glue and Gelatin. Jerome Alexander. American Chemical Society Monograph Series. 230 pp. Price, $3.00. The Chemical Catalog Co., Inc., New York.

Inorganic Chemical Synonyms and Other Useful Data. Elton Richmond Darling. 2nd edition, revised and enlarged. 126 pp. Price, $1.00. D. Van Nostrand Co., New York.

Inorganic Chemistry: Study Questions and Problems in Inorganic Chemistry. For Colleges and Universities. Alexander Silverman. 2nd edition, revised. 90 pp. Price, $1.00. D. Van Nostrand Co., New York.

Laboratory Manual: An Advanced Laboratory Manual of Organic Chemistry. Michael Heidelberger. 103 pp. Price, $2.00. The Chemical Catalog Co., Inc., New York.

Leather: The Manufacture of Chrome Leather. M. C. Lamb. 450 pp. Illustrated. Price, 26s. The Anglo-American Technical Co., Ltd., London.

Metals: El Arte de los Metáles. Translated from the Spanish of Alvaro Alonso Barba by Ross E. Douglas and E. P. Mathewson. 276 pp. Price, $3.50. John Wiley & Sons, Inc., New York.

Modern Industrialism. Frank L. McVey. 358 pp. Price, $2.50. D. Appleton & Co., New York.

Oil Analysis. Augustus H. Gill. 10th revised edition. 223 pp. Illustrated. Price, $2.50 net. J. B. Lippincott Co., Philadelphia.

Optical Methods in Control and Research Laboratories. Vol. I. J. N. Goldsmith, S. Judd Lewis, and F. Twyman. 2nd edition. 56 pp. Price, 1s. 8d. Adam Hilger, Ltd., London.

Ore Analysis: Notes on Technical Ore Analysis for Students. A. H. Low. 95 pp. Price, $1.75. John Wiley & Sons, Inc., New York.

Our Farm in Cedar Valley. Edward Hart. 250 pp. Price, $1.50. Chemical Publishing Co., Easton, Pa.

Oxyacetylene Welding and Cutting. P. F. Willis. 254 pp. Price, $1.50. Norman W. Henley Publishing Co., New York.

Paracelsus, His Personality and Influence as Physician, Chemist, and Reformer. J. M. Stillman. 184 pp. Price, 10s. net. The Open Court Publishing Co., London.

Petroleum Industry. Edited by A. E. Dunstan. 346 pp. Illustrated. Price, $5.00. D. Van Nostrand Co., New York.

Photography: The Theory of Development. A. H. Nietz. Monograph No. 2 from the Research Laboratory of Eastman Kodak Co. 190 pp. Illustrated. Price, $2.50. D. Van Nostrand Co., New York.

Plant Products: An Introduction to the Chemistry of Plant Products. Vol. II. P. Haas and T. G. Hill. 140 pp. Price, $2.50. Longmans, Green & Co., New York.

Quantitative Agricultural Analysis. E. G. Mahin and R. H. Carr. 329 pp. Price, $2.75. McGraw-Hill Book Co., Inc., New York.

Richter's Organic Chemistry. Vol. III. Heterocyclic Compounds. Translated from the 11th German edition by E. E. Fournier D'Albe. 326 pp. Price, 25s. Kegan Paul, Trench, Trubner & Co., Ltd., London.

Rubber: The Preparation of Plantation Rubber. Sidney Morgan. 331 pp. Illustrated. Price, 21s. net. Constable & Co., Ltd., London.

Steel: The Properties of Some Nickel-Chromium Steels. Research Department, Woolwich. R. D. Report No. 55. 51 pp. Price, 7s. 6d. H. M. Stationery Office, London.

Steel Thermal Treatment. John W. Urquhart. 351 pp. Illustrated. Price, $8.00. D. Van Nostrand Co., New York.

Steel: Technical Analysis of Steel and Steel Works Materials. F. T. Sisco. 543 pp. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

NEW JOURNAL

The Explosives Engineer, a Magazine for Users of Explosives. Published monthly by The Hercules Powder Co., Wilmington, Del. Harry Roberts, Jr., and N. S. Greensfelder, Editors. Price, $3.00 a year.

RECENT JOURNAL ARTICLES

Alcohol Fuel Mixtures. H. R. Adam. *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, Vol. 23 (1922), No. 6, pp. 112–18.

Ammonium Sulfate: La Fabrication du Sulfate d'Ammoniaque dans les Usines à Gaz. A. Grebel. *Chimie et Industrie*, Vol. 9 (1923), No. 1, pp. 26–42.

Blast Furnace: Use of Magnetic Ore in the Blast Furnace. G. P. Pilling. *The Blast Furnace and Steel Plant*, Vol. 11 (1923), No. 2, pp. 148–52.

Bleaching of Ligno-Cellulose. C. G. Schwalbe and H. Wenzyl. *Paper*, Vol. 31 (1923), No. 17, pp. 9–13, 19. Translated from *Der Papierfabrikant*.

Combustion Control for Steam Boilers. Charles H. Smoot. *Power*, Vol. 57 (1923), No. 10, pp. 354–56.

Dyes: Classifying and Measuring Color by the Ostwald Method. H. T. Tenen. *American Dyestuff Reporter*, Vol. 12 (1923), No. 4, pp. 127–32.

Dyes: Details of a Method for Determining Relative Fastness of Dyestuffs and Physical and Practical Basis of Same. Hibbard S. Busby. *Textile Colorist*, Vol. 45 (1923), No. 531, pp. 151–56.

Fatty Oils: Some Problems Connected with the Saponification of Fatty Oils. H. M. Langton. *Journal of the Society of Chemical Industry*, Vol. 42 (1923), No. 7, pp. 51*t*–57*t*.

Glass: The Action of Water and Steam under Pressure on Some Soda-Lime-Silicate Glasses. F. W. Hodkin and W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. 6 (1922), No. 24, pp. 291–302.

Glass: The Manufacture and Properties of Oven Glass. R. F. Brenner. *The Glass Industry*, Vol. 4 (1923), No. 2, pp. 23–24.

Lehrs. W. S. Mayers. *The Glass Industry*, Vol. 4 (1923), No. 2, pp. 21–23.

Mercerization: Notes on Mercerization. A. J. Hall. *Textile Colorist*, Vol. 45 (1923), No. 530, pp. 83–86.

Mercury Arc Lamp in Dye Testing. Oscar R. Flynn. *Textile World*, Vol. 63 (1923), No. 8, pp. 25–31.

Modern Equipment for Dyeing, Bleaching, and Finishing Operations. E. A. Turner. *American Dyestuff Reporter*, Vol. 12 (1923), No. 5, pp. 165–69.

Steel: British Practice in High-Speed Steel. H. K. Ogilvie. *The Iron Age*, Vol. 111 (1923), No. 10, pp. 679–81.

Steel: Heat Treatment of Electric Carbon and Alloy Forging Steels. Larry J. Barton. *Forging and Heat Treating*, Vol. 9 (1923), No. 2, pp. 102–05.

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

Additions, Removals, and Changes in Permissible List of Explosives from March 15 to December 31, 1922. S. P. Howell. *Reports of Investigations* 2430. 4 pp. Issued, January, 1923.

Combustion Products from a Radiant-Type Natural-Gas Heater and Suggestions Regarding Its Operation. G. W. Jones, W. P. Yant, and L. B. Berger. *Reports of Investigations* 2443. 15 pp. Issued February, 1923.

Condensation Losses Due to Transmission of Carbureted Water Gas under High Pressures. W. A. Dunkley. *Reports of Investigations* 2447. 7 pp. Issued February, 1923.

Jet. W. M. Myers. *Reports of Investigations* 2452. 4 pp. Issued March, 1923.

Metallurgical Possibilities of the Descloizite Ores at Goodsprings, Nevada. H. A. Doerner. In coöperation with Mackay School of Mines, University of Nevada. *Reports of Investigations* 2433. 19 pp. Issued January, 1923.

Petroleum Engineering in the Skull Creek Oil Pool, Northeastern Osage County, Oklahoma. T. E. Swigart. *Reports of Investigations* 2450. 9 pp. Issued February, 1923.

Quarry Problems from the Engineer's Viewpoint. Oliver Bowles. *Reports of Investigations* 2429. 5 pp. Issued January, 1923.

Report of Lignite Carbonizing Experiments Conducted at Grand Forks in 1922. W. W. Odell. *Reports of Investigations* 2441. 26 pp. Issued February, 1923.

Road Loading at Lime-Plant Quarries. Oliver Bowles. *Reports of Investigations* 2446. 5 pp. Issued February, 1923.

Specifications for Petroleum Products and Methods for Testing. Federal Specifications Board Standard Specification No. 2. Revised October 31, 1922. *Technical Paper* 323. 88 pp. Paper, 10 cents. Issued January, 1923. These specifications were officially adopted by the Federal Specifications Board on February 3, 1922, for the use of the Departments and Independent Establishments of the Government in the purchase of materials covered by them.

Subject List of Reports of Investigations Issued during 1922. The list of all reports issued up to December 31, 1922, was published as *Reports of Investigations* 2316, in January, 1922. (The present list covers all reports issued during the calendar year 1922.) *Reports of Investigations* 2440. 7 pp. Issued January, 1923.

Tests of Large Boiler Fired with Powdered Coal. Henry Kreisinger and John Blizard. *Reports of Investigations* 2438. 2 pp. Issued January, 1923.

The Use of Vapor-Tight Tankage in the Oil Fields. Ludwig Schmidt. *Reports of Investigations* 2442. 11 pp. Issued February, 1923.

The Value of Oxygen-Breathing Apparatus to the Mining Industry. E. H. Denny and M. W. von Bernewitz. *Reports of Investigations* 2445. 5 pp. Issued February, 1923.

Bureau of Standards

Copper. *Circular* 73. 2nd ed. 108 pp. Paper, 20 cents.

Formula for the Rate of Exhaustion of a Large Tank by a Reciprocating Air Pump. E. Buckingham. *Technologic Paper* 224. Paper, 5 cents.

Scientific Papers of the Bureau of Standards, Vol. 17, 1922. Contents and Index. (Prior to Vol. 15 this series was called the "Bulletin of the Bureau of Standards.") 5 pp.

Soap. *Circular* 62. 3rd ed. 24 pp. Issued January 24, 1923. Paper, 5 cents.

The International Metric System of Weights and Measures. *Miscellaneous Publication* 2. 2nd ed. 16 pp. Paper, 5 cents.

United States Government Specification for Asphalt Varnish. *Circular* 104. 2nd ed. Federal Specifications Board, Standard Specification 19. 7 pp. Paper, 5 cents.

Bureau of the Census

Mines and Mineral Resources, 1919. General Report and Analytical Tables, and Reports for States and Selected Industries. 14th Census of the United States, 1920: Mines and Quarries, 1919. Prepared under the supervision of E. F. Hartley by F. J. Katz, assisted by E. B. White, M. M. Harrison, and M. B. Nevius. 443 pp. Cloth, $1.25.

Congress

Airplanes to Distribute Boll-Weevil Insecticides. To enable the Secretary of Agriculture, in coöperation with the Secretary of War, to investigate and develop the use of the airplane as a means of distributing insecticides for the control of the boll weevil and other cotton insects, including the employment of persons and means in the city of Washington, District of Columbia, and elsewhere, and all other necessary expenses, to remain available until June 30, 1924, $40,000, or so much thereof as may be necessary. *Public* 543 (*H. R.* 14,408). 10 pp. Approved March 4, 1923.

Customs Service. Customs Service Reorganization Bill, report to accompany S. 4245 (to provide necessary organization of Customs Service for adequate administration and enforcement of Tariff Act of 1922 and all other customs revenue laws); submitted by Mr. Calder, January 23, 1923. *S. Rep.* 1065. 8 pp. Paper, 5 cents.

Customs Service. Reorganization of Customs Service, hearings on S. 4245. 7 pp. 1923.

Customs Service. An Act to provide the necessary reorganization of the Customs Service for an adequate administration and enforcement of the Tariff Act of 1922 and all other customs revenue laws. *Public* 502 (*S.* 4245). Approved March 4, 1923. 2 pp.

Naval Stores. A Bill establishing standard grades of naval stores, preventing deception in transactions in naval stores, regulating traffic therein, and for other purposes. *Public* 478 (*S.* 1076). 7 pp. Approved March 3, 1923.

Nitrate Plant at Muscle Shoals. Communication from the President of the United States, transmitting, together with an accompanying letter from the Director of the Bureau of the Budget, a supplemental estimate of appropriation in the sum of $30,000 for payment of awards for lands condemned for use by the War Department at United States Nitrate Plant No. 2, Muscle Shoals, Ala. *S. Doc.* 340. Read, referred to the Committee on Appropriations, and ordered to be printed, March 1, 1923. 2 pp.

Nitrate Plants. A Bill to authorize and direct the Secretary of War to sell to John Kissell, nitrate plant numbered 1, nitrate plant numbered 2, the Waco Quarry, the interest of the Government in the Gorgas Warrior River steam plant; and to lease to the corporation to be incorporated by John Kissel dam numbered 2 and dam numbered 3, including power stations, when constructed as provided herein, and for other purposes, all in the State of Alabama. *H. R.* 14,445. Referred to the Committee on Military Affairs and ordered to be printed, February 28, 1923. 17 pp.

Statistics of Foreign Commerce. An Act to consolidate the work of collecting, compiling, and publishing statistics of the foreign commerce of the United States in the Department of Commerce. *Public* 379 (*S.* 3295). 1 p. Approved, January 5, 1923.

Tariff. Hearing on proposed Tariff Act of 1921 (*H. R.* 7456) (*S. Doc.* 108). Revised and indexed. 8 vols.

- American Valuation, Dyes Embargo. Vol. 1. 775 pp. Paper, 60 cents.
- Chemicals, Oils, and Paints. Schedule 1, Vol. 2. 829 pp. Paper, 65 cents.
- Metals and Manufactures. Schedule 3, Vol. 3. 948 pp. Paper, 75 cents.

Department of Agricultrue

Probable Cause of the Toxicity of the So-Called Poisonous Greensand. J. W. Kelly. *Journal of Agricultural Research*, 23 (January 20, 1923), 223–8.

Significance of Wheat Hairs in Microscopical Examination of Flour. G. L. Keenan. *Department Bulletin* 1130. 8 pp. Paper, 5 cents.

The Lead-Cable Borer or "Short-Circuit Beetle" in California. H. E. Burke, R. D. Hartman, and T. E. Snyder. *Department Bulletin* 1107. 56 pp. Paper, 20 cents.

Geological Survey

A Geologic Reconnaissance in the Gulf Coastal Plain of Texas near the Rio Grande. A. C. Trowbridge. *Professional Paper* 131-D. Separate from shorter contributions to general geology, 1922. 33 pp. Published February 12 1923.

Gold, Silver, Copper, Lead, and Zinc in Idaho and Washington in 1921. Mines Report. C. N. Gerry. Separate from Mineral Resources of the United States, 1921, Part I. 30 pp. Published February 12, 1923.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1921. Mines Report. V. C. Heikes. Separate from Mineral Resources of the United States, 1921, Part I. 30 pp. Published February 10, 1923.

Mineral Waters in 1921. W. D. Collins. Separate from Mineral Resources of the United States, 1921, Part II. 8 pp. Published February 5, 1923.

Structure and Oil and Gas Resources of the Osage Reservation, Oklahoma. David White and others. *Bulletin* 686. 427 pp.

Surface Water Supply of the United States, 1918. Part XII. North Pacific Drainage Basins. B. Snake River Basin. N. C. Grover, G. C. Baldwin, G. L. Parker, A. B. Purton, and F. F. Henshaw. Prepared in Coöperation with the States of Oregon, Nevada, and Washington. *Water-Supply Paper* 483. 171 pp. Paper, 15 cents.

Public Health Service

An Experimental Study of the Relation of Hydrogen-Ion Concentrations to the Formation of Floc in Alum Solutions. E. J. Theriault and W. M. Clark. *Public Health Reports*, 38 (February 2, 1923), 181–98.

A Toxin-Producing Anaërobe Isolated Principally from Fly Larvae. Its Relation to the Organisms Hitherto Known to Be Causative Factors in the Production of Botulism. I. A. Bengston. *Public Health Reports*, 38 (February 23, 1923), 340–4.

Some New Sulfonphthalein Indicators. A Preliminary Note. Barnett Cohen. *Public Health Reports*, 38 (February 2, 1923), 199.

MARKET REPORT—MARCH, 1923

[Supplied by Drug & Chemical Markets]

The most significant thing which has developed in the American chemical market during the past month is undoubtedly the broader inquiry from the British Isles and the Continent for supplies of American chemicals. The inquiries have come in each instance from chemical importers abroad who either represented a German manufacturer or had previously been buying their stocks on the open market in Germany. The Ruhr occupation, with its consequent shut-down on supplies of coal and other raw materials for German factories outside of the occupied area, has been steadily tightening its grip. While at first many of the chemical factories continued to ship for export in large lots, the situation has now reached a point where importers of England and some of the continental countries have been all but cut off from their sources of supply. As a reflection of this condition, the importers abroad are turning to America for such products as can be supplied by manufacturers here in competition with the European producers.

During the past month the chemical business as a whole has been active and a large quantity of goods has been shipped into consuming channels. Prices as a whole have risen steadily since the first of the year, as might be expected as a result of steady absorption of reserve stocks. With surplus supplies reduced to a minimum, practically all industrial chemical factories have now resumed operations on a full-time schedule.

Manufacturers of heavy chemicals report a steady demand from the consuming industries for nearly all lines. The main difficulty has been in making deliveries, owing to the handicaps caused by snowstorms and rail embargoes. The basic chemicals, such as heavy acids and alkalies, are moving in greater volume than at any time since 1920. Sulfuric acid production has been increasing by leaps and bounds, and some makers are unable to supply the demand. Hydrochloric acid is also in active demand. Oleum is very difficult to obtain. Caustic-soda and soda-ash deliveries were larger for February than for January. The recent strength in the market for metals was reflected by advances in nearly all products derived from copper, lead, and tin.

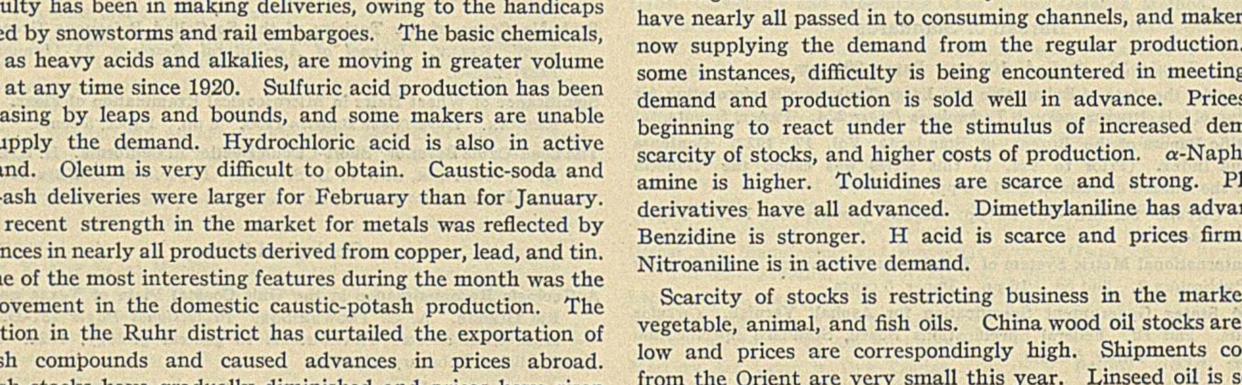
One of the most interesting features during the month was the improvement in the domestic caustic-potash production. The situation in the Ruhr district has curtailed the exportation of potash compounds and caused advances in prices abroad. Potash stocks have gradually diminished and prices have risen to the point where American producers are now competing with the imported material. Potassium carbonate has also advanced.

Imported chemicals have been in steady demand in the New York market. Prices have held firm owing to the higher replacement costs of these products abroad. Export demand has improved and inquiries for American products are coming in from countries all over the world. Ammonium sulfate is very scarce and prices have advanced considerably. Acetone prices have been advanced. Makers have advanced prices on sodium bicarbonate. Competition in sodium dichromate has settled prices. Bleaching powder continues in active demand with prices firm. Refiners of saltpeter have reduced their prices. Prussiates are slightly easier.

In the crude coal-tar products, considerable excitement was stirred up by the sudden rise in phenol prices. A sudden buying movement on the part of consumers during the past month found supplies were to be had only in limited quantities, and holders immediately advanced prices sharply. Coincidentally prices in England rose 300 per cent after reported heavy buying on the part of Japanese interests. In New York prices advanced from 35 to 50 cents a lb., and in some cases sales were made at higher figures. The list of coal-tar crudes shows scarcity of supplies in every item except benzene, though no large surplus of this material exists. Cresylic acid has been scarce for some time and the situation is growing worse. Domestic producers of phenol and cresylic acid are able to supply only a small part of the American demand, while high prices due to the tariff rates forbid importing these products. Toluene and solvent naphtha are at a premium and no supplies are expected to be had for several months. A supply of English xylene has been offered in the American market recently. Naphthalene scarcity has also developed and prices have been slowly creeping up.

Demand for intermediates has improved considerably and is covering a broader field than at any time since 1920. Old stocks have nearly all passed in to consuming channels, and makers are now supplying the demand from the regular production. In some instances, difficulty is being encountered in meeting the demand and production is sold well in advance. Prices are beginning to react under the stimulus of increased demand, scarcity of stocks, and higher costs of production. α-Naphthylamine is higher. Toluidines are scarce and strong. Phenol derivatives have all advanced. Dimethylaniline has advanced. Benzidine is stronger. H acid is scarce and prices firm. p-Nitroaniline is in active demand.

Scarcity of stocks is restricting business in the market for vegetable, animal, and fish oils. China wood oil stocks are very low and prices are correspondingly high. Shipments coming from the Orient are very small this year. Linseed oil is scarce on spot, and crushers have advanced their prices. Castor oil is higher. Soy-bean oil supplies are limited and prices strong. Peanut oil is scarce. Cottonseed oil prices have advanced. Demand for animal oils and products has been very active and prices are generally higher. Tallow is higher. Stearic acid and red oil have advanced. Lard oil is higher. Fish oils can be had only in limited quantities and holders are asking higher prices. Turpentine has been quite steady.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

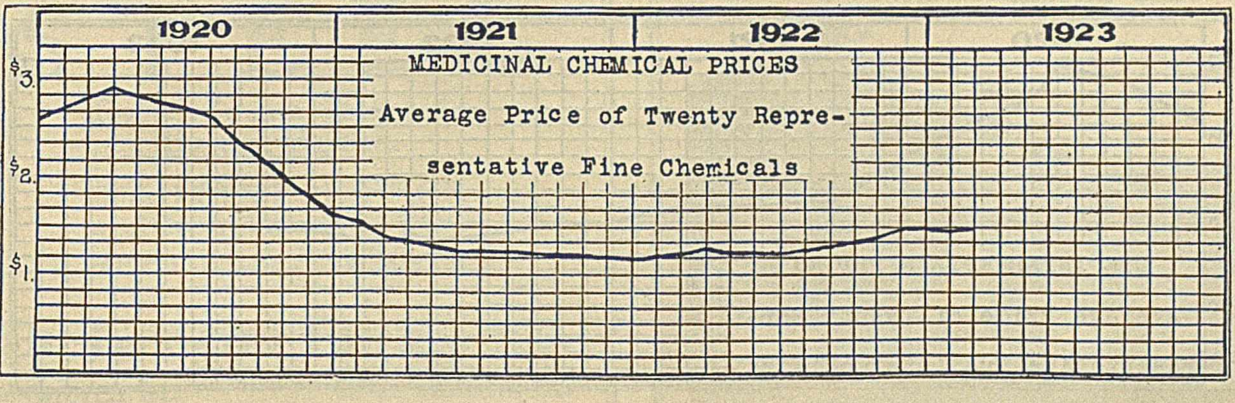
INORGANIC CHEMICALS

	Feb. 1	Feb. 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11½	.11½	.11½
Hydrochloric, comm'l, 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/l wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.09	.08
Sulfuric, C. P............lb.	.08	.08	.07
66° tks. wks........ton	15.00	15.00	15.00
Oleum, 20%........ton	18.00	18.00	18.00
Alum, Ammonia, lump........lb.	.03½	.03½	.03½
Potash, lump............lb.	*.03¼	*.03¼	*.03½
Chrome.............lb.	.05½	.05½	.05½
Soda, ground............lb.	.04	.04	.04
Aluminium Sulfate (iron-free)..lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd...lb.	.09	.09	.09½
Chloride, white gran......lb.	.08	.08	.07¾
Ammonia, anhydrous.........lb.	.30	.30	.30
Ammonia Water, drums, 26°..lb.	.07½	.07½	.07½
Arsenic, white...............lb.	.15½	.15½	.15½
Barium Choride.............ton	*90.00	*90.00	*92.50
Nitrate.................lb.	*.07½	*.07¾	*.07½
Barytes, white...............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works ....100 lbs.	2.15	2.15	2.15
Borax, cryst., bbls............lb.	.05½	.05¼	.05½
Bromine, pure, wks...........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	24.50
Chlorine, liquid...............lb.	.05¼	.05¼	.05¼
Copper Sulfate..........100 lbs.	6.25	6.50	6.25
Iodine, resublimed...........lb.	4.55	4.55	4.50
Lead Acetate, white crystals....lb.	.13	.13½	.13
Nitrate.................lb.	.22	.22	.22
Red................100 lbs.	10.65	11.40	10.60
White (Carb.)...........lb.	.09	.09¾	.08½
Lime, live and hydrated, bbl. .lb.	.01¾	.01¾	.01½
Oyster shell.............lb.	.03	.03	.03
Lime Acetate...........100 lbs.	3.50	3.50	3.50
Magnesium Carbonate, tech...lb.	.08	.07¾	.08
Magnesite, calcined..........ton	55.00	55.00	55.00
Phosphorus, yellow...........lb.	*.28	*.28	*.28
Red.....................lb.	*.30	*.30	*.30
Plaster of Paris, tech........bbl.	3.30	3.30	3.30
Potassium Bichromate........lb.	.10	.10	.10
Bromide, imported.......lb.	.14½	*.14½	.14½
Carbonate, calc., 80–85%.lb.	*.05¾	*.05¾	*.05½
Chlorate, cryst...........lb.	*.08½	*.08½	*.05½
Hydroxide, 88–92%......lb.	*.07½	*.08	*.08
Iodide, bulk, U. S. P.....lb.	3.60	3.75	3.60
Nitrate..................lb.	.06½	.06	.06½
Permanganate, U. S. P...lb.	*.16	*.20	*.16
Prussiate, red...........lb.	*.80	*.80	*.90
Yellow..............lb.	*.37½	*.37½	*.38
Salt Cake, bulk.............ton	28.00	28.00	28.00
Silver Nitrate...............oz.	.44	.43	.44
Soda Ash, 58%, bags.....100 lbs.	*1.80	*1.80	*1.85
Caustic, 76%, N. Y..100 lbs.	3.70	3.70	3.50
Sodium Acetate..............lb.	.07¼	.07¼	.07¼
Bicarbonate.........100 lbs.	2.00	2.00	2.00
Bichromate..............lb.	.07½	.07½	.07¾
Bisulfite, powd...........lb.	.04	.04	.04
Chlorate.................lb.	.06½	.06½	.06½
Cyanide, 96–98%........lb.	.23	.23	.23
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls....100 lbs.	3.25	3.25	3.60
Nitrate, 95%........100 lbs.	2.62	2.67	2.57½
Nitrite...................lb.	.08½	.08½	.08½
Prussiate, yellow.........lb.	.19	.18¾	.18½
Phosphate (di-sod.), tech. lb.	.03½	.03½	.03½
Silicate, 40°.........100 lbs.	.80	.80	.80
Sulfide, 60%, fused.......lb.	.05	.05	.05
Strontium Nitrate............lb.	*.08¾	*.08¾	*.08¾
Sulfur, flowers............100 lb.	3.00	3.00	3.00
Crude, mines.......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n.....lb.	.10¼	.13½	.10¼
Oxide...................lb.	.44	.54	.43
Zinc Chloride, U. S. P.........lb.	.20	.20	.20
Oxide, bbls..............lb.	.07½	.07½	.07½

* Resale or Imported (not an American makers' price).

ORGANIC CHEMICALS

	Feb. 1	Feb. 15	Jan. 1923
Acetanilide, U. S. P., bbls.....lb.	*.35	*.35	*.35
Acid, Acetic, 28 p. c......100 lbs.	3.17½	3.17½	3.17½
Glacial.........100 lbs.	12.50	12.50	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drs...............lb.	.37	.42	.32
50- to 110-lb. tins.....lb.	.39	.44	.34
Citric, crystals, kegs......lb.	*.48½	*.48½	*.48½
Oxalic, cryst., bbls., wks..lb.	.12½	.12½	.13½
Pyrogallic, resublimed....lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.45	.50	.45
Tannic, U. S. P., bbls.....lb.	.70	.70	.70
Tartaric, cryst., U. S. P....lb.	*.30½	*.30½	*.32
Acetone, drums..............lb.	.21	.22	.21
Alcohol, denatured, complete.gal.	.41	.41	.45
Ethyl, 190 proof, bbls....gal.	4.70	4.70	4.70
Amyl Acetate...............gal.	3.00	3.50	2.50
Camphor, Jap, refined, cases...lb.	.86	.91	.86
Carbon Bisulfide, c/l.........lb.	.06¾	.06¾	.06¾
Tetrachloride............lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums...lb.	.35	.35	.35
Creosote, U. S. P............lb.	.40	.40	.40
Cresol, U. S. P...............lb.	.25	.25	.25
Dextrin, corn...........100 lbs.	3.09	3.09	3.09
Imported Potato.........lb.	.09	.09	.09
Ether, U. S. P., 100 lbs,.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.16	.16	.16
Glycerol, dynamite, drums....lb.	.17½	.17	.16½
Methanol, pure, bbls........gal.	1.30	1.30	1.35
Methylene Blue, med.........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.03¾	.04½	.03¾
Pyridine.....................gal.	2.75	2.35	2.75
Starch, corn, pow'd......100 lbs.	2.47	2.47	2.47
Potato, Jap.............lb.	.06¾	.06¾	.06¾
Sago....................lb.	.03½	.03½	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Feb. 1	Feb. 15	Jan. 1923
Beeswax, pure, white.........lb.	.36	.36	.36
Castor Oil, No. 3.............lb.	.13	.13½	.13
Ceresin, yellow..............lb.	.08½	.08½	.08½
Corn Oil, crude, tanks, mills...lb.	.09¾	.10⅛	.09¾
Cottonseed Oil, crude, f. o. b. mill....................lb.	.10	.10¼	.09⅝
Linseed Oil, raw, c/l.........gal.	.90	.99	.87
Menhaden Oil, crude, mills...gal.	.53	NOM.	.53
Neat's-foot Oil, 20°..........lb.	.18½	.18½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	6.25	6.40	6.25
Rosin Oil, first run..........gal.	.45	.47	.45
Shellac, T. N................lb.	.81	.78	.80
Sperm Oil, bleached winter, 38°....................gal.	1.09	1.09	1.02
Stearic Acid, double pressed...lb.	.13	.14½	.12½
Tallow Oil, acidless..........lb.	.11½	.11¾	.11½
Turpentine, spirits of........gal.	1.50	1.54	1.56

METALS

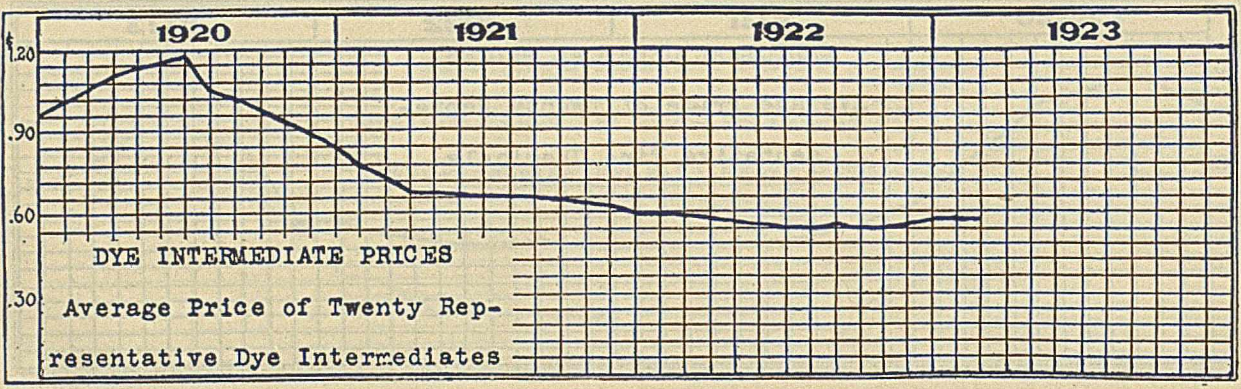
	Feb. 1	Feb. 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.23	.24½	.23
Antimony, ordinary......100 lbs.	6.75	8.87½	6.75
Bismuth.....................lb.	2.65	2.75	2.75
Copper, electrolytic..........lb.	.15	.17	.14¾
Lake...................lb.	.15⅛	.17⅛	.14¾
Lead, N. Y.............100 lbs.	8.50	8.62½	7.80
Nickel, electrolytic...........lb.	.36	.25	.36
Platinum, refined, soft........oz.	110.00	110.00	118.00
Quicksilver, flask......75 lbs. ea.	69.00	75.00	73.00
Silver, foreign...............oz.	.63	.68¼	.63
Tin.........................lb.	.40⅛	.49½	.39
Tungsten Wolframite....per unit	7.00	7.75	7.50
Zinc, N. Y.............100 lbs.	8.25	8.50	8.25

FERTILIZER MATERIALS

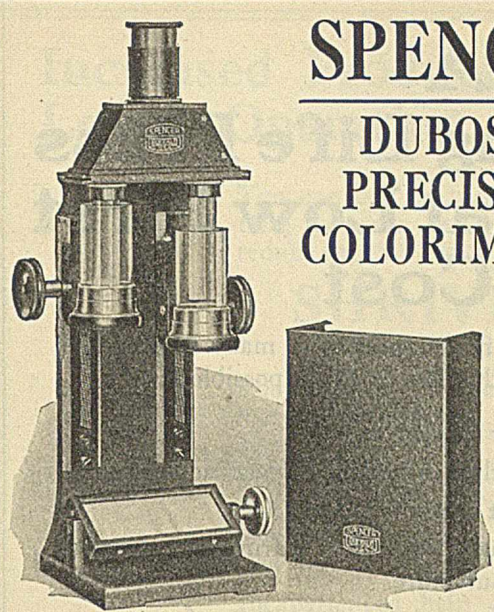
	Feb. 1	Feb. 15	Jan. 1923
Ammonium Sulfate, expt. 100 lbs.	3.55	3.90	3.90
Blood, dried, f. o. b. N. Y...unit	4.70	4.75	4.70
Bone, 3 and 50, ground, raw..ton	32.00	32.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	5.35 & .10	5.35 & .10	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	3.00
Tennessee, 78–80%......ton	3.00	3.00	3.00
Potassium Muriate, 80%....unit	.70	.68	.70
Tankage, high-grade, f. o. b. Chicago...............unit	4.75 & .10	4.50 & .10	4.75 & .10

COAL-TAR CHEMICALS

	Feb. 1	Feb. 15	Jan. 1923
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.30	.30	.30
Naphthalene, flake...........lb.	.06½	.06½	.06½
Phenol, drums...............lb.	.33	.50	.32
Crudes (*concluded*)			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, tanks..................gal.	—	—	—
Intermediates			
Acids:			
Anthranilic.............lb.	1.10	.98	1.10
Benzoic, tech...........lb.	.65	.65	.65
Cleve's................lb.	1.05	1.05	1.25
Gamma.................lb.	1.80	1.80	1.85
H......................lb.	.80	.80	.80
Metanilic..............lb.	.60	.60	.60
Monosulfonic F.........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.60	.60	.60
Nevile & Winther's.......lb.	1.15	1.15	1.15
Picric..................lb.	.20	.20	.20
Sulfanilic..............lb.	.20	.20	.19
Tobias'................lb.	1.30	1.30	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.17	.17	.17
Aniline Salt.................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech...........lb.	.65	.65	.65
U. S. P..................lb.	1.40	1.40	1.40
Benzidine Base..............lb.	.84	.84	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	3.75	3.80	3.75
Dianisidine..................lb.	4.50	4.10	4.50
p-Dichlorobenzene...........lb.	.18	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline.............lb.	.41	.43	.41
Dinitrobenzene..............lb.	.19	.19	.19
Dinitrotoluene...............lb.	.19	.19	.20
Diphenylamine..............lb.	.50	.48	.50
G Salt......................lb.	.60	.60	.60
Hydroquinol.................lb.	1.05	1.05	1.05
Monochlorobenzene...........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.24	.24	.26
a-Naphthylamine............lb.	.29	.35	.29
b-Naphthylamine............lb.	.90	.90	.95
m-Nitroaniline..............lb.	.80	.78	.80
p-Nitroaniline..............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	.72	.90	.72
o-Nitrotoluene.............lb.	.10	.10	.10
p-Nitrotoluene.............lb.	.65	.60	.65
m-Phenylenediamine.........lb.	1.00	.98	1.00
p-Phenylenediamine.........lb.	1.50	1.55	1.50
Phthalic Anhydride..........lb.	.35	.35	.35
R Salt......................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.50	1.50	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.58	.62	.62
Thiocarbanilide.............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.30	.27	.30
o-Toluidine................lb.	.15	.15	.15
p-Toluidine................lb.	1.00	1.00	1.00
m-Toluylenediamine.........lb.	.95	.95	.95
Xylidine....................lb.	.41	.41	.42



Courtesy of Drug & Chemical Markets



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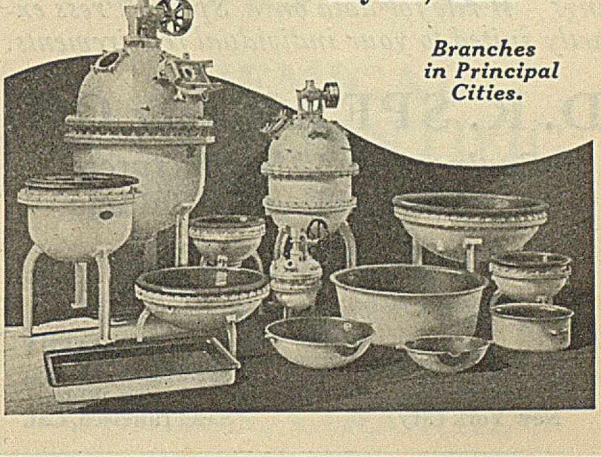
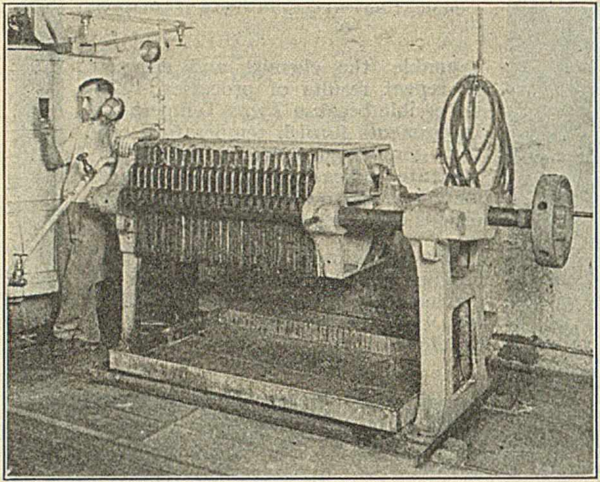


SPERRY FILTER PRESSES

In Action No. 3



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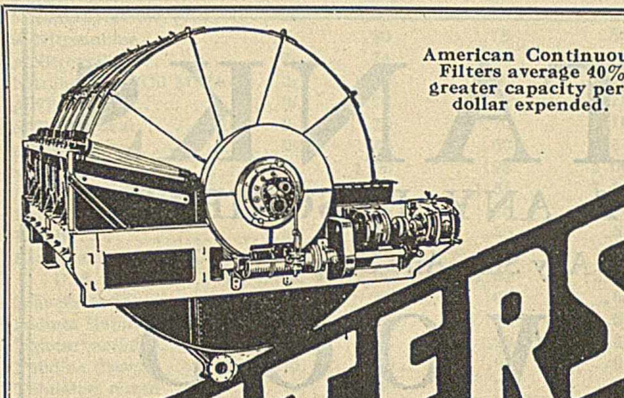

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