Industrial and Engineering Chemistry

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The Privy Council Report

THE Committee of the Privy Council for Scientific and Industrial Research of Great Britain has recently issued its eleventh report, which contains much food for thought. We have examined with interest the summaries of the work carried on by some twenty-six trade associations, the formation of which has been encouraged by the British Government for the prosecution of research. Of these, twenty-two have been in existence for more than five years, two have terminated their existence, while a third has temporarily suspended operations. Some of the activities of the British Council could be duplicated in our own country with much advantage; for example, a "survey of the state of scientific and industrial research in the country in order to afford an opinion as to how far its development could be further assisted."

The Department of Scientific and Industrial Research finds some of the greatest opportunities, and indeed the largest demand at present, for trained men to be in the borderlands between chemistry and agriculture, chemistry and botany, chemistry and physics, and other such subjects. Reference is also made to the proper relationships between government and industry in the prosecution of research. Here we find it stated that "the limits (speaking of money grants) must be dictated not only by the distinction of the worker and the nature of the work but also by the undesirability of using public funds to provide assistance which would more properly come from other sources." And while the Council, which has been given some large funds for disbursement in support of scientific work, has stood ready to assist researches in new fields of knowledge, particularly those which appear to be of potential benefit to industry, it clearly believes that the Government's function is to encourage research in neglected fields, occasionally to take the lead in these new researches, but always to be careful that the Government does not undertake research which can better be done by the industries themselves. "The main problem with which we are faced is how to encourage and assist the movement for industrial research without taking over functions which are best carried out by industry itself.*** A large portion of the work of a government research department must necessarily be directed toward helping industry to help itself." At the same time it must be recognized that there are certain types of research problems of such wide interest or of such importance to the welfare of the state that they cannot be left wholly to private initiative.

Again we find the Council clear in the opinion that pure and applied research cannot be promoted as it should be until public opinion is fully aroused to its necessity, an argument that has been used with justification throughout the development of the A. C. S. News Service. Another point of mutual interest is the insistence that industry build up a reserve of scientific knowledge in the creation of which the expenditure of stockholders' money is amply justified, and look upon industrial research "not as a cure for but as a prevention of bankruptcy."

One other reference, and perhaps one of the most important, is to the rock upon which several programs of trade association research have grounded—namely, the application to the industry of the results of industrial research. It is not difficult, as the report points out, to prepare reports of research results, but to make sure that the members of the association apply these results and thus directly benefit from the work they support is quite another matter. As soon as the time comes when they think that the return is not adequate for their expenditure, there is either a curtailment of funds or internal dissension that may even cause the suspension of association work. The remedy would seem to be the creation of an educational section and of a strong utilization section in any trade association research organization and perhaps even in the scientific groups of our larger industries.

After all, science in industry is a comparatively recent innovation. More thought is being given to it than at any other period, and we may confidently expect even the major problems to be reduced to their component parts, which will be solved one by one.

Table d'Hote

A MENU offering so wide a choice as to meet the diversified tastes of chemists is in preparation for the Institute of Chemistry of the American Chemical Society. Preliminary announcements have been made and booklets, filled with detail, are available to those who will write for them. The Institute is not to be confused with any other chemical activity in this country. It is unique. It is designed for a special purpose, and we predict that those who procrastinate may find themselves deprived of one of the best opportunities which has been afforded American chemists.

If you are intent upon working every minute, the program of the Institute will afford opportunity for the utilization of your energy. The News Editions of May 10 and 20 indicated a number of courses which may be attended at will by those who desire no college credit for their summer's work. In this way a variety of topics, presented by specialists, can be heard. The morning until 11 o'clock can be thus occupied, while each day at that hour a general conference, for which some of the topics have been announced, will take place. Here recognized authorities will sum up for you the present status of the science in a particular topic, followed by general discussion. At the close of the conference interested groups will undoubtedly continue the discussion in the institute dining halls. Thereafter you may gather under the trees, at golf, or attend other courses. The laboratories will be open and every chance given for work. In the early evening scientific motion pictures and later additional lectures and similar events for instruction or entertainment will be offered. No doubt in many cases groups will continue discussions "and so on far into the night."

Are you less ambitious? Then look over the program and take what suits you, just as you choose from any table d'hote menu. There are the courses—many of them—the daily conferences, the contacts with those who share your interests, the motion pictures, the evening lectures. Certainly a wide variety!

Perhaps you are not in the mood for anything bordering on work. In that case not only can you do as you please, scientifically speaking, but you will find at State College the real recreation which mountains, streams, highways, and sports afford, with the opportunity always at hand to get just that degree of mental exercise you may desire, especially after a few days of simon-pure loafing have passed.

And all this at a cost which those who have seen the schedule of fees and living expenses agree is most reasonable!

Announcements relative to speakers, lecturers, and teachers clearly indicate the desirability of being at State College for at least a part of July. You are urged to reach a decision and to obtain full details from the several issues of the News Edition or direct from A. W. Kenney, Institute of Chemistry of the American Chemical Society, State College, Pa. This is an event of the Society so important to you as an individual that you cannot afford to disregard it in making your summer plans.

Department Chairmen

IT IS inevitable that the growth of appreciation of science on the part of industrial organizations should decimate the ranks of college and university professors, not leaving untouched department heads and chairmen. Much has been said regarding this policy, believed by many to be shortsighted, but while it should be clear that a shortage may soon develop in the supply of adequately trained scientific men if the machinery for their development becomes crippled, industry generally is inclined to let the future care for itself and to obtain for the direction of its own research men who have demonstrated leadership in the scientific field.

We sometimes think the freedom from some types of executive work is a part of the appeal which the industrial laboratory makes to the academic man, though a department head doubtless looks upon it as a different sort of administrative job, the details of which are more attractive. Certainly the farsighted industries offer a freedom for scientific work quite as much unhampered as that which the academic laboratory affords. Our schools are, therefore, faced with a new competition in which changing conditions have lost to them some of their former advantages.

Our colleges and universities should adopt a new policy if they are to attract and hold the professors necessary to train in America men satisfactory for the research laboratories of academic and industrial life. We see frequent examples of one major disadvantage in present policies. This is the promotion of a successful teacher or director of research to an executive position for which he may not be temperamentally fit and which really does not attract him, so far as its duties and opportunities are concerned. Many a good scientist has been spoiled to make a poor executive. The obvious way out of this difficulty is to recognize at once that there is a place in any great development for an executive head, call him what you will, who does not necessarily have to be the greatest man in his specialty. Of course he must have a broad sympathy with the science and some actual experience in it, but if he is the right sort of man he will not hesitate to secure for the department the best available teachers and directors of research, even if all of them rank far above him in scholastic standing and perhaps in monetary remuneration as well. Such an executive would work for the advancement of these men according to their results. He would not disturb them in the work of their choice, but would see that everything possible was done to make the productive men more productive and to eliminate quickly the non-producers. Such an executive would also relieve those successful in teaching research of multitudinous committee meetings, the details concerning purchases, and a host of other activities which now serve merely to divert them from their main purpose. Such an arrangement might appear as an addition to overhead, but it is the kind of overhead that becomes a good investment through releasing productive men from non-productive activities.

Another factor worthy of serious consideration is the precedent that has become established of considering members of the faculty as appointed for life after they have been promoted to a given rank, without regard to their productivity or their effort to remain abreast of the times. Promotion is slow but in most institutions it is certain, granted only good behavior and reasonable activity, and some men are passed along from grade to grade until they have a life position from which they cannot be budged except for grave misdemeanors. In consequence, we find here and there a faculty so loaded down with deadwood that its progress can be measured only in terms of geologic time, and science suffers as a result.

Several suggestions have been made for the correction of this situation. One is the adoption of the foreign plan, whereby professors are paid a small salary by the institution, deriving the remainder of their income from fees paid by their students who are given considerable leeway in choosing their courses. It is said that this plan is satisfactory to the successful leader of students, and soon indicates to the unsuccessful and unpopular man the desirability of seeking another location. No doubt there are other ways out, but it is high time that some practical solution should be developed and put into operation.

All that has been written and said concerning the need for the support of pure science research can be heartily endorsed, but unless great care is taken we shall find ourselves without an adequate scientific staff when the research funds become available.

Surprises in September

IT HAS been a matter of general regret that recent expositions of the chemical industries, while quite complete as regards equipment, have not displayed the actual products of the chemical industry, and particularly of chemicals, to the extent which all would have desired. We are glad to note that chemical products are to have a prominent place in the Eleventh Exposition, which opens September 26. The present list of exhibitors includes nearly fifty—a number are of foreign origin—which can be classified as chemical. The nature of these exhibits cannot be disclosed, but surprises are certain and it is hoped that many of them will be presented by the American chemical manufacturers.

Almost a new generation has made its appearance in the chemical industry since chemicals and chemical compounds were featured at the exposition. Manufacturers who have felt that all potential customers had been reached in former shows must now consider this new audience, which has come from the educational institutions and found its place in industry, as purchasers and users of equipment and materials.

The coincidence of a large number of new exhibits with visits by many who have but recently entered the chemical industry should make the Eleventh Exposition a long remembered event.

Anniversaries

THREE notable silver anniversaries have already come to us in 1927. We congratulate the American Electrochemical Society, the American Society for Testing Materials, and our contemporary, *Chemical and Metallurgical Engineering*, on rounding out a quarter of a century of very useful service. The societies celebrate with special meetings, while *Chemical and Metallurgical Engineering* has already issued its special anniversary number. To some, including our friends abroad, twenty-five years seems altogether too brief a time to deserve special notice but the records of the past quarter-century show that in a country so young as ours there has been much accomplished that is an inspiration for future growth and stimulation for continued development.

Lower Cost Arsenate

ONE interesting result of investigations made by the Chemical Warfare Service looking to the better control of the cotton boll weevil, the preliminary report of which we present in this issue, has been the development of a process which promises calcium arsenate in acceptable physical form at lower costs. The extent to which the cotton farmer can employ calcium arsenate is determined by the price of cotton and its relation to the price of this chemical compound. While both prices fluctuate between wide limits, it is obvious that a uniformly low-priced arsenate would encourage its more frequent and extensive use, thereby affording a more complete control of the boll weevil and consequent lower production costs for the cotton farmer. The perfection of the process is another indication of the peacetime utility of the Service. The careful consideration of its work in this field is recommended to all interested in the insecticide and fungicide question.

Youth No Handicap

THOUSANDS of young men and women will soon leave our colleges and universities to find their places in our economic structure. Some may feel bewildered when they consider what has been accomplished and have impressed upon them the seriousness of living and pursuing their work without the protection of student days. Few of us realize how much good work has been done by young men. It is to emphasize this that we pass along a note taken from *The Oil Can:*

> Martin Luther was twenty-nine when he wrote the manifesto that led to the Reformation.
>
> John Calvin was twenty-six when he wrote "The Institutes of Theology."
>
> Patrick Henry was twenty-seven when he made his speech against the Stamp Act.
>
> Thomas Jefferson was thirty-three when he drafted the Declaration of Independence.
>
> Alexander Hamilton was aide-de-camp of Washington at twenty, and at thirty-two first Secretary of the Treasury.
>
> Napoleon was twenty-seven when he was appointed to the command of the Army of Italy, and thirty-five when he crowned himself Emperor of the French.
>
> Alexander had conquered the known world and was dead at thirty.
>
> Charlemagne was master of France and Germany at thirty.
>
> James Fox was Lord of the Admiralty and a thorn in the side of George III at twenty-one.
>
> William Pitt became Chancellor of the Exchequer at twenty-three, and Prime Minister at twenty-four.
>
> Charles Dickens was twenty-four when he began "Pickwick Papers" and twenty-five when he wrote "Oliver Twist."
>
> Poe was doing some of his best work at twenty-five.
>
> Balzac wrote seventy-nine novels between the ages of thirty and forty-three.
>
> James Bryce had written "The Holy Roman Empire" at twenty-six.
>
> Benjamin Franklin had written "Poor Richard's Almanac" at the same age.
>
> David Hume at twenty-six had shocked all Christendom with his highly heretical "Treatise on Human Nature."
>
> Ruskin wrote "Modern Painters" at twenty-four.
>
> Stevenson had completed "Treasure Island" at thirty-three.
>
> Keats, Shelley, and Byron were dead at twenty-five, thirty, and thirty-six, respectively.
>
> Sheridan wrote "The School for Scandal" at twenty-seven.
>
> Shakespeare had completed ten of his greatest plays at thirty-two.
>
> Newton formulated the law of gravitation at twenty-four.
>
> McCormick and Westinghouse were twenty-three when they invented the reaper and airbrake.
>
> Michelangelo did his statue of David at twenty-six.

The list does not pretend to be complete. You can add your own heroes and heroines. Also, if you care to take the time, you will find an equally imposing list of men who did their best work after forty. The moral is, "There is no dead line on achievement, but it pays to start young."

In the American Manner

OUR contemporary, *Chemistry and Industry*, the official publication of the Society of Chemical Industry, has paid us the compliment of commenting editorially upon the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY, which holds its initial session at State College, Pa., beginning July 5. How we wish our British cousins in considerable numbers might find it possible to join us at State College! They would see a demonstration of how American chemists utilize such occasions to further projects similar to those which engage their attention at home. If, at times, progress has seemed slow we believe one cause to be the comparatively limited and often strictly selective acquaintance of the average British chemist with his fellows.

Not so long ago it was our privilege and pleasure to journey to the Pacific and return with a group of eminent British scientists, including some thirty chemists. We secured a list and set out to learn more of the activities and affiliations of these visitors. We began our inquiry by approaching a few of those chemists whom we had previously met. Imagine our astonishment upon finding that these chemists from overseas not only did not know each other but saw no particular reason why they should. These men had had the enterprise to journey from Great Britain; they had come on the same vessel; they had spent nearly two weeks together in Canada and were now setting out on a round trip journey across the American continent; and still they were unacquainted. It was a new experience to see two fellow scientists dining at the same small table in the diner of the special train quite in silence because they had never been introduced. And there were similar occasions quite beyond the understanding of the few Americans on the trip, to whom we believe some credit is due for the change in attitude of many individuals before the end of the journey. In consequence they not only took home some new acquaintances but left many lifelong friends in America.

Now if we could have a few of our British friends at State College, we would show them that a holiday and the science of chemistry can be admixed without detriment to either. They would find in the relaxation and informal discussions at the Institute of Chemistry many opportunities to ripen acquaintanceship into friendship and to further that type of wholesome coöperation and delightfully informal contacts which, in a very large degree, have been responsible for such progress as has been made, not only by the AMERICAN CHEMICAL SOCIETY, but by the American chemical industry and, indeed, by chemistry itself.

If adopted as a British policy, who can tell but that Chemistry House and a united association of all British chemists might not automatically follow?

Progress of Electrometric Control Methods in Industry[1]

By Henry C. Parker

Research Department, The Leeds & Northrup Co., Philadelphia, Pa.

A review is given of the present status of electrometric control in industry. Installations in various industries are described, including mercerizing, sulfuric acid manufacture, waste disposal, sugar manufacture, and in the waterworks and power plant fields. Several of the difficulties encountered in new applications are mentioned and the various advantages gained by electrometric control are discussed. The progress made within the last few years has been mainly due to improvements in the requisite apparatus.

DURING the past few years the progress in the use of electrometric control in industry has been quite marked. However, the advantages of these methods are only just beginning to be appreciated in the commercial world. The future progress in the field appears to be limited only by the complexity of some of the problems and by the not infrequent necessity for specifically adapting the control principles to individual cases. Although this engineering development work increases the cost of these installations, the advantages gained by obtaining a true record of concentration, as well as a more accurate control, have been proved to far outweigh the initial expense in at least the majority of cases where electrometric methods have been tried.

Recent Improvements in Apparatus

Cells and Electrodes—The recent progress in electrometric control has been given considerable impetus by the development of improved electrodes and cells. One of the first satisfactory types of industrial conductivity cell is shown in Figure 1. The electrodes are made of brass rods capped with gold and molded with Bakelite into a brass tube. The whole may be inserted through a gate valve, making a conveniently removable and sturdy cell, suitable for neutral or slightly acid solutions. The Bakelite makes tight joints with the brass rods and tube, which are capable of withstanding 300 pounds hydrostatic pressure without the use of any packing glands or cements. The gold caps are platinized and then sand-blasted to drive the platinum back into the gold, forming a surface which is such that polarization is negligible and which, under normal conditions of operation, requires no subsequent platinizing. This new type of surface has relieved the operator of the only remaining manipulation which is reminiscent of the research laboratory. At present these cells are being successfully used for measuring surface condenser leakage in a number of power plants in various parts of the country.

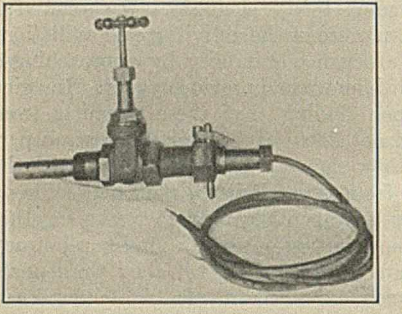
Figure 1—Removable-Type Conductivity Cell

It has not been found possible to eliminate the use of glass in the construction of cells for some types of service. In Figure 2 are shown two of the most convenient glass cells. The cell to the left is used as a standard for automatic temperature compensation,[2] while that to the right is the test cell. These cells are giving satisfaction in several types of service. When installed they are generally protected by a metallic or composition case.

Most of the improvements in H-ion measuring apparatus have been described previously.[3] In Figure 3, however, is shown for the first time a flow-type quinhydrone electrode which has been giving satisfaction in several types of service for over a year. The quinhydrone is put into cloth bags which are placed in the adapter at the base of the flow channel. The test solution flows past these bags of quinhydrone, becoming sufficiently saturated to supply the gold electrode. This apparatus can be used advantageously to obtain a record or a control through a pH range of about 3 to 7.5. In most solutions correct results will be given to a pH of 8.5, but the increased solubility of the quinhydrone makes its operation rather expensive. The rate of solution may be governed to some extent by using cloth bags of heavier material. This method of introducing the quinhydrone is much more convenient than regulating the rate of dropping of a saturated solution.

Conductivity Recorder—Not all of the recent improvements have consisted in the development of cells and electrodes. In Figure 4 is shown a connection diagram for a conductivity recorder which has several advantages. By moving the main slide wire the resistance of only a single bridge arm is altered, while in the conventional bridge one arm is increased while the other is diminished. A bridge connected as shown in the figure gives a scale which is linear in terms of conductance units. Since, in the large majority of solutions and over a short range of concentration, the conductance is proportional to the concentration, it is obvious that we can use a linear scale in connection with this Wheatstone bridge which reads per cent concentration in terms of a standard solution which is placed in the cell to the left in Figure 2. This scale is shown in Figure 5, where the recorder reads from 60 to 120 per cent. This scale means that if a 3 per cent solution is placed in the standard cell, and if the recorder reading is 100 per cent, the test has a concentration

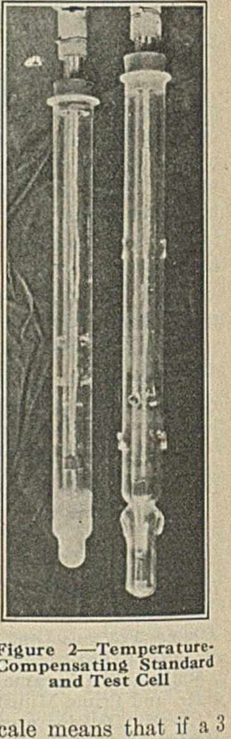
Figure 2—Temperature-Compensating Standard and Test Cell

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[1] Received March 9, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Bishop, U. S. Patent 933,015 (August 31, 1909).

[3] Parker and Dannerth, This Journal, 17, 637 (1925); Parker, *Ibid.*, 737 (1925).

of 3 per cent. If the recorder reading is 90 per cent, the concentration of the test solution is 90 per cent of the standard or 2.7 per cent, etc.

The dial marked *A*, Figure 5, is connected with the slide wire, *A*, in Figure 4. This slide wire gives a convenient means for adjusting the bridge for a difference in the constants of the two cells. It will be noted that the test cell (to the right in Figure 2) has a constant which is adjustable by raising or lowering the center tube. This adjustment is made while both cells are immersed in and measuring the same standard solution. The dial *A* is set at zero, the recorder is stopped at 100 per cent, and the center tube is then adjusted until the galvanometer is nearly balanced. Fine adjustment may be made by turning the dial *A*. If the test solution is being controlled at a concentration reading 100 per cent, and if it is desired to change the controlled concentration by 10 per cent, for example, this change may be made by turning the dial *A* through ten divisions. In this case the concentration of the test solution is found by adding or subtracting the reading of dial *A* from that indicated on the recorder. Changing the control point by shifting the dial *A* is easier than by turning the control disk.

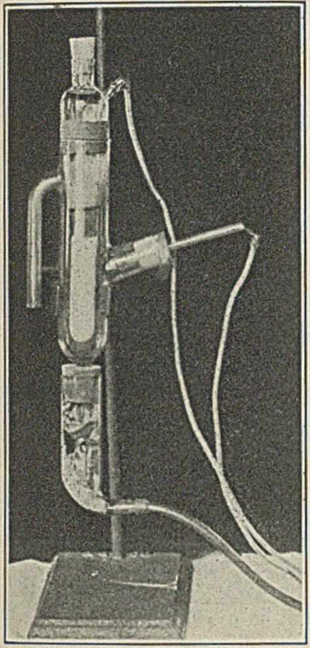

Figure 3—Flow-Type Quinhydrone Electrode

A similar diagram of connections forms the basis of a new portable conductivity bridge which reads in either ohms or reciprocal ohms on a linear scale,[4] and a bridge which reads directly in specific conductance units. This latter bridge was designed especially for measuring sugar ash.

AUTOMATIC TEMPERATURE COMPENSATION—Besides the above improvements, automatic temperature compensation has been developed for both H-ion and conductivity apparatus.

CONTROL IN VARIOUS INDUSTRIES

In the following sections it has been found most convenient to divide up the description of the different types of control under the headings of the various industries in which the particular control is operating. In a few industries both H-ion and conductivity controls are being utilized but in the majority the development has not progressed to this extent.

Mercerizing Industry

Some of the first adaptations of conductivity control were made in the mercerizing industry.[5] Among the several possible applications in this industry, the control of the acid bath, which is used for neutralizing the caustic carried over in the yarn from the mercerizing bath, is one of the most important. Close control in this bath is essential both to increase the uniformity of the dyeing and to prevent the deterioration of the yarn. The control obtained automatically is several times as accurate as that obtained by other methods.

In Figure 6 is shown a record obtained during the operation of automatic control in a plant that has been using the method successfully for about four years. In this type of control a solenoid valve, placed in the acid line, is operated automatically to keep the bath in the neighborhood of 3 per cent acid. When the record is at the left of the line on the chart, which represents a concentration of 3 per cent, the valve is open, and when at the right it is closed. If increased accuracy is desired, a by-pass may be used in the chemical supply line, to supply the minimum requirements of the system, while the solenoid valve supplies a slight excess. However, this type of control is capable of accuracy only in those cases where a tank or pond is available in which the cells may be placed and in which both mixing and equalization may take place. It is also limited to those cases where the flow is essentially constant.

In Figure 7 are shown the acid bath (at another plant) and the conductivity cell (indicated at *A*). Figure 8 shows the concentrated acid tank *A*, the solenoid valve *B*, and the recorder-controller.

Power Plants

SURFACE CONDENSER LEAKAGE—In power plants there are many problems that may be solved by electrometric control. One of the most important of these is the detection of surface condenser leakage, especially in stations using salt water for cooling. The prompt detection of leakage by conductivity instruments operating with alarm contacts has eliminated the expense of cleaning boilers which otherwise would have been "salted up." The same measurement in plants using surface water for cooling is only of slightly less importance, since measurements of leakage are necessary to prevent scaling of the boilers and to determine the efficiency of the turbines.

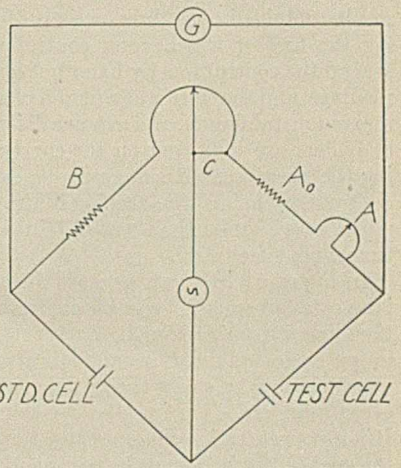

Figure 4—Bridge Circuit for Conductivity Recorder

The United States Navy was one of the first to adopt signal-light conductivity control for detecting condenser leakage. Figure 9 shows a four-point controller used on the new airplane carriers. The conductivity cell used most widely in these measurements has been shown in Figure 1.

If a recorder is used, with a cell in the condensate, the readings may be interpreted as parts per million of dissolved solids. If a measurement of the pounds of water per hour leaking into the condenser is required, it is also necessary to measure a sample of condensed steam which is free from leakage.[4,6]

H-ION CONTROL OF BOILER FEED WATER—H-ion control of boiler feed water has recently been perfected.[7] This is another important power plant application. The automatic installation in the Public Service Gas & Electric Company's

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[4] To be published in the near future.

[5] Parker, Greer, and Barba, *Am. Dyestuff Reptr.*, **16**, 49 (1927).

[6] Keeler, *Power*, **55**, 126 (1922).

[7] Parker and Greer, *J. Am. Water Works Assoc.*, **16**, 602 (1926).

station at Perth Amboy, N. J., is shown in Figure 10. The control is operating to regulate the addition of caustic soda and sodium phosphate to the boiler feed water and to keep the latter at a constant pH. The advantages are an increase in uniformity of the alkalinity in the individual boilers from day to day, and also in the boilers as a whole. This has resulted in less blow-downs. The control likewise acts as a degree of protection from condenser leakage, since additional chemicals will be added automatically to compensate for any leakage. In Figure 11 are shown the daily operating results obtained over three periods of two months each, during the first of which hand control was in use, during the second the control was by hand but governed by the recorder readings, and the third was a period of automatic control. The maximum, minimum, and average daily alkalinities of the bank of boilers are indicated on the curves—the circles representing the averages. It can easily be seen that the automatic control has enabled the keeping of the boiler alkalinity within much closer limits than was obtained by either of the other two types of control.

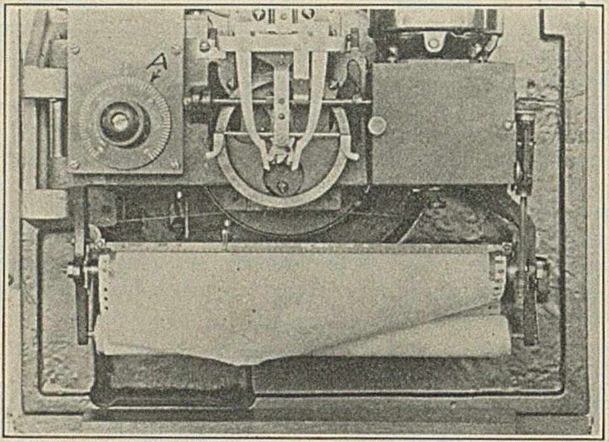

Figure 5—Conductivity Recorder

In Figure 12 is shown a record of the H-ion control. This illustrates a second type of control, which may be called the time lag–proportional step type. The recorder operates in two cycles—a recording and a controlling cycle—the timing of which may be easily changed to suit the conditions of any given problem. During the recording period a record of H-ion concentration is made and this period continues until the record has had time to register the effect of the last operation of the motor-operated valve. At this point the control cycle begins and an auxiliary e. m. f. is thrown in circuit, which is equal to the e. m. f. of the electrodes when the H-ion concentration is at the desired value. The recording carriage immediately starts to move over to the e. m. f. represented by this control point and the valve starts operating in such a direction as to correct the H-ion concentration to its desired value. When the recording carriage reaches the control voltage, the motor, which operates the valve, is thrown out of circuit. The displacement of the valve is thus proportional to the deviation of the H-ion record from the desired value.

From the record in Figure 12 it is evident that the plant was shut down about 1:00 A. M. The caustic added during the last operation of the valves was sufficient to keep the water in the feed heaters alkaline until the feed pumps operated for a short time at 3:00 A. M.

Since the position of the valve never deviates much from that required to supply the correct quantity of chemicals, this type of control is applicable even in those cases where no equalizing tank is available and where there is a considerable change in flow.

The proper setting of the control point is determined from the daily alkalinity analysis of the boiler water. By changing the setting to correspond to this analysis, it is, of course, evident that any errors due to inequalities among the tungsten electrodes are largely eliminated. When operated in this manner, electrodes have been in successful use over periods as long as six weeks. In this particular installation, where the pH averages about 8, it has been found that the electrodes are practically free from drift.

ACID TREATMENT OF ZEOLITE-SOFTENED WATER—In some of the plants using zeolite-softened water, sulfuric acid is being added both to reduce the boiler alkalinities, which may build up to a dangerously high value, and to maintain a required sulfate-caustic ratio. The flow-type quinhydrone electrode (Figure 3) has been successfully used, in this application, to hold the acid-treated water to a definite H-ion concentration. Automatic control appears feasible, but at present the recorder readings are used as a guide for the proper setting of a flow-proportioning device. When kept at a constant H-ion concentration, additional acid is added if the alkalinity of the untreated water increases. It would therefore be expected that this control would supply a feed water having an approximately constant sulfate-bicarbonate ratio which, after being concentrated and broken down (to caustic) by a definite degree in the boiler, would provide a definite sulfate-caustic ratio. In the first plant to use H-ion control this desirable result has been accomplished within close limits. This method presupposes an accurate control of the boiler blow-down and this has been supplied by conductivity measurements.

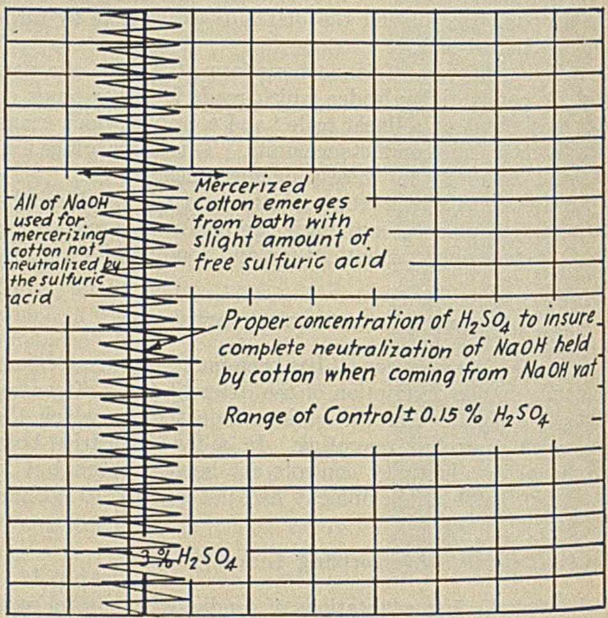

Figure 6—Conductivity Record in Control of Acid Bath in Mercerizing Process

CONTROL OF BOILER BLOW-DOWN POINT—The control of the boiler blow-down point is a very important electrometric application, from the standpoint of both saving heat and the prevention of priming and scaling. Conductivity measurements have been used successfully for this purpose for several years. When a very uniform method of feed-water treatment is used, such as zeolite softening or automatic H-ion control, the conductivity of the boiler water (at a definite temperature) may be related to its concentration. In some cases the alkalinity has been found practically proportional to the conductivity. Conductivity measurements, of course, cannot distinguish between the accumulation of salts and the alkalinity. The hydroxyl ion has approximately twice the mobility of any other ion in such a mixture, so the conductivity measurements, in most cases, are found to be rather closely related to the causticity. When the salts and the causticity are kept in a definite ratio, as best boiler operation undoubtedly dictates, it is evident that the conductivity may be used to measure the total concentration.

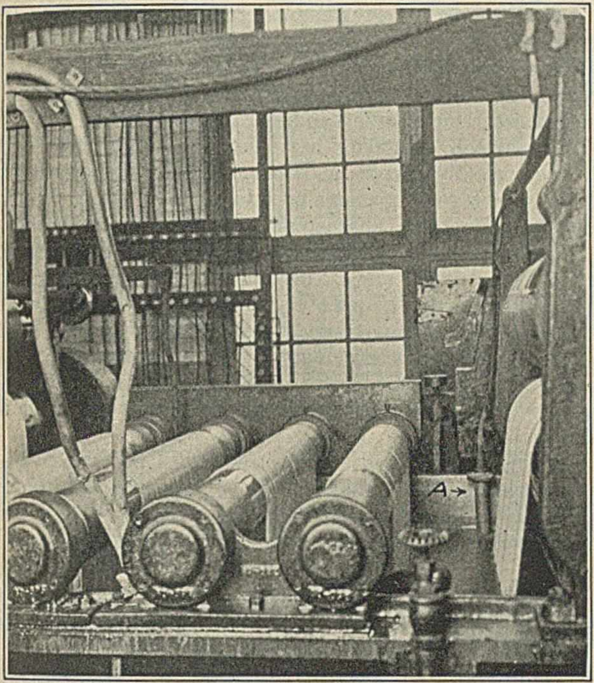

Figure 7—Mercerizing Bath with Conductivity Cell Installed

Measuring the conductivity of boiler water with a portable instrument, calibrated in conductance units, is considerably easier than an analysis by titration. The ideal method of measurement would consist in the installation of a cell inside the boiler. This is impracticable, at least for high-pressure boilers. However, in Figure 13 is shown a cell which has been installed in a continuous blow-down line at 150 pounds pressure. Indications are that the insulation will last at least two months under these conditions, after which it may be renewed. In this installation a record of boiler-water conductivity is being obtained and the blow-down valve is adjusted to keep this quantity constant. Analysis has shown that by this method the alkalinity of the boiler has been kept within ±10 p. p. m.

Control of Concentration in the Tail Race of Evaporators—The control of evaporator blow-downs is closely related to that of boilers, with the advantage in the former that the conductivity cells may be installed either in the blow-down line or directly in the evaporator. These measurements have resulted in less scale formation and in the saving of heat. An alarm may be used to indicate the correct time for a blow-down. It would also be feasible to operate a blow-down valve automatically, to keep the conductivity in the evaporator at a constant value.

Automatic Discarding of Contaminated Distillate—Evaporators are frequently subject to priming, and in several plants automatic controls have been installed for by-passing to the sewer any distillate having a conductivity above a certain value. This is an important precaution in those plants which, in increasing numbers, are supplying "make up" by evaporators. In this application a controller alone has been used without a record being obtained.

Waste Disposal

An automatic H-ion control has been recently installed at Winston-Salem in the sewage disposal plant which is being operated by the "direct oxidation" method. The control is of the time lag-proportional step type. The recorder-controller, gear reduction, and milk-of-lime dosing apparatus are shown in Figure 14. The last mentioned device[8] consists of a short flume with a wier at each end. One end of the flume serves as an overflow return, while the chemical feed flows over the wier at the other end. The flume is tilted automatically to supply more or less lime to the sewage.

Although H-ion or conductivity control operate to add chemicals in proportion to the flow, in this installation it was found that the combination of a long-time lag and exceedingly rapid fluctuations in the flow prevented the required accuracy from being obtained. Consequently, the apparatus shown in Figure 15 was installed in connection with a flowmeter. This device operates upon the "follow up" principle, and if the flow increases or decreases the chemical feed is increased or reduced in approximately the same proportion. The H-ion control serves to correct this rough adjustment to give a solution of constant H-ion concentration. The effluent is being kept at about 50 p. p. m. excess causticity and, as it is well known, this lies well over on the insensitive part of an H-ion titration curve. A slight difference in voltage of the tungsten electrodes is liable to introduce a considerable error. At this causticity the electrodes also exhibit a very slow drift to higher voltages. These difficulties have been overcome by using two electrodes in parallel, by changing one electrode every day, by using them in rotation and keeping them in a saturated sodium phosphate

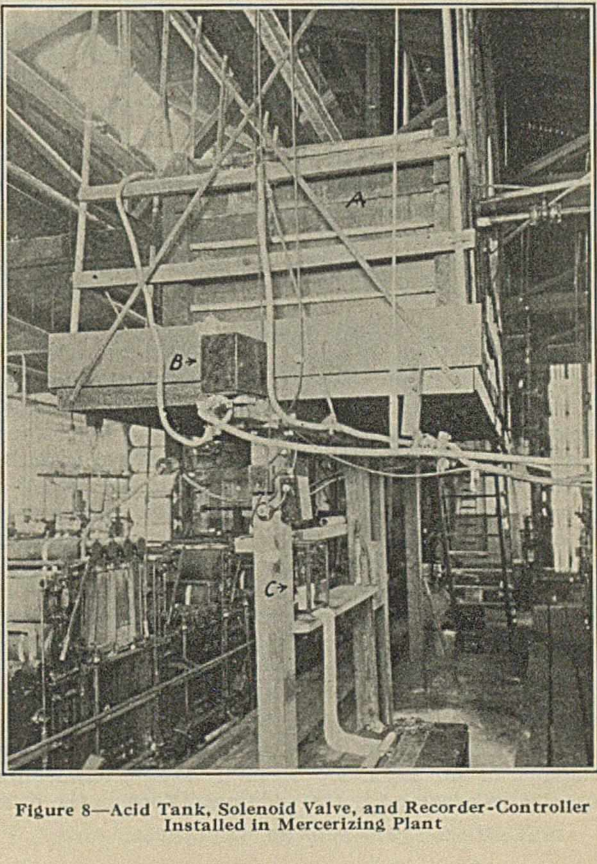

Figure 8—Acid Tank, Solenoid Valve, and Recorder-Controller Installed in Mercerizing Plant

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[8] Designed by the Direct Oxidation Process Corporation.

solution when not in use. The effluent is titrated for causticity shortly after placing a new electrode in service and the setting of the control points adjusted accordingly.

This installation represents the most difficult that has been met in practice. At a lower causticity the drift in voltage disappears and the electrodes become more sensitive. In spite of these difficulties, however, the combined control has been able to keep the effluent within approximately ±15 p. p. m. causticity. In most waste disposal problems it is believed that the addition of lime could be controlled more accurately and without the necessity for the flow-proportioning device.

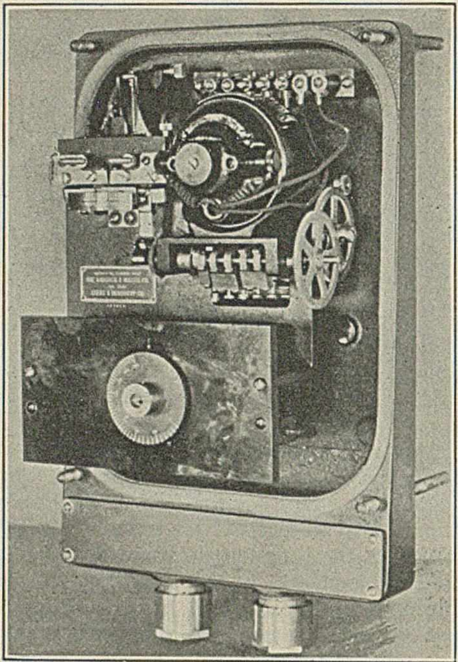
Figure 9—Four-Point Signal-Light Salinity Controller

Another application which promises success in the sewage disposal field is a control upon the addition of acid, which is necessary for obtaining satisfactory rates of filtration, in the activated sludge process. The flow-type quinhydrone electrode has been tested in this application and preliminary results are encouraging.

Sugar Industry

In both the beet and cane sugar industries there are several important applications for electrometric control. Probably none of these is more important than the second carbonation of beet sugar. H-ion records have been obtained with the tungsten electrode, in both this process and in the defecation of cane sugar.[9] In both cases a considerable improvement in control was obtained when the operator was using the recorder chart to determine the proper setting of the valve.

An experimental installation of automatic control of the liming of raw cane juice is being operated during the present season in Porto Rico. Tungsten electrodes are being used in connection with the time lag–proportional step type of control and the tilting weir box shown in Figure 14.

Another installation is using an H-ion recorder during the present campaign in Cuba. The recorder readings are being used in connection with signal lights to determine the proper valve opening for the addition of lime in the defecation process. This recorder has a scale reading in pH units. The readings of the tungsten electrode are checked against the quinhydrone electrode, and if there is a discrepancy in the readings the pen is shifted to give the correct value. The flow-type tungsten electrode (Figure 16) is used in this application. The solution is cooled to the neighborhood of 60° C. by flowing through the cooling coil to the left. It then flows up past the tungsten electrodes and calomel cell. Automatic temperature compensation is provided. The additional valves shown in the photograph provide means for draining the cooling oil and blowing live steam through the apparatus for cleaning and sterilizing purposes.

The tungsten electrodes have invariably been found to indicate correctly *changes* in H-ion concentration. In some solutions, however, they have been found to possess a slightly different pH-voltage characteristic from that determined with buffer solutions. In these cases, if an auxiliary method for checking is used, and if the control setting or the pen is shifted accordingly, a quite satisfactory control or record may be obtained. Since some type of auxiliary check, such as a titration or a measurement with the quinhydrone electrode, is generally in use already, this limitation is not serious. A check is usually necessary not more frequently than once a day.

The dip-type quinhydrone electrode with portable potentiometer, as shown in Figure 17, is being used satisfactorily by several sugar companies for the determination of H-ion concentrations. This combination has been found exceedingly convenient, and routine measurements may be taken probably more rapidly than by any other method. This method is particularly adapted to the measurement of the dark-colored solutions where colorimetric methods fail.

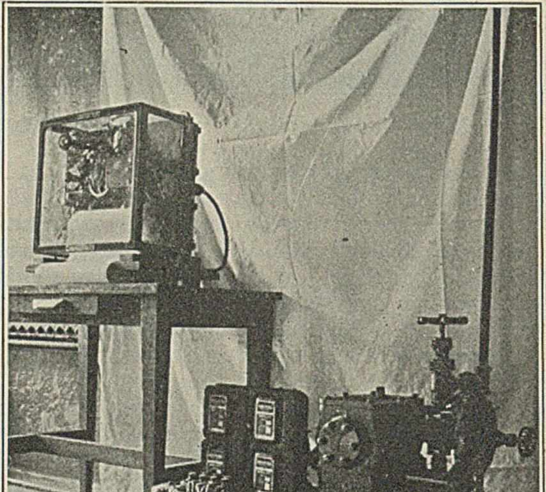
Figure 10—Recorder-Controller and Automatic Valve Used in Boiler Feed-Water Control

Many sugar companies are likewise using the conductivity method for the determination of sugar ash.[10] A new bridge, which reads directly in specific conductance, and which has hand temperature compensation, has been developed for this measurement. This bridge (Figure 18) has

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[9] Balch and Paine, *Planter Sugar Mfr.*, **75**, 347 (1925).

[10] For various references regarding this method see Zerban and Sattler, *Facts About Sugar*, **21** (December 4, 1926).

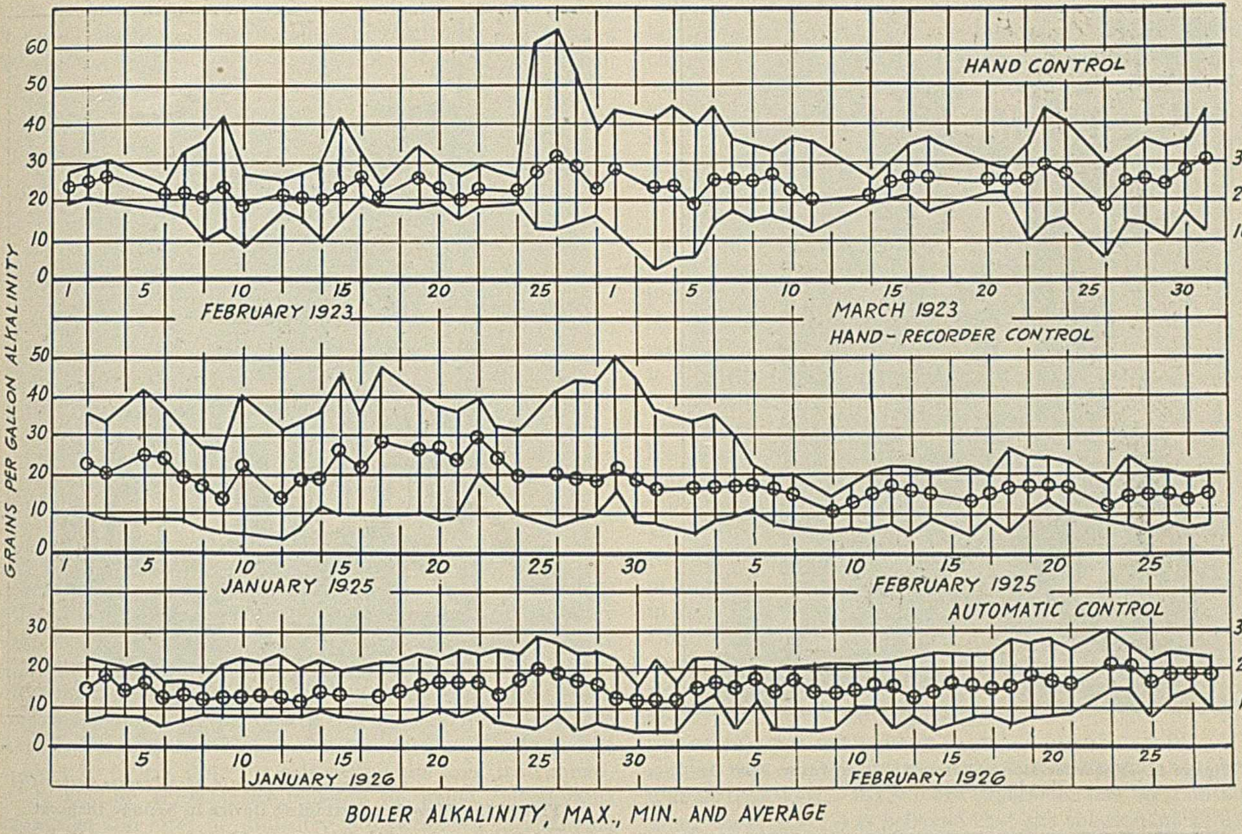

Figure 11—Improvement in Alkalinity Control of Boilers during Automatic Control

simplified the measurement to the point where the determination is easy even for a person who has never previously made a conductivity measurement.

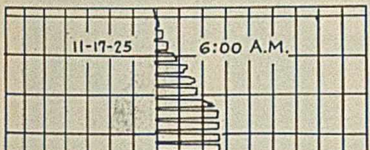

Figure 12—Record of Automatic Control of Boiler Feed Water

The Waterworks Field

The waterworks field presents many problems which may be satisfactorily solved by electrometric control. It is well known that there is a certain pH value at which a minimum quantity of alum is required for best clarification. Consequently, the recording of pH is an important factor in this field. Some success has been obtained with the tungsten electrode,[11] but in cases where the pH is below 8 an increase of accuracy (to ±0.05 pH) has been obtained with the flow-type quinhydrone electrode.

Many water purification plants add lime as a corrective to raise the pH and prevent troubles from corrosion and "red water." In this application the tungsten electrode has given satisfaction and where the pH averages less than 8 the quinhydrone electrode is applicable. Figure 19 shows an H-ion record obtained at the Montebello Filters, Baltimore, Md. The record was made with tungsten electrodes while recording the pH of the water after the addition of lime. The record to the right was obtained before the operator was told to watch the recorder chart, and that to the left while the operator was opening the valve in such a manner as to keep the pH at the proper value.

Sulfuric Acid Manufacture

Figure 13—Boiler Water Cell

In the contact process of sulfuric acid manufacture the double-cell principle of conductivity measurements has been in use many years for keeping the concentration of the absorbing acid at its proper value. Up to this time the measurements have been made with portable indicators and recorders. Owing to the rapid change of conductivity over the required range of concentration, it is evident that automatic control should be capable of giving considerable accuracy.

Miscellaneous Applications

In nickel-plating baths the dip-type quinhydrone electrode has proved very successful for measuring pH.[12] In

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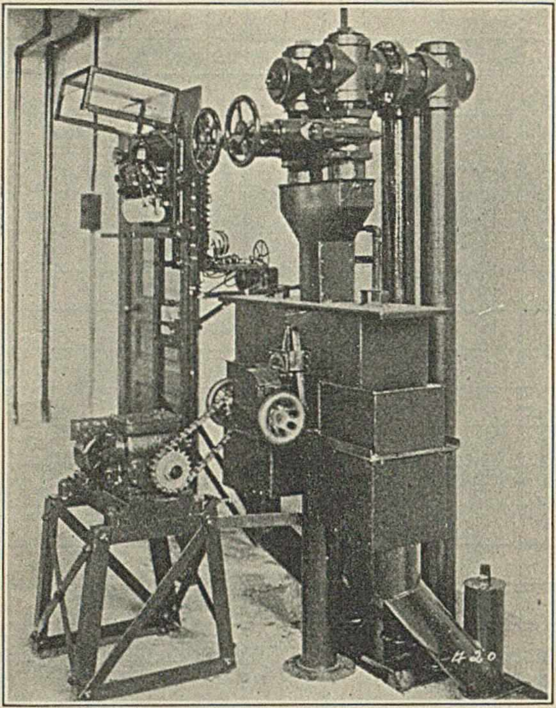
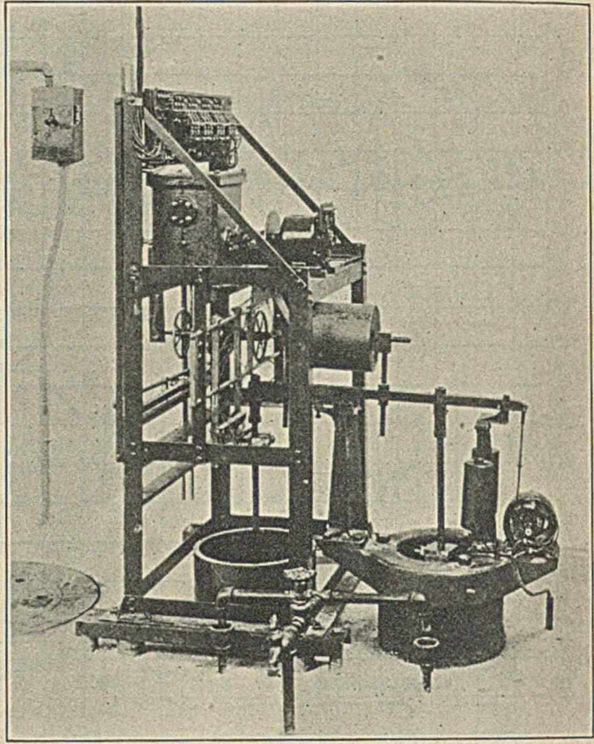
[11] Parker and Baylis, *J. Am. Water Works Assoc.*, **15**, 22 (1926).

[12] Parker and Greer, *Trans. Am. Electrochem. Soc.*, **49**, 451 (1926).



Courtesy of Direct Oxidation Process Corporation

Figure 14—Recorder-Controller and Tilting-Lime-Feed Device in Sewage Disposal



Courtesy of Direct Oxidation Process Corporation

Figure 15—Flow-Proportioning Device in Sewage Disposal

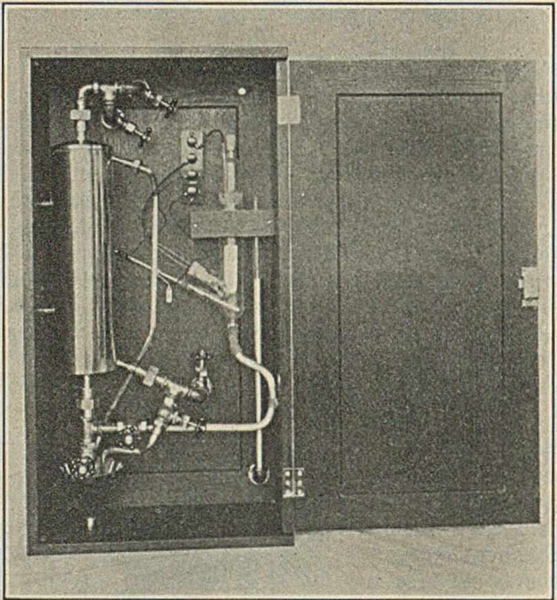


Figure 16—Flow-Type Tungsten Electrode as Used in Sugar Manufacture

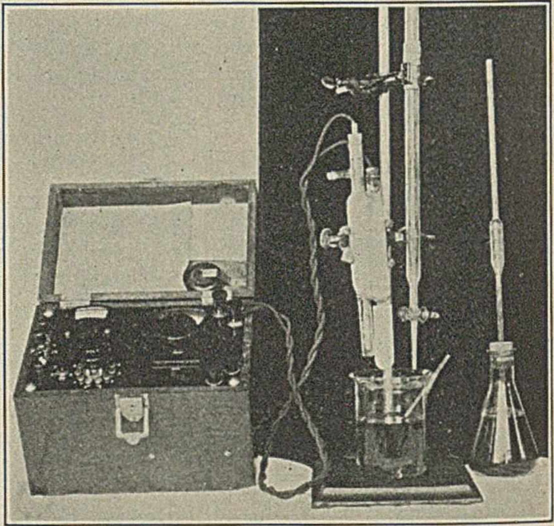


Figure 17—Dip-Type Quinhydrone Electrode with Portable Potentiometer

larger installations it is quite likely that automatic control of this quantity would be found advantageous.

Many other industries, such as the paper, baking, flour, dairy, tanning, ceramic, lithopone, etc., have found the dip-type quinhydrone electrode to be the most convenient method of making H-ion measurements and are gradually adopting it.

There are several miscellaneous uses to which conductivity and H-ion measurements have been put. Chemical laboratories which rely greatly upon the purity of their distilled water have installed conductivity recorders. The leakage of river water into artesian wells has been detected by conductivity methods. These measurements have also been used to detect the presence of water in oil wells, to detect contamination of river water by trade wastes, to measure concentration in various types of solutions, etc. In fact, there seems to be scarcely an industry in which chemistry plays an important role that would not find some advantageous use for electrometric measurements or control.

DISCUSSION

The progress of electrometric control has depended almost entirely upon the development of simplified and fool-proof cells and electrodes. The electrical measuring and control apparatus has been in a high state of perfection for several years. The present expansion has been due almost entirely to recent improvements in cells and electrodes which have finally been demonstrated to be commercially practicable.

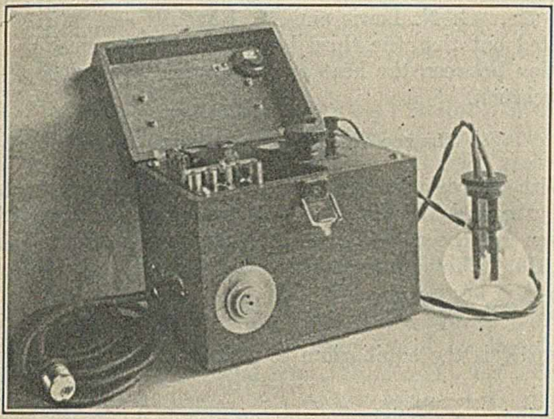


Figure 18—Specific Conductivity or Sugar-Ash Bridge

In applying electrometric control to industry, it is at times very difficult to predict whether a given problem is likely to be solved by this means. It is likewise almost impossible to predict the correct range for a recorder or controller, without making preliminary measurements at the plant in which the control is to be installed. Frequently it is advisable to permit the operator to make preliminary measurements in order to collect data for calibrating the final instrument. While making these measurements he gains considerable knowledge and later no difficulty is experienced in changing over to recording or control apparatus.

Recording apparatus which can be applied to a large number of quite different problems has helped to solve this difficulty. The recorder that uses a reference cell, in which various solutions may be placed, is a good example of this adaptability. Even in using this instrument, however, the proper range must be employed in order to obtain the desired sensitivity. Instruments have also been made with variable ranges in an attempt to solve these difficulties.

While the preceding description included the most important fields where electrometric control is at present employed in industry, no attempt will be made to summarize the possible uses to which such control may be applied in the future. In all the cases cited there are at least one or more installations in successful operation at the present time. Present progress is necessarily slow, owing to the necessity for overcoming various obstacles, many of which are peculiar to particular installations. After more experience has been obtained along these lines, it is believed that the subsequent progress will be relatively rapid.

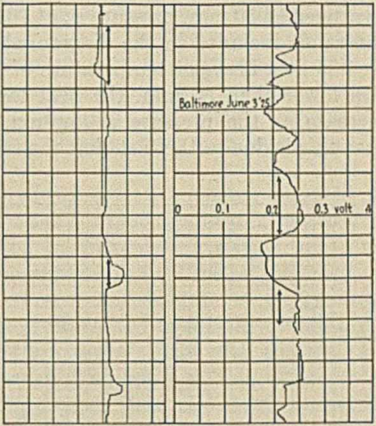


Figure 19—H-Ion Record, with Tungsten Electrode, at the Montebello Filters, Baltimore, Md.

Flames of Atomic Hydrogen[1,2]

By Irving Langmuir

Research Laboratory, General Electric Company, Schenectady, N. Y.

The heat carried away from an incandescent wire by a surrounding inert gas at ordinary temperatures increases roughly in proportion to the 1.9th power of the absolute temperature, T, of the filament.[2] This relation holds, for example, for such gases as nitrogen, argon, and mercury vapor up to the temperature of melting tungsten, 3660° K. In the case of hydrogen, however, abnormal results were obtained in experiments made at high temperatures. Up to about 1700° K. the normal exponent of 1.9 was observed, but at higher temperatures the exponent increased until at 2600° K. and above it was about 5.0. At 3400° K. the heat conducted by hydrogen was twenty-three times as great as that carried by nitrogen under similar conditions.

Nernst[3] in 1904 had developed the theory of heat conduction in a dissociating gas and had shown that dissociation results in a great increase in the heat conductivity. The dissociation products diffuse from the hot portions of the gas into the cold portions and there, by recombining, give up the large energy of the chemical reaction. This suggested that the abnormal heat conductivity of hydrogen at high temperatures is due to dissociation of the hydrogen into atoms according to the reaction

$$H_2 = 2H \qquad (1)$$

An abnormal heat conductivity might, however, be due to the formation of an endothermic polymorphic form of hydrogen such as H_3, corresponding, for example, to ozone. According to the law of mass action, the degree of dissociation of a gas into atoms must be greater at low pressures than at high, whereas the opposite would be true if molecules containing more than two atoms were formed.

At temperatures below 1700° K. the heat carried away by convection and conduction was greater at higher pressures of hydrogen than at lower pressures. For example, a wire of 0.0706 mm. diameter at 1500° K. dissipated over twice as much energy in hydrogen at 760 mm. as in hydrogen at 50 mm. pressure. At temperatures above 2700° K., however, more energy was dissipated at 50 mm. than at 760 mm. There are evidently two factors acting in opposite directions. Since the heat loss by convection and normal conduction increased with temperature according to a law which had been determined, it was possible to extrapolate

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[1] Received April 19, 1927. A major part of the subject matter of this paper was covered in an address under the same title delivered at the General Meeting of the American Chemical Society, Philadelphia, Pa., September 8, 1926. Preliminary publications have appeared in the *Gen. Elec. Rev.*, **29**, 153, 160 (1926).

[2] Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911); *Phys. Rev.*, **34**, 401 (1912); *J. Am. Chem. Soc.*, **34**, 860 (1912).

[3] Boltzmann Festschrift, p. 904 (1904).

to the higher temperatures, and then by subtracting this from the observed heat loss at the higher temperatures it was possible to find the energy that was carried from the filament by the dissociation (or association) that occurred. A portion of the data obtained in this way with a filament of 0.0706 mm. diameter at a series of different pressures is given in Figure 1.[4]

At temperatures from 2000° to 2400° K. more than twice as much heat is carried in this way from the filament in hydrogen at 50 mm. pressure as at 760 mm., but data beyond the range included in the diagram show that this ratio falls to 1.55 at a filament temperature of 3400° K. At pressures still lower than 50 mm. the heat loss does not continue to increase as the pressure is lowered, but calculation shows that this is due to the fact that the free path of the gas molecules is no longer negligible compared with the diameter of the wire so that there is a "concentration drop" of the modified hydrogen at the surface of the wire analogous to the temperature drop discovered by Smoluchowski.

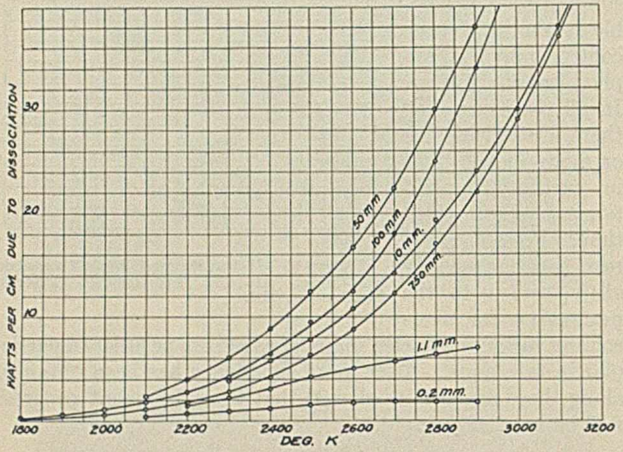

Figure 1—Heat Loss from a Tungsten Filament Due to Dissociation of Hydrogen by Filament in Hydrogen at Various Pressures

The marked increase in heat loss as the pressure was lowered proved that the heat was carried from the filament by a dissociation of the hydrogen into atoms. In fact, the amount of the increase was in quantitative agreement with a mathematical theory of the effect based on an assumed dissociation.

When the pressure was lowered to 10, 1.1, and 0.2 mm. the heat loss decreased with decreasing pressure (Figure 1), and decreased much more rapidly at the high temperatures than at the lower ones, so that finally (at 0.21, 0.04, and 0.015 mm.) it became independent of the filament temperature at temperatures above 2600° K. This indicates that the dissociation under these conditions is nearly complete, so that the rate of dissociation, which determines the heat loss, is limited only by the rate at which the molecules strike the surface of the wire. Quantitative calculations based on the kinetic theory confirmed this conclusion.

By means of these theoretical considerations it was possible to determine the degree of dissociation and the heat of the reaction by which atoms combine to form molecules. The results that were published in 1915 gave 90,000 calories as the heat of combination of 2 grams of hydrogen atoms at constant pressure and at 3000° K. The degree of dissociation,[5] x, expressed as the fraction of the molecules which have been dissociated, was found to be, at atmospheric pressure, 0.00165 at 2000° K., 0.0109 at 2400° K., and 0.0421 at 2800° K.

Since these experiments were made, more accurate data for determining the temperatures of tungsten filaments have come into use. G. N. Lewis and M. Randall[6] and others have pointed out that the third law of thermodynamics gives a relation between the heat of dissociation and the degree of dissociation.

Degree of Hydrogen Dissociation

With this relationship and the new temperature scale of Forsythe and Worthing,[7] the degree of dissociation of hydrogen has been recalculated from the experimental data of 1914. The results are expressed by the equation

$$\log_{10} K = -\frac{21{,}200}{T} + 1.765 \log_{10} T - 9.85 \times 10^{-5}\, T - 0.256 \qquad (2)$$

where K is the equilibrium constant defined by

$$K = p_1^2/p_2 \qquad (3)$$

p_1 being the partial pressure of atomic hydrogen and p_2 the pressure of molecular hydrogen, both expressed in atmospheres. Then if P is the total pressure, p_1 and p_2 are given by

$$p_1 = 2Px/(1 + x);\; p_2 = (1 - x)\,P/(1 + x) \qquad (4)$$

where x is the degree of dissociation.

The equilibrium constant K in equation (2) is also given by

$$K = 4Px^2/(1 - x^2) \qquad (5)$$

Table I gives the equilibrium constant K and the degree of dissociation at various temperatures as calculated from equations (2) and (5).

Note—This revision in the calculation of x changed the values of x calculated in 1915 to the following values:

T (° K.)	Old	New
2000	0.00165	0.00122
2400	0.0109	0.0104
2800	0.0421	0.0488
3200	0.117	0.154

From equation (2), by applying the Clapeyron equation, we can calculate H, the heat absorbed by the dissociation of the molecular hydrogen (at constant pressure), as follows:

$$H = 97{,}000 + 3.5\, T - 0.00045\, T^2 \qquad (6)$$

This is expressed in small calories per gram-molecule of hydrogen (2.016 grams). The heat of reaction Q at constant volume is

$$Q = 97{,}000 + 1.5\, T - 0.00045\, T^2 \qquad (7)$$

Note—This result for the heat of dissociation which was published in March, 1926,[1] is in excellent agreement with the value 98,570, subsequently found by Witmer[8] from studies of a hydrogen band spectrum found by Lyman. In a later paper[9] from a more careful analysis of similar data Witmer concludes that Q_0 is 100,000 ± 5000 calories.

Table I—Degree of Dissociation of Hydrogen into Atoms

T ° K.	K Atmos.	x (At 1 atmos.)	T ° K.	K Atmos	x (At 1 atmos.)
300	2.63×10^{-67}	2.56×10^{-34}	2800	9.58×10^{-3}	4.88×10^{-2}
1000	5.50×10^{-17}	3.71×10^{-9}	3000	3.30×10^{-2}	9.03×10^{-2}
1200	2.48×10^{-13}	2.48×10^{-7}	3200	9.78×10^{-2}	0.154
1400	1.04×10^{-10}	5.08×10^{-6}	3400	0.256	0.245
1600	9.81×10^{-9}	4.95×10^{-5}	3600	0.598	0.361
1800	3.42×10^{-7}	2.92×10^{-4}	3800	1.24	0.488
2000	5.93×10^{-6}	1.22×10^{-3}	4000	2.56	0.625
2100	2.02×10^{-5}	2.24×10^{-3}	4500	10.9	0.855
2200	6.18×10^{-5}	3.92×10^{-3}	5000	34.7	0.9469
2300	1.71×10^{-4}	6.54×10^{-3}	6000	169.0	0.9884
2400	4.36×10^{-4}	1.04×10^{-2}	7000	649.0	0.9969
2500	1.04×10^{-3}	1.61×10^{-2}	8000	1560.0	0.9987
2600	2.30×10^{-3}	2.40×10^{-2}	9000	3030.0	0.9993
2700	4.82×10^{-3}	3.48×10^{-2}	10000	5000.0	0.9996

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[4] Langmuir and Mackay, *J. Am. Chem. Soc.*, **36**, 1708 (1914).

[5] Langmuir, *Ibid.*, **37**, 417 (1915); **38**, 1145 (1916).

[6] "Thermodynamics," p. 470, McGraw-Hill Book Co., New York, 1923.

[7] *Astrophys. J.*, **61**, 146 (1925).

[8] *Proc. Natl. Acad. Sci.*, **12**, 238 (1926).

[9] *Phys. Rev.*, **28**, 1233 (1926).

Chemical Properties of Atomic Hydrogen

While the measurements of the heat losses from filaments in hydrogen were being made, other experiments[10] showed that hydrogen which had been in contact with heated filaments acquired entirely new chemical properties, and they were quite in accord with those to be expected of an atomic form of the element.

If a tungsten or platinum filament is heated to 1300° K. or more in dry hydrogen at low pressures, preferably less than 1 mm., a limited amount of the hydrogen gradually disappears or cleans up. When the limiting clean-up has taken place no additional clean-up occurs if a second filament is lighted, so we know that the gas is not absorbed by the filament. It was found that part of the hydrogen can be recovered by heating the bulb. The amount of hydrogen that can be cleaned up increases considerably, but not indefinitely, when the bulb is kept cooled by liquid air. If the liquid air is removed after the filament has been allowed to cool, the excess of absorbed hydrogen is evolved but does not recondense when the liquid air is replaced unless the filament is again lighted. The hydrogen on the bulb is thus not in the form of liquefied or solidified atomic hydrogen, but is held there rather as an adsorbed film. Hydrogen atoms striking a bare glass surface can condense, but if they strike atoms already on the surface they combine with these and the molecules escape.

The maximum amount of hydrogen that can be adsorbed by glass cooled in liquid air was found to be 0.03 cu. mm. per sq. cm., the hydrogen being measured at atmospheric pressure and temperature. This corresponds to 1.5×10^{15} atoms per sq. cm. If these are arranged in a close-packed lattice on the surface their distance between centers would be 2.78×10^{-8} cm. The diameter of the electron orbit in the Bohr hydrogen atom is 1.06×10^{-8} cm. This result confirms the theory that impinging hydrogen atoms combine with adsorbed hydrogen atoms which they strike. If the glass surface is allowed to warm up to room temperature some of the atoms can react with adjacent atoms and thus escape as molecules.

The atomic hydrogen adsorbed on glass is capable of reacting rapidly with oxygen at room temperature and slowly even at liquid-air temperature. Thus if hydrogen is cleaned up by a heated filament on to a bulb cooled in liquid air, and oxygen is admitted after cooling the filament, the oxygen disappears very slowly; but when the liquid air is removed an amount of oxygen suddenly disappears which is the chemical equivalent of the hydrogen that was previously cleaned up. This removal of the adsorbed hydrogen makes it then possible to clean up another portion of hydrogen on to the bulb when the filament is lighted.

Atomic hydrogen from a filament in hydrogen at low pressure, even after diffusing through several feet of glass tubing at room temperature, can manifest itself by reducing such metallic oxides as WO_3, CuO, Fe_2O_3, ZnO, or PtO_2.[11] The blackening of WO_3 or ZnO thus serves as a means for detecting atomic hydrogen. An oxidized piece of copper rapidly acquires a metallic luster. The fact that the atoms can pass through a long crooked tube proves that adsorbed hydrogen atoms can evaporate from glass surfaces at room temperature. Experiments showed that no atomic hydrogen passed through a trap cooled in liquid air, so that at this temperature the evaporation of the atomic hydrogen does not occur. A plug of glass wool in a tube at room temperature also stops the passage of the atoms.

A well-exhausted tungsten filament lamp was connected through a glass tube to a Hale-Pirani vacuum manometer[12] which contained pure platinum wire 0.028 mm. in diameter and 45 cm. long heated to about 125° C. by the passage of a current of 0.0092 ampere. The resistance of the platinum wire was used to measure the pressure of the residual gas in the lamp. After the lamp had run about 50 hours at normal efficiency (2400° K.) the resistance of the platinum wire had *increased* 0.12 ohm, the original resistance having been about 96 ohms. Investigation showed that this increase of 0.125 per cent in resistance was caused by atomic hydrogen which diffused into the platinum wire. The increase in resistance persisted for days after the tungsten filament was turned off, but the resistance returned to normal either after heating the platinum wire or after admitting a little oxygen and then pumping it out again, the platinum wire being kept at 125° C.

The dissociation of hydrogen by a tungsten filament at 1500° K., which causes a fairly rapid clean-up of dry hydrogen, is entirely prevented by pressures of oxygen or water vapor of an order of magnitude of 10^{-9} mm.[13] A very remarkable phenomenon occurs if a mixture of oxygen and hydrogen at low pressure is admitted to a bulb containing a filament at 1500° K. The oxygen reacts with the filament rapidly to form WO_3, which evaporates at this temperature as fast as formed. The oxygen thus cleans up at a rate proportional to its own pressure and the pressure of oxygen thus falls to half value about every 2 minutes in a bulb of ordinary size. All this occurs exactly as though no hydrogen were present. During this time there is no measurable disappearance of hydrogen. After 10 or 15 minutes the oxygen is nearly all gone and then for 5 or 10 minutes more the gas pressure remains apparently constant and corresponds exactly to that of the hydrogen which was admitted. Then suddenly, when the pressure of oxygen is low enough (10^{-9} mm.), the hydrogen begins to disappear by dissociation and in a few minutes the pressure falls practically to zero. Water vapor has an effect similar to oxygen in preventing the dissociation of hydrogen. At filament temperatures of 1750° K. some of the hydrogen disappears while the oxygen is cleaning up, but the kink in the curve still occurs when the oxygen is gone. Water vapor and oxygen are thus powerful catalytic poisons for the reaction of the hydrogen dissociation.

Arcs in Hydrogen at Atmospheric Pressures

Several years ago in this laboratory studies were made of arcs between tungsten electrodes in various gases. Arcs in hydrogen were remarkable because of the high voltage drop and small cross section. A 10-ampere, direct-current arc between heavy tungsten electrodes about 7 mm. apart in a bulb containing pure hydrogen at atmospheric pressure appeared as a sharply defined, brilliant red line about 0.5 mm. in diameter along which the potential gradient was 150 volts per centimeter, making a power dissipation of 1500 watts per centimeter of length, this being about fifteen times as great as in nitrogen or argon. This abnormal behavior of hydrogen was attributed to the dissociation which carried energy so rapidly out of the arc.

Arcs in Hydrogen at Low Pressures

In attempting to obtain the Balmer spectrum of hydrogen without contamination by the secondary spectrum, Wood[14] built very long vacuum tubes of moderate bore, in which he passed currents as large as 20 amperes through moist hydrogen at about 0.5 mm. pressure. He observed

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[10] Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912).

[11] Langmuir, *Proc. Am. Inst. Elec. Eng.*, **32**, 1894 (1913); *Trans. Am. Electrochem. Soc.*, **29**, 294 (1916).

[12] Hale, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911).

[13] Langmuir, *J. Am. Chem. Soc.*, **38**, 2271 (1916); *Trans. Am. Electrochem. Soc.*, **29**, 261 (1916); *Gen. Elec. Rev.*, **25**, 445 (1922).

[14] *Proc. Roy. Soc.*, **102**, 1 (1922); *Phil. Mag.* **44**, 538 (1922).

many remarkable phenomena. Short pieces of tungsten wire projecting into the discharge were heated to incandescence, although a fine thread of glass or a platinum wire in a similar position was apparently not heated by the discharge. On drying the hydrogen with phosphorus pentoxide the secondary spectrum (due to molecular hydrogen) appeared strongly and the Balmer spectrum (due to atomic hydrogen) nearly disappeared. The heating of the tungsten wire was also prevented by drying the hydrogen.

In correspondence with Professor Wood, the writer pointed out that oxygen and water vapor decrease the rate of dissociation of hydrogen in contact with tungsten and must thus also tend to prevent the recombination of hydrogen atoms on a tungsten surface. He also suggested that moisture poisons the catalytic activity of the dry glass surfaces that otherwise converts atomic into molecular hydrogen. Thus with moist hydrogen the tube becomes filled with nearly pure atomic hydrogen and the diffusion of this to the catalytically active tungsten wire causes the heating of the latter. Calculations based on the measured heat of dissociation proved that a pressure of only 0.16 mm. of atomic hydrogen at 500° C. would suffice to maintain a tungsten filament at 2400° K.

These conclusions were confirmed by Wood's observations that the walls of the tube became only slightly heated if the hydrogen was moist, whereas they were strongly heated with dry hydrogen. A tungsten wire was heated red hot even when mounted in a side tube (of 5 mm. diameter) at a distance of 4 cm. from the discharge tube, showing that the hydrogen atoms could diffuse in relatively large quantities out of the discharge.

It occurred to the writer that it should be possible to obtain even higher concentrations of atomic hydrogen by passing powerful electric arcs between tungsten electrodes in hydrogen at atmospheric pressure and this atomic hydrogen could be blown out of the arc by a jet of molecular hydrogen directed across the arc.

Preliminary Experiments with Flames of Atomic Hydrogen

To try out the possibility of blowing atomic hydrogen out of an arc, 20-ampere arcs from a constant-current transformer were passed between two tungsten rods 6 mm. in diameter mounted transversely in a horizontal alundum tube (10 cm. diameter) through which a stream of hydrogen flowed. With voltages from 300 to 800, arcs could be maintained with electrode separations up to 2 cm. The magnetic field of the arc caused it to move transversely so that it became fan-shaped. Iron rods 2 or 3 mm. in diameter melted within 1 or 2 seconds when they were held 3 to 5 cm. above the arc.

By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame. To maintain the arc in a stable condition the electrodes were brought close together (1 to 3 mm.), but the arc did not remain entirely between the electrodes, but extended as a fan to a distance of 5 to 8 mm. The flame of atomic hydrogen, however, extended far beyond the arc. At distances of 1 or 2 cm. from the arc molybdenum (m. p. 2900° K.) melted with ease. Near the end of the arc tungsten rods and even sheet tungsten (m. p. 3660° K.) could be melted.

The use of hydrogen under these conditions for melting and welding metals has proved to have many advantages. Iron can be melted without contamination by carbon, oxygen, or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminum, silicon, or manganese can be melted without fluxes and without surface oxidation.

Temperature of Atomic Hydrogen Flame Compared with Other Flames

Let us suppose we could obtain atomic hydrogen in bulk at atmospheric pressure and room temperature and that we could then let this "burn" to the molecular form in a flame. What would be the temperature of this flame and how would it compare with that of other flames? Taking the heat of reaction (for 2 grams) to be 98,000 calories and taking the specific heat of molecular hydrogen (for 2 grams) to be 6.5 + 0.0009 T, we find that the heat of the reaction would be sufficient to heat the hydrogen to 9200° K.

The dissociation of the hydrogen, however, would prevent the temperature from rising to any such high value. If x is the degree of dissociation at the maximum temperature reached, the available heat of recombination is only $(1-x)$ 98,000.

The heat in calories, Q, needed to raise the temperature of a gram molecule of gas from room temperature (300° K.) to T at constant pressure is[15]

For H (atomic) $Q_1 = 4.97\ T - 1490$

H_2 $Q_2 = 6.50\ T + 0.00045\ T^2 - 1990$

CO or O_2 $Q_3 = 6.50\ T + 0.00050\ T^2 - 2000$

H_2O $Q_4 = 8.81\ T - 0.00095\ T^2 + 7.4 \times 10^{-7}\ T^3 - 2570$

CO_2 $Q_5 = 7.0\ T + 0.00355\ T^2 - 6.2 \times 10^{-7}\ T^3 - 2400$

Thus the temperature that could be reached by the recombination of hydrogen atoms starting from room temperature and atmospheric pressure can be calculated by the equation

$$(1 - x)\ H_0 = 2xQ_1 + (1 - x)\ Q_2 \tag{8}$$

where H_0 is the heat of combination of 2.016 grams of atomic hydrogen at room temperature (98,000 calories). Introducing the values of Q_1 and Q_2 in this equation and solving for x we find

$$x = \frac{100{,}000 - 6.50\ T - 0.00045\ T^2}{97{,}000 + 3.44\ T - 0.00045\ T^2} \tag{9}$$

We can thus plot a curve giving x as a function of T. But the data of Table I enable us to plot another curve of x as a function of T. These two curves intersect at T = 4030° K. and x = 0.642. Thus atomic hydrogen at room temperature and atmospheric pressure would heat itself to 4030° K. and the degree of dissociation would then be 0.642.

The temperature of the oxyhydrogen flame can be calculated in an analogous manner, taking into account the dissociation of the water vapor into oxygen and hydrogen and the dissociation of the molecular hydrogen into atomic. This rather laborious calculation shows that the combustion of a mixture of two volumes of hydrogen with one of oxygen at room temperature (300° K.) and atmospheric pressure produces enough heat to raise the reaction products to 3130° K. The reaction is

$$2H_2 + O_2 = 1.652\ H_2O + 0.249\ H_2 + 0.198\ H + 0.174\ O_2 \tag{10}$$

Thus the composition (by volume) of the flame gases at this maximum temperature is water vapor 72.68, molecular hydrogen 10.95, atomic hydrogen 8.71, and molecular oxygen 7.66 per cent. At this temperature the equilibrium constant for the dissociation of hydrogen according to the data of Table I is K = 0.068 atmosphere. The corresponding equilibrium constant for the dissociation of water vapor at 3130° K. is[16]

$$K = (H_2)^2\ (O_2)/(H_2O)^2 = 0.00170 \tag{11}$$

where the parentheses represent pressures in atmospheres.

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[15] The specific heats for these calculations were taken from a table on p. 80 of Lewis and Randall's "Thermodynamics."

[16] Langmuir, *J. Am. Chem. Soc.*, **28**, 1357 (1906).

In the flame gases the water vapor is 17.4 per cent dissociated and the hydrogen is 27.4 per cent dissociated.

For the combustion of acetylene with oxygen we may consider the reactions:

$$C_2H_2 + {}^5/_2\, O_2 = 2\, CO_2 + H_2O + 302{,}000 \text{ calories} \qquad \text{I}$$
$$C_2H_2 + {}^3/_2\, O_2 = 2\, CO + H_2O + 166{,}000 \text{ calories} \qquad \text{II}$$
$$C_2H_2 + O_2 = 2\, CO + H_2 + 102{,}600 \text{ calories} \qquad \text{III}$$

In a flame having the proportion of oxygen given in the first reaction the flame gases would contain a relatively large amount of oxygen owing to the dissociation of both the carbon dioxide and the water vapor. For oxy-acetylene welding such strongly oxidizing flames are avoided and the oxygen ratio is cut down nearly as low as that in reaction III.

Let us calculate the temperature and flame composition for this case. The reaction does not go to completion as indicated above in reaction III, but should be written

$$C_2H_2 + O_2 = 2\, CO + n_2H_2 + n_1H \qquad (12)$$

where

$$n_2 + {}^1/_2 n_1 = 1 \qquad (13)$$

The heat of the reaction, $102{,}600 - (1 - n_2)\, 98{,}000$ calories, must equal the heat content of the reaction products $2Q_3 + n_2Q_2 + n_1Q_1$. From the resulting equation we find

$$n_1 = \frac{108{,}600 - 19.5\ T - 0.00145\ T^2}{48{,}500 + 1.72\ T - 0.000225\ T^2} \qquad (14)$$

The partial pressures of H and H_2 are

$$p_1 = \frac{n_1}{2 + n_1 + n_2} = \frac{n_1}{3 + {}^1/_2\, n_1} \qquad (15)$$

and

$$p_2 = \frac{1 - {}^1/_2\, n_1}{3 + {}^1/_2\, n_1} \qquad (16)$$

so that the equilibrium constant is

$$K = \frac{p_1^2}{p_2} = \frac{n_1^2}{(1 - {}^1/_2\, n_1)(3 + {}^1/_2\, n_1)} \qquad (17)$$

At any assumed temperature we can calculate n_1 and thus get K as a function of T. We also get K as a function of T from Table I. The intersection of the two curves gives $T = 3270°$ K.; $n_1 = 0.5676$; $n_2 = 0.7162$.

Thus we conclude that when acetylene burns with an equal volume of oxygen the maximum temperature may rise to 3270° K. and at this temperature the composition of the flame gas is carbon monoxide 60.9 per cent, molecular hydrogen 21.8 per cent, and atomic hydrogen 17.3 per cent by volume.

There is another factor which tends greatly to increase the temperature of the atomic hydrogen flame even above the calculated value of 4030° K. The atomic hydrogen, instead of being originally at room temperature, is already at a high temperature at the moment of its escape from the arc. The conditions are analogous to those in an oxy-hydrogen flame in which both gases are preheated. Thus the upper limit of temperature is fixed only by the degree of dissociation of the hydrogen and the rate at which heat is lost by radiation or contact with bodies of lower temperature.

Rate of Surface Heating by Flames

Although the high temperature of the atomic hydrogen flame is of great importance when it is desired to melt substances of very high melting point such as tungsten, a factor of even greater importance in ordinary welding operations is the rapidity with which heat can be delivered to a surface per unit area.

In order to determine this rate of surface heating for various kinds of flames, the device shown in Figure 2 was constructed. It consists essentially of a short rod of tungsten, *A*, so arranged that heat from the flame can be applied only to the circular surface forming its upper end, while its lower end is in good thermal contact with a large mass of copper, *B*, which removes the heat from the tungsten rod as fast as it is delivered by the flame. To prevent the flame from striking the sides of the rod, a water-cooled circular plate or guard ring of copper, *C*, is used. To obtain good thermal contact between the tungsten rod and the copper, the mass of copper *B* was made by casting it around the tungsten rod which had previously been covered with copper by heating with copper in an atmosphere of hydrogen. The tungsten rod had a diameter of 0.77 cm. and the portion extending out of the copper mass had a length of about 0.8 cm. The hole in the copper plate was 0.95 cm. in diameter. The weight of the copper block *B* was 8100 grams and the diameter of its cylindrical part was 10 cm.

The temperature of the copper block was measured at half-minute intervals by means of a mercury thermometer placed in a hole which had a diameter only slightly larger than the thermometer and into which oil had been introduced to make better thermal contact between the thermometer and copper.

When the atomic hydrogen or other flame was directed against the tungsten tip the rate of temperature rise of the copper block gave a measure of the rate of surface heating. The flame was applied for a definite time which ranged from 2 to 5 minutes, during which time the temperature rose 40° to 80° C. After the flame was removed the thermometer readings continued to rise for a couple of minutes because of the time needed for the heat to become uniformly distributed throughout the copper block. Readings were continued for several minutes more in order to determine the rate of cooling so that correction could be made for the slight loss of heat that occurred before the maximum temperature was reached. This correction rarely amounted to more than 5 per cent.

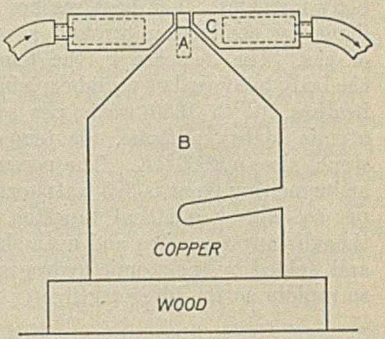

Figure 2—Apparatus for Measuring Rate of Surface Heating Produced by Flames

Table II—Rate of Surface Heating Produced by Various Flames

		Watts/sq. cm.
(1)	Ordinary Bunsen burner (gas-air) at tip of inner cone. Flame 15 cm. high, cone 4.5 cm. high	51
(2)	Ordinary blast lamp (gas-air), 14 cm. from burner tip in flame 25 cm. long, nozzle 0.60 cm. diameter	57
(3)	Same at 19 cm. from burner tip (hottest part)	73
(4)	Ordinary blast lamp (hydrogen-air), 13 cm. from burner tip	100
(5)	Blast lamp for quartz blowing (gas-oxygen) 2.5 cm. from burner tip	450
(6)	Same with hydrogen-oxygen	520
(7)	Acetylene welding torch, adjusted for maximum effect (several different tips gave about the same result)	670
(8)	Atomic hydrogen flames:	

Amperes	Volts	Mm. from tips	
20	100	3	580
		5	640
		7	400
40	75	3	1000
		5	1140
		7	900
		10	620
60	65	5	1300
		7	1100
		10	850
		15	500
		20	330
		30	190
		40	130
		50	95

The rate of surface heating in watts per square centimeter was then calculated from the temperature rise, the time of application of the flame, the area of the end of the tungsten tip (0.466 sq. cm.), the mass of copper and its specific heat (0.394 watt second per gram per degree). A summary of the results is given in Table II. Except where specifically noted, the conditions for the use of each flame were chosen to give the greatest possible rate of surface heating.

The rate at which heat is delivered to a tungsten surface by the atomic hydrogen flame produced by a 60-ampere arc (1330 watts per sq. cm.) is thus twenty-six times as great as that from a Bunsen burner flame and about double that from the flame produced by the ordinary oxy-acetylene welding torch.

According to the Stefan-Boltzmann law the heat radiated from a body at high temperature is

$$W_R = 5.7\,E\left(\frac{T}{1000}\right)^4 \text{ watts per sq. cm.} \qquad (18)$$

where E is the emissivity of the body ($E = 1$ for a black body).

If a Bunsen burner flame delivers 51 watts per sq. cm. to the whole surface of a black body, it would thus heat it to 1730° K. If heat is applied by the flame to one side of a plate-shaped body and the heat is radiated from both sides, the temperature would be 1450° K. The fact that the Bunsen flame does not heat bodies so hot as this indicates that the rate of surface heating decreases as the temperature of the body increases. The heat reaches the surface from such a flame by conduction through a relatively stationary film of gas. The decrease in the temperature gradient when the body becomes hot would explain the lower rate of surface heating. With 1330 watts per sq. cm. delivered by the atomic hydrogen flame, the temperature of a black body would rise to 3900° K. The power radiated from tungsten at its melting point is 395 watts per sq. cm., and 1330 watts per sq. cm. should heat tungsten to about 5300° K. Although tungsten wires and even sheet metal can be melted and welded by the atomic hydrogen flame, it does not occur so rapidly as the foregoing figures would lead us to expect.

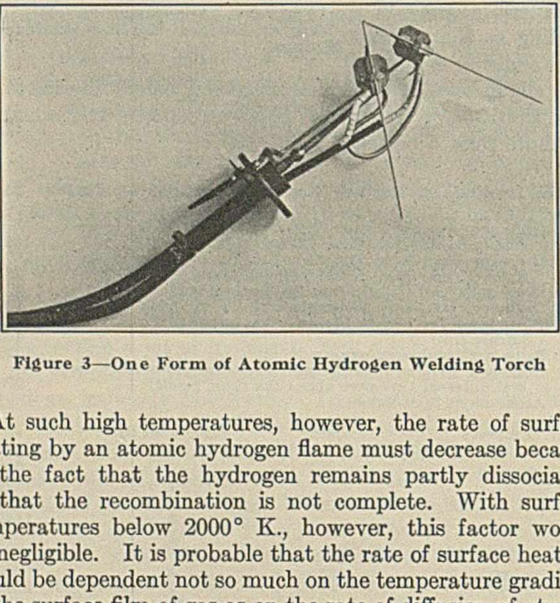

Figure 3—One Form of Atomic Hydrogen Welding Torch

At such high temperatures, however, the rate of surface heating by an atomic hydrogen flame must decrease because of the fact that the hydrogen remains partly dissociated so that the recombination is not complete. With surface temperatures below 2000° K., however, this factor would be negligible. It is probable that the rate of surface heating would be dependent not so much on the temperature gradient in the surface film of gas as on the rate of diffusion of atomic hydrogen through this film. Thus we may expect the rate of delivery of energy to a metal surface to remain nearly constant until the surface reaches a temperature of at least 2000° K.

To test this conclusion and also to find out whether different metals are heated at different rates, another device like that shown in Figure 2 was constructed, but the tip which was heated was of copper instead of tungsten, being made by turning down a large block of copper. When energy is delivered at the rate of 1000 watts per sq. cm. the temperature gradient in the tungsten tip is about 1100° K. per cm., while with a copper tip it is 260° K. per cm. Thus the surface of the tungsten tip was probably at a temperature of at least 1400° K. while the copper surface was not over 600° K. The observed rates of surface heating with the copper and tungsten tips were, however, not measurably different. This seems to indicate that up to 1400° K. the temperature of the surface does not affect the rate of heating and also that copper and tungsten are equally effective in causing recombination of hydrogen atoms on their surfaces.

Total Heat Delivered to Surfaces

The foregoing method measures the intensity of surface heating in watts per square centimeter. It was of interest to determine what fraction of the total energy in an arc or a flame could be delivered to a large flat surface against which the flame was directed. For this purpose a cylinder of copper 10.5 cm. in diameter and 9.8 cm. long was used, which weighed 7950 grams. The flame was directed against one of the flat polished ends, and the rate of temperature rise was measured as before.

An atomic hydrogen flame was produced by a 60-ampere a. c. arc using a torch like that shown in Figure 3. The voltage across the electrodes was 70 volts. A wattmeter showed that the power consumption in the arc was 3510 watts, which gives a power factor of 0.84. The electrodes were tungsten rods 3.2 mm. in diameter, which made an angle of 55 degrees with one another. The rate of flow of hydrogen which bathed the electrodes was 14.2 liters per minute (30 cubic feet per hour). From the temperature rise of the copper block the heat delivered to the surface was found to correspond to 3100 watts when the electrode tips were 3 to 5 mm. from the copper surface. This decreased to 2800 watts at 13 mm., 2500 at 25 mm., and 2200 at 35 mm. With the arc turned off but the molecular hydrogen burning in the air, the rate of heating corresponded to 250 watts with the electrodes 6 mm. from the surface. Subtracting this energy delivered by the combustion of the hydrogen in the air, we find that the energy carried to the metal by the atomic hydrogen ranged from 2850 to 1950 watts. Thus with the electrodes 3 mm. from the metal 82 per cent of the power input into the arc was delivered to the copper surface. This efficiency became 78 per cent at 6 mm., 71 at 13 mm., 65 at 25 mm., and 55 per cent at 35 mm. The energy corresponding to the complete combustion of 14.2 liters of hydrogen per minute is 2360 watts. Actually, only 250 watts or 11 per cent of this reaches the copper. The total energy of the arc and the flame of molecular hydrogen is 5870 watts, of which 3100 watts or 53 per cent is delivered to the copper.

An oxy-acetylene flame from a standard welding torch consuming 30.6 liters of oxygen per minute (64.8 cubic feet per hour) and 28.6 liters of acetylene per minute (60.6 cubic feet per hour) delivered energy at the rate of 4400 watts to the copper surface. A smaller torch consuming 13.7 liters of oxygen per minute and 13.0 of acetylene (29.0 and 27.5 cubic feet per hour, respectively) gave energy to the copper at the rate of 3900 watts. If we take the heat of combustion of the acetylene to be 302,000 calories corresponding to complete oxidation according to reaction I, the efficiency of the heat delivery by these flames is 17.6 per cent with the larger torch and 34.2 with the smaller. The energy delivered is, however, 52 and 101 per cent, respectively, of the heat energy generated if the combustion proceeded only as far as indicated by reaction III.

The data in Table II and the foregoing results show that the intense heat of the atomic hydrogen flame extends a considerable distance beyond the arc between the electrodes. Some measurements were also made of the length of time required to melt the ends of rods 6.3 mm. in diameter (1/4 inch) of Armco iron which were held in the flame at different distances from the electrode tips, the axis of the rods being perpendicular to the direction of motion of the flame gases. The rods were at room temperature when introduced into the flame. Table III gives the time in seconds before fusion of the end of the rod occurred.

Table III—Time Required to Melt Ends of 6.3-Mm. Iron Rods in Flame from 60-Ampere Arc

DISTANCE FROM ELECTRODES		TIME
Mm.	*Inches*	*Seconds*
6.3	1/4	4
9.5	3/8	7
13	1/2	8
19	3/4	14
25	1	18
38	1 1/2	27
51	2	36
64	2 1/2	80
76	3	240

Action of Atomic Hydrogen on Various Refractory Substances

Every refractory material which has been tried, except carbon, can be melted with comparative ease by the atomic hydrogen flame. Many substances vaporize very rapidly. The flame from a 60-ampere arc was directed against a large piece of calcium oxide. After considerable shrinkage and cracking a surface of several square centimeters can be maintained in a molten condition (m. p. of CaO, 2850° K.),[17] but evaporation occurs with remarkable rapidity. The flame becomes very brilliant and of a red color, and a spectroscope shows many hundreds of lines extending over nearly the whole spectrum. An optical pyrometer with a red screen ($\lambda = 0.66\ \mu$) sighted on the fused lime when at its highest temperature showed that the luminous intensity corresponded to that of a black body at 3500° K. A large fraction of this light was undoubtedly emitted by the gas.

Pure magnesium oxide (m. p. 3070° K.) melts with much greater difficulty. When it reaches high temperatures the arc shows a strong tendency to short-circuit on to the heated mass and rapid evaporation occurs where the arc leaves and enters the oxide. The end of a rod of oxide 4 × 7 mm. in cross section was heated just to fusion for 1.5 minutes and its weight decreased from 1.74 to 1.01 grams. The observed black-body temperature just at fusion was 3070° K., but the apparent temperature could be raised to 3200° K. Relatively little light was emitted by the flame gases.

Pure thorium oxide, ThO_2 (m. p. > 3070° K.), when just fused gave a black-body temperature of 3360° K., but the apparent temperature could be raised to 3700° K. at the points where the arc short-circuited on to the hot oxide. Evaporation was very rapid under these conditions.

With none of these oxides, or with alumina, was there any direct indication of reduction of the oxide to metal. A water-cooled, polished copper surface held in the flame just over the heated oxide rapidly became coated with oxide, but no metal was observed. It may well be, however, that the apparent volatility of the oxides is in large part due to reduction of the oxides and evaporation of the resultant metal, but as the temperature of the flame gas is lowered by cooling, the metal vapor reacts with the water vapor or oxygen derived from the original oxide.

Quartz glass seems peculiarly difficult to fuse. At least, with the most intense heat of the arc it retains a very considerable viscosity. For example, when the atomic hydrogen flame is directed against the central part of a thin piece of quartz glass about 3 mm. thick, it does not seem possible to *melt* a hole through the sheet of glass. Right under the arc, however, the silica evaporates rapidly so that after perhaps half a minute, but without any further increase in temperature, the glass becomes so thin that a hole forms. The hottest part remains clear and the surface clean, but this region is surrounded by a ring where the surface is covered by a fairly thick film of silicon or lower silicon oxides. On cooling the sample by removal from the flame, this ring appears black or dark brown with a peculiar luster, but in the flame the central part appears dark because of its low emissivity while the surrounding ring is bright. Pyrometer readings of the sample when strongly heated give black-body temperatures of 2530° K. for the central part and 2690° K. for the inner edge of the ring.

The inability to get the silica in a more fluid condition is due partly to its inherently high viscosity. Cooling by rapid evaporation, and perhaps failure of the quartz to catalyze the reaction involving the recombination of the hydrogen atoms, probably limit the temperature to which the quartz can be heated.

Evaporation of Metals

Pieces of various metals weighing 3 to 6 grams were placed upon cupels made from pure magnesium oxide, and were heated as strongly as possible by an atomic hydrogen flame from a 60-ampere arc. Cracks which formed in the cupels, through which molten metal could escape, were repaired by fusing small amounts of lime into the surface. Of course, a flame directed against the surface of a liquid cannot raise the temperature of the liquid to the boiling point, for cooling by evaporation will hold the temperature below this point. Thus, a Bunsen burner flame playing on the surface of water in a small dish heats the water to only about 85° C. Table IV gives maximum temperatures to which various metals could be heated by the atomic hydrogen flame.

Table IV—Maximum Temperatures of Metals Heated by Atomic Hydrogen Flame

METAL	$T_{Max.}$	$T_{b.p.}$	RADIATION	EVAPORATION	RATE OF EVAPORATION	EMISSIVITY
	° *K.*	° *K.*	*Watts per sq. cm.*		*G./cm./cm./sec.*	
Ni	2870	3650	140	60	0.0095	0.36
Cu	2840	3110	37	300	0.058	0.11
Ag	2660	2740	20	330	0.125	0.07

These temperatures were calculated from the pyrometer readings by means of the emissivities given in the last column. The boiling points in the third column were obtained from measurements of the rate of evaporation from these metals in vacuum.[18]

The rate of radiation of energy from the surface of the metal in watts per square centimeter is given in the fourth column while the heat energy corresponding to the cooling of the metal by its evaporation in the flame is given in the fifth column. The observed rate of loss of weight in grams per square centimeter per second is in the sixth column. It is clear that the cooling by evaporation limits the temperature to which molten metals can be heated except in the case of such difficultly volatile metals as molybdenum and tungsten.

Application of Atomic Hydrogen Flames to Welding of Metals

The high temperature of this flame, together with its powerful chemical reducing action and the avoidance of gases containing oxygen and nitrogen, render it particularly useful for welding, not only for iron and its alloys, but for

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[17] These melting points are taken from the International Critical Tables.

[18] These data will soon be published by H. A. Jones and the writer in *Phys. Rev.*

such metals and alloys as contain aluminum, magnesium, chromium, manganese, etc.

Since a general account of these applications has already been published,[19] only a brief summary will be given here. The technical development of these processes is largely the work of R. A. Weinman.

Figure 3 illustrates one of the later forms of torch used for welding. Two tungsten rods, as electrodes, are held at a definite angle to one another by easily adjustable clamps, and a jet of hydrogen is directed from a small nozzle along each of these rods near its end. The hydrogen thus bathes the heated parts of the electrodes and forms a gentle blast of gas which passes through the arc between the electrode tips, and blows the atomic hydrogen away from the electrodes so that these are not unduly heated. Other torches have been built suitable for automatic welding using machine feed.

The electrodes are ordinarily separated 3 or 4 mm. and the arc assumes a fan shape extending 6 to 10 mm. from the electrodes. Alternating current is generally used.

Figure 4 illustrates some welds made by the use of this method. At the center is shown a weld between two pieces of 1/8-inch sheet steel (low carbon). The weld is of very high strength and ductility, as is shown by its ability to stand the three mechanical embossing operations to which it was subsequently subjected.

The small sample to the left illustrates a particularly severe test for ductility. The 1/16-inch sheet metal (low carbon steel) after being welded, as in the case just discussed, was folded double along the line of the weld and then folded double a second time at right angles to the first fold. The sample shows a piece cut from the corner of this double fold. The metal shows no signs of cracking.

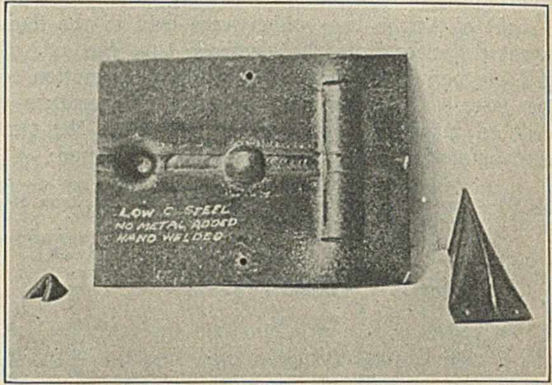

Figure 4—Welds of Low Carbon Steel Made with Atomic Hydrogen Torch

Left—Welded sheet 1/16 inch thick, folded twice
Center—Weld 1/8 inch thick, tested by embossing
Right—Tube made by welding sheet 1/32 inch thick, subsequently subjected to tests

The third sample at the right illustrates a cylindrical tube made from low carbon steel sheet metal 1/32 inch thick. After being welded the tube was flattened at its ends in two directions at right angles to each other. The weld showed no signs of failure.

[19] Weinman and Langmuir, *Gen. Elec. Rev.*, **29**, 160 (1926).

Measurement of the Abrasion Resistance of Rubber[1]

By Ira Williams[2]

Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

Abrasion is the process of wearing away the surface layers by doing work on the surface. The amount of work done depends upon the resistance which the rubber exerts when it is moved against the abrasive. Under the same conditions the resistance offered by two samples of rubber may vary 100 per cent. The usual type of abrasion machine disregards this factor. A machine has been devised which measures the power consumed in abrasion and the results are expressed as volume loss per unit of work done. The relation between abrasion resistance and tire treadwear is rather complicated and a study of a number of factors including rolling resistance of the tread and tread design would assist in determining the value of a tread stock.

THE purpose of the measurement of the resistance to abrasion of a rubber compound is to determine the life in actual service of an article produced from the rubber. This may be done either by interpreting the results obtained with an abrasion machine directly into service or by comparison with a second compound of known service life. The reliability of the test depends upon the extent to which the particular abrasion machine duplicates actual service conditions. This at once raises a question in regard to the type of abrasion machine to be employed and requires a knowledge on the part of the operator, not only of the peculiar action of the abrasion machine, but of the detailed stresses, strains, loads, conditions of slip, temperature, etc., imposed upon the article during service. The lack of this detailed information explains much of the lack of confidence in the results obtained by any particular abrasion machine and is sufficient reason for placing final reliance only on actual service tests.

Varieties of Abrasion Machines

Attempts to duplicate service conditions are responsible for the existence of a large variety of abrasion machines which in the final analysis are seen to be quite similar. Each machine gives due consideration to the abrasive, the area of rubber exposed, the pressure between abrasive and rubber, and the duration of the test or the amount of slipping, apparently on the assumption that the only remaining variable is the rubber itself. The mechanical differences in the abrasion machines arise largely from the different methods employed to produce slipping between the rubber and abrasive, and from this standpoint the various machines may be divided roughly into three classes:

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[1] Presented under the title "The Measurement of the Abrasion Resistance of Rubber and Some Relations between Abrasion and Treadwear" before the Division of Rubber Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa. The data presented in this paper were secured during the course of an extended investigation of accelerators and of vulcanization, which was sustained by the Grasselli Chemical Company of Cleveland, Ohio, during the period 1923–1927.

1—A flat rubber surface is moved against a flat abrasive surface in the same plane. The area of the rubber exposed to the abrasive is usually maintained constant in all tests and is pressed against the abrasive by a standard pressure. The test is usually conducted for a standard time at a fixed speed.

2—The rubber, either a prepared disk or blocks attached to the periphery of a wheel, is rotated against a rotating abrasive surface, the two axes of rotation being neither perpendicular nor parallel. The amount of sliding action between the rubber and abrasive is determined by the relative position of the two axes. The load is maintained constant while the area of contact may remain constant or may increase, depending on the shape of test piece and the relative position of the axes. The test is usually conducted for a standard time at a fixed speed.

3—The rubber is subjected to the impact of loose abrasive. The usual procedure consists in rapidly rotating a disk of rubber in a vessel of loose abrasive.

Principle of Abrasion

Abrasion seems to be the process of wearing away the surface by friction and is an action which in itself involves only the surface layer. Motion between the rubber and the abrading surface is necessary and a force must be applied to create the motion. The product of this motion and force represents the amount of work which is actually done on the surface of the rubber. The uniform conditions of surface contact, load, and amount of slip which are generally imposed on the test sample do not assure the expenditure of a uniform amount of work, which under these uniform conditions is a direct function of the resistance to motion which the rubber exerts. This factor, which has formerly been neglected, may differ as much as 100 per cent between two samples of rubber. Since the surface of the rubber can be removed only by the application of work, the measurement of volume loss on abrasion is incomplete without a simultaneous measurement of the total work expended on the rubber.

Apparatus

The accompanying picture illustrates an abrasion machine for measuring the volume loss of rubber per unit of work expended. The principle is that of a Prony brake in which the rubber test pieces are made the friction surfaces of the brake. The disk *A*, carrying the abrasive, is mounted on a hollow shaft and rotates in a vertical plane at a speed of 37 r. p. m. Two rubber test blocks, each 2 cm. square and 1 cm. thick, are mounted on the under side of the bar *B*, one being placed at each end and at a distance of 4.5 inches (11.4 cm.) apart. The bar *B* is permanently attached to a rod which extends through the hollow shaft carrying the abrasion disk. A weight *E* attached to the end of this rod by means of a cord over a pulley holds the test pieces against the abrasive. The lever arm, *C*, carries at the end an adjustable weight which is made just great enough to prevent the rotation of the bar *B*. This weight varies from 500 to 1000 grams. The spring balance, *D*, serves for the final adjustment of the load. The abrasive generally used is No. 0 emery paper. The abrasive surface is cleaned by means of air jets which are not shown. Brushes are not efficient. This machine measures the volume loss in the usual manner which, together with the simultaneous measurement of rate of work, permits the calculation of volume loss per unit of work done.

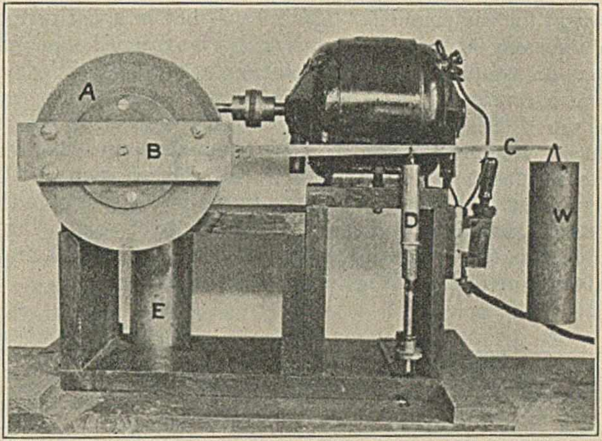
Calculation

The calculation of the volume loss on a work basis is simple and after the first calibration of the machine can largely be taken from curves or tables. The calculations necessary for the calibration employ the ordinary Prony brake formula,

$$\text{H. p.} = \frac{2\pi NRW}{33{,}000}$$

where N = r. p. m. of the disk carrying the abrasive
R = distance expressed in feet from the axis of rotation to the weight tending to prevent rotation
W = weight in pounds applied to prevent rotation

It is obvious that three calculations will be necessary. First, the work represented by the weight of the lever, *C*, with the Vernier balance, *D*, attached but hanging free. The factor, *W*, in this calculation can be obtained conveniently by supporting the lever with a spring balance. The weight indicated by the balance is *W*, and the factor *R* is the distance from the axis of revolution to the point at which the lever was supported. The work indicated by this calculation will be constant in all tests. In the second calculation *W* is the weight applied at the end of the lever and *R* is the distance from the axis of revolution to the point of application of the weight. A table or curve can be constructed showing the horsepower corresponding to any weight *W*. In the third calculation *W* is the load indicated on the spring balance and *R* is the distance to the point of application of the balance. A table or curve can also be constructed showing variations of horsepower with variation of load indicated by the balance. The rate of work during any test will then be the sum of these three factors. Volume loss per horsepower-hour can be found by means of the formula $V = \frac{L \times 60}{\text{h.p.} \times T}$, where L is the volume loss during the test and T is the duration of the test in minutes.



Apparatus for Measuring Abrasion Resistance of Rubber

The type of abrasive employed in the test will influence the final results and, of course, must be constant during any comparison. Fine abrasive will remove fine particles from the surface of the rubber, while coarse abrasive will remove the rubber as large particles. It is improbable that the work required to remove a given volume of rubber as fine particles would be the same as that required to remove an equal volume as large particles. In order to secure uniform results, fresh paper should be used for each test.

Experimental

In order to illustrate the action of the abrasion machine, five tread-type compounds have been prepared. The compounds tested are shown in Table I. Compounds 1 and 5 were milled first. Compounds 2, 3, and 4 were then prepared by mixing together the proper proportions of compounds 1 and 5. The physical properties of these stocks are listed in Table II and the abrasion data are shown in Table III. The abrasion test was made with an 8-pound (3.6-kg.) weight holding the test blocks against the abrasive.

Table I—Compounds Tested

	No. 1	No. 2	No. 3	No. 4	No. 5
Smoked sheet	100.0	75.0	50.0	25.0	0.0
Tire reclaim	0.0	25.0	50.0	75.0	100.0
Zinc oxide	10.0	9.75	6.5	4.75	3.0
Carbon black	39.0	31.65	24.5	17.25	10.0
Stearic acid	0.0	0.37	0.75	1.13	1.5
Pine tar	0.0	0.50	1.0	1.5	2.0
Sulfur	3.1	2.87	2.65	2.43	2.2
Accelerator	1.00	1.00	1.00	1.00	1.0

Table II—Physical Tests

Compound	Cure at 140° C.	Load at Elongation of 400 Per Cent		Tensile at Break		Elongation at Break	Hardness with Durometer
	Minutes	*Pounds*	*Kg./sq. cm.*	*Pounds*	*Kg./sq. cm.*	*Per cent*	
1	55	2225	156.4	4590	323.0	587	65
2	45	2260	159.0	4060	285.2	600	70
3	35	2215	155.6	3030	212.7	500	72
4	30	1845	130.0	2040	144.0	412	75
5	25	...		1080	82.8	250	76

The rate at which work is done on the test samples is seen in Table III to fall gradually from 0.0206 horsepower (15.4 watts) for compound 1 to 0.0136 horsepower (10.1 watts) for compound 5. This means that in equal periods of time only 66 per cent as much energy is expended on sample 5 as on sample 1. If only volume loss in equal periods of time is considered, compound 5 is shown to have 36 per cent as much resistance to abrasion as compound 1. When reduced to volume loss on the basis of equal energy expended, the resistance of compound 5 is only 23 per cent that of compound 1. These compounds by no means illustrate the extreme variations which may be met in rate of work. Compounds have been tested which vary in rate of work from 0.0083 to 0.0221 horsepower (6.2 to 16.4 watts).

Table III—Abrasion Tests under Equal Loading

Sample	Loss in Weight	Sp. Gr.	Volume Loss	Time Tested	Weight Applied	Spring Balance (Av.)	Power		Loss		Value with Sample 1 as Standard on Work Basis	Value on Volume Loss per Hour
	Grams		*Cc.*	*Min.*	*Grams*	*Grams*	*Watts*	*H. p.*	*Cc./h. p. hour*	*Cc./kw. hour*		
1	2.413	1.100	2.193	20	580	600	15.4	0.0206	319	914	1.0	1.0
2	2.788	1.153	2.420	20	580	445	13.9	0.0187	388	454	0.82	0.91
3	3.439	1.207	2.850	20	462	425	12.0	0.0161	531	690	0.60	0.77
4	4.956	1.259	3.941	20	382	405	10.7	0.0143	826	1074	0.39	0.56
5	6.006	1.315	6.09	15	363	380	10.1	0.0136	1380	1794	0.23	0.36

The rate at which work is done during a single test decreases slowly as the test progresses. Adjustment for this change is made by changing the tension in the spring balance, and readings must be taken at intervals which will permit an average value to be obtained. If the points form an irregular curve when plotted against time, the average is best obtained by means of a planimeter. If the curve is regular, a sufficiently accurate average can generally be obtained by inspection.

The reason for the decrease in rate of work is not entirely clear, but may be due to a number of factors. It can be said, in general, that the load on the spring balance decreases farther and more rapidly for low-grade compounds than for compounds of high quality. That the decrease is not due entirely to changes in temperature is shown by Table IV, which records the temperature while the data in Table III were being obtained and which shows no parallel between load decrease and temperature increase. While the greatest temperature change takes place in the first 3 minutes, the load continues to change regularly. That temperature has only a small influence is also shown in Table V. The sample was tested for 15 minutes, after which the machine was stopped and the load removed from the test blocks until the temperature had returned to normal. The test was then continued for another 15-minute period. Cooling the test sample increased the load 70 of the 185 grams necessary to produce the original value of 635 grams. Loss in the abrasive action of the paper used in the test also has some effect in reducing the power consumption.

Table IV—Spring Balance and Temperature Readings during Abrasion

	No. 1		No. 2		No. 3		No. 4		No. 5	
Min.	*Grams*	*° C.*	*Grams*	*° C.*	*Grams*	*° C.*	*Grams*	*° C.*	*Grams*	*° C.*
0	650	22	625	22	645	22	630	22	620	22
3	705	26.3	590	26.3	605	26.3	555	24.8	550	25.2
5	710	26.9	565	26.6	515	27.4	510	25.5	430	26.9
10	625	27.2	485	27.7	380	27.7	375	26.3	285	27.7
15	500	28	315	28.2	315	27.9	305	27.0	205	28.8
20	425	28.6	220	28.8	270	28.5	260	27.8		

Table V—Effect of Temperature on Power Consumed

Minutes test was run	0	5	10	15	15	20	25	30
Grams indicated on balance	635	620	530	450	520	430	370	340
Temperature, ° C.	25.0	28.1	28.2	28.7	25.0	28.4	29.4	30.0

The abrasion machine may be operated in still another manner. Instead of subjecting the abrasion blocks to a uniform load and measuring the rate of work, it is possible by varying the load during the test to do work at any predetermined rate on the rubber. The series of five tread stocks were tested in this manner. The weight, *W*, and the balance, *D*, were adjusted to produce a rate of work of 0.0180 horsepower (13.4 watts). As the energy consumed tended to decrease, shot was poured into the hollow weight, *E*, until the rate of 0.0180 horsepower was maintained. The data are given in Table VI. In this case the relative value of the stocks will be the same whether considered on a volume-loss basis or on volume-loss per horsepower hour, since work was done at the same rate on all samples. The results are in good agreement with the figures given in Table III.

Table VI—Abrasion Tests at an Equal Rate of Work

Sample	Time Tested	Volume Loss on 20-Minute Basis	Loss		Value with Sample 1 as Standard
	Minutes	*Cc.*	*Cc./h. p. hour*	*Cc./kw. hour*	
1	20	1.88	312	420	1.0
2	20	2.46	410	550	0.77
3	20	3.45	573	718	0.55
4	15	5.06	842	1128	0.37
5	10	8.90	1480	1990	0.21

Other Factors Affecting Treadwear

The question of treadwear involves much more than the abrasion resistance of the tread stock. A tread can be worn away only by doing work on the surface. The work required to drive a car forward at a definite speed and for a definite distance against the normal rolling resistance could be determined, and this amount of work must be done on the rear tires, irrespective of the stock of which the treads are composed. Work is done on both front and rear tires due to rolling friction. This is caused by the difference in circumference of the tire at the center of the tread and at the tread shoulder which necessitates slip, and by the change in area of the inflated tire when it deflects to carry the load. The amount of work will depend on tread design with its effect on the amount of slip, on the coefficient of friction between the rubber and road surface, on the stress-strain relationship, and on the mechanical efficiency of the rubber. It is obvious that if the coefficient of friction could be reduced to zero slipping would take place but no work would be done. If the coefficient of friction could be made infinitely great, no slipping would occur and no work would be done on the surface, but the stress due to the strain resulting in the rubber would be stored in the rubber in a reversible manner. Under normal conditions both slip and strain in the rubber result. Any point on the tread of a tire at the time of coming into contact with the road will slip until the pressure against the road increases to a definite value, which depends upon the existing coefficient of friction and the stress-strain relationship of the rubber, after which energy is stored in the rubber due to the strain imposed. As the rolling motion of the tire proceeds until the point of the tread is about to leave the road, any energy stored in the rubber due to strain will be available to cause slip and do work on the surface of the rubber.

Many of these factors are extremely variable under road conditions and tend to be minimized by dusty or wet roads which reduce the friction. While the work done on the rear tires due to driving force and on the front tires due to steering thrust must be constant for any tread stock, the work due to rolling, camber, and toe-in will vary with the road conditions and tread compound. While the present development of the abrasion machine makes possible a comparison of the abrasion resistance of any compound, it should not be expected to replace actual road tests in the selection of a tire tread.

Evaporation of Sulfite Waste Liquor[1]

By W. L. Badger

Chemical Engineering Department, University of Michigan, Ann Arbor, Mich.

This paper deals with the problem of disposal of waste sulfite liquors by considering the design of suitable evaporating equipment. Apparatus for large experiments are described and the data obtained from their operation are discussed.

THE problem of the disposal of sulfite waste liquors, though not especially acute at present, promises to be more serious in the near future, owing to the increasing stringency of stream pollution laws. Although the ultimate solution of this problem must involve finding some new uses for the material, it is obvious that, whatever these uses may be, the first step will undoubtedly be an evaporation of the liquor. This will be particularly true in those cases where the only possible disposal of the wastes will be to burn them. Consequently, since all recovery processes are based on a preliminary evaporation, the first step in the general problem will be to design suitable evaporating equipment.

The difficulties met in attempts to evaporate sulfite liquor are threefold: (1) The extreme viscosity of the solution; (2) the very serious scale-forming tendencies of the liquor; and (3), the corrosive nature of unneutralized liquors. The third item was not considered in this investigation.

It is now generally accepted that the velocity with which a liquid will be moved past the heating surface is by far the most important factor in determining the capacity of an evaporator. In the ordinary evaporator, whether of the vertical tube or horizontal tube type, this circulation is accomplished by natural convection and by the evolution of steam bubbles. Obviously, as the liquid becomes more viscous, the circulation produced by both of these means rapidly decreases, with the result that it is very difficult to concentrate this liquid to high densities without using either excessively large evaporators or very large temperature differences. Since the cost of the disposal of sulfite liquor must be held to very low figures, and since the principal cost of evaporation is the cost of steam, it follows that an evaporator of the largest possible number of effects is desirable. This, however, results in a small temperature drop per effect, which, as has been shown above, makes operation exceedingly difficult or impossible. This line of reasoning, therefore, leads to the conclusion that a satisfactory evaporator must employ some means of artificial circulation.

Mechanism of Scale Formation—It is now generally accepted that the cause of scale formation is the presence in solution of a substance with an inverted solubility curve—that is, one whose solubility decreases with increasing temperature. Calcium sulfate is such a substance, and its presence in sulfite liquors gives them their scale-forming tendencies. Next the heating surface there is a stagnant film of liquid whose temperature is higher than that of the bulk of the liquid. If a substance with an inverted solubility curve is present when the solution is concentrated, the solution will become saturated with respect to this substance in the stagnant film before the bulk of it is saturated. Therefore, the substance with an inverted solubility curve will be precipitated first in the stagnant film and will continue to deposit in this film, producing a characteristic compact scale. If there is present in the liquid other solid material in a finely divided state, this solid material is very apt to be included in the scale, increasing the rate at which it forms. Without the presence of a substance whose solubility curve is inverted, no true scale can form. If this explanation is correct, anything which decreases the thickness of this stagnant film or which brings into contact with the stagnant film particles which could act as nuclei, and therefore start the crystallization, should diminish the formation of scale, although it would seem that such a method could not completely prevent scale but merely decrease its rate of formation. Therefore, both the viscosity of the liquid and its tendency to form scale lead to the same conclusion—namely, that some form of artificial circulation is desirable.

Apparatus

One of the evaporators of this laboratory was modified to carry out these ideas. A diagram of the experimental apparatus is shown in Figure 1. The shell of the evaporator was of cast iron, 30 inches I. D. and 12 feet high. It was

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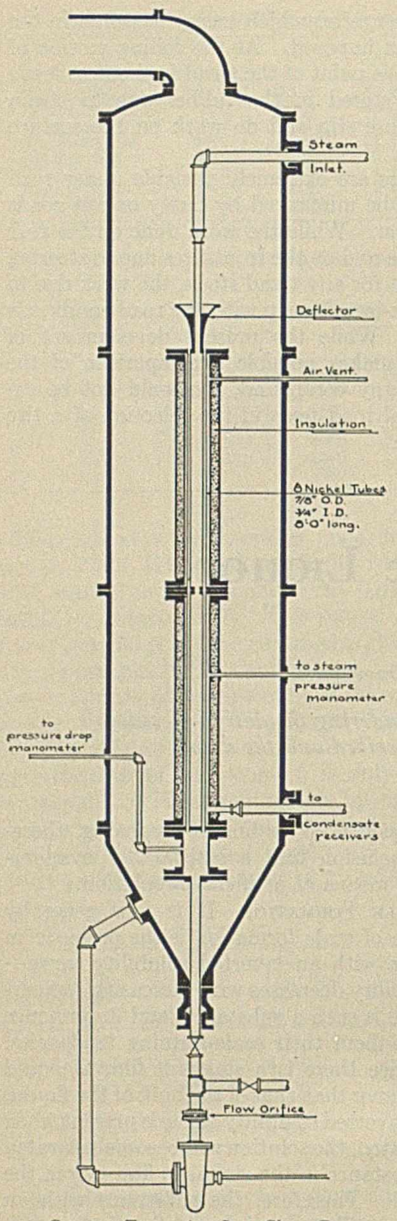
[1] Received March 14, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.



Courtesy Trans. Am. Inst. Chem. Eng.

Figure 1—Experimental Evaporating Apparatus

closed at the bottom with a 60-degree cone. A number of heating units were made, each 5 inches in diameter, 4 feet long, and closed at each end by a tube sheet.

Between these tube sheets in each unit were expanded eight nickel tubes $^{7}/_{8}$ inch O. D., $^{3}/_{4}$ inch I. D. The shell of the unit was surrounded by an outer jacket of sheet iron, welded on. The annular space between this shell and the wall of the unit was filled with Sil-O-Cel powder. Suitable connections were made for removing condensate, for measuring steam pressure, and for venting noncondensed gases. The baskets were so arranged that any number of them could be assembled end to end, thus giving total tube lengths of multiples of 4 feet.

In these tests two such units were so assembled as to give an equivalent length of 8 feet. Steam was introduced into the center of the top tube sheet and a steam connection was made between the two units through the intermediate tube sheets. A liquor distribution chamber was attached to the bottom tube sheet, and this was connected through the shell of the evaporator to a pump in such a way that liquid could be drawn out of the machine, pumped into this liquor-distributing chamber, and from the chamber pass up through the tubes. Since the liquor issued from the tubes at the top at very high velocities, a deflector was placed above the top unit to throw this spray against the walls of the machine.

Calculations

The most important figure to be obtained from these tests was the heat transfer coefficient, which is expressed as B. t. u. transmitted per square foot of heating surface per degree Fahrenheit temperature difference per hour. The total amount of heat transferred was determined by collecting the condensate in calibrated drip receivers. The receivers were insulated, and no correction was made for radiation from the relatively short pipe lines between the basket and these receivers. Steam temperature was calculated from the steam pressure inside the baskets. This pressure was measured by a mercury manometer and the temperature calculated from the steam tables.

In the same way the boiling point of the liquid was calculated from the steam tables, using the pressure in the vapor space as measured by a mercury manometer. This boiling point was not corrected for the elevation of boiling point of sulfite liquor, since Moore[2] has shown that this elevation is very small. The temperature drop was taken as the difference between steam and liquor temperatures determined as above and is therefore the "apparent" temperature drop, and the coefficients calculated from it will therefore be "apparent" coefficients.

An orifice was calibrated with liquor of various densities at the actual temperatures at which they were handled. The results of these calibrations were calculated in terms of entrance velocities in the heating tubes in feet per second. A mercury manometer had one arm connected to the liquor-distributing chamber and the other arm connected to the vapor space of the evaporator. Its reading, therefore, gave the pressure drop which occurred in the tubes. This pressure drop is the principal resistance which must be overcome by the circulating pump and is, therefore, a measure of the power consumed in the operation.

A tank car of neutralized sulfite liquor was supplied by the Hammermill Paper Company. It was desired to control the operation of the evaporator by specific gravity determinations and the only data available on the relation between specific gravity and concentration at different temperatures are those given by Moore[2] (Figure 2). Since there is considerable variation in the composition of the liquor from one mill to another, it was not certain that Moore's figures would apply to this liquor. A sample was evaporated in the laboratory to different concentrations and for each of these samples specific gravity and total solids were determined. These figures were compared with Moore's data with the following results:

Per Cent Solids (Detd.)	Specific Gravity (Detd.)	Specific Gravity (Moore)
6.87	1.0320	1.031
8.50	1.0405	1.037
13.17	1.0630	1.063
16.09	1.0800	1.080
20.93	1.1107	1.106
29.29	1.1512	1.153
49.90	1.1990	1.270
53.50	1.3050	1.29+ (est.)

The checks are sufficiently good, with the exception of one sample, to justify the use of Figure 2 for this work. At the end of these experiments the concentrations were carried so high that they came outside the range of Moore's data and their values had to be estimated. All concentrations above 50 per cent solids, therefore, may be more or less in error.

It was desired to duplicate in these experiments the concentration of this liquor to 50 per cent solids in a quadruple-effect evaporator operated with forward feed, assuming that the exhaust steam would be at 240° F. (approximately 10 pounds gage) and the vacuum, 26.5 inches on a 30-inch barometer. From Moore's data it was estimated that the boiling point elevations in the four effects would be 0°, 1°, 1°, and 3° F., respectively. This would leave a total temperature drop of 115° F., which, it was assumed, would be divided between the effects to give temperature drops of 22°, 23°, 25°, and 45° F., respectively. The conditions in the four effects under these assumptions would be as follows:

	° F.
Steam to first effect	240
Boiling point, first effect	218
Vapor from first effect	218 (2 lbs. gage)
Boiling point, second effect	195
Vapor from second effect	194 (9-inch vacuum)

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[2] *Trans. Am. Inst. Chem. Eng.*, **15**, Pt. II, 245 (1923).

	° F.
Boiling point, third effect	169
Vapor from third effect	168 (18-inch vacuum)
Boiling point, fourth effect	123
Vapor from fourth effect	120 (26.5-inch vacuum)

The conditions actually maintained were as follows:

	° F.
Steam to first effect	231
Vapor from first effect	211
Steam to second effect	214
Vapor from second effect	194
Steam to third effect	192
Vapor from third effect	167
Steam to fourth effect	175
Vapor from fourth effect	131

In other words, the test conditions correspond reasonably well with the assumption, except that we did not carry quite so high a vacuum nor could we carry quite so much steam pressure on the first effect as we desired.

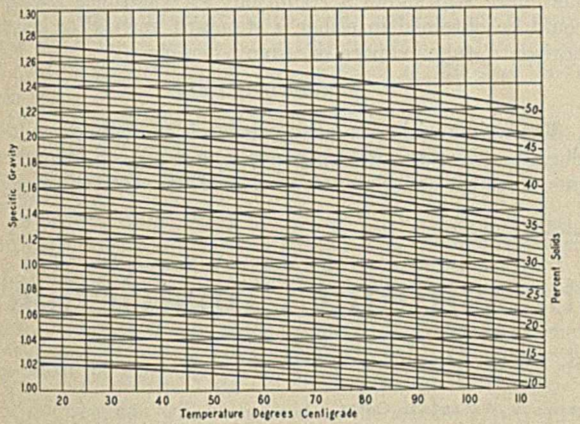

Figure 2—Relation between Specific Gravity and Concentration (Moore)

The total solid content of the thin liquor was about 7.5 per cent. On the assumption of an approximately equal distribution of evaporation between the four effects, this would give, for the concentration leaving each effect, the following:

	Per Cent Solids		Per Cent Solids
First effect	10	Third effect	21
Second effect	15	Fourth effect	50

Operation

The machine was filled with thin liquor to the desired level, steam and boiling point adjusted to the desired conditions, and evaporation continued, thin liquor being fed as became necessary, until the concentration reached the limit for that effect. After that, thick liquor was pumped out of the machine and thin liquor fed to maintain concentration approximately constant. During this operation actual runs were made for the determination of heat transfer coefficients. A run lasted 20 minutes, during which time the amount of condensate was measured and all temperatures and pressures read at frequent intervals. The data for each run were calculated in duplicate. These runs followed each other at short intervals. The total time of operation was recorded each day and the figures in Table I indicate the total time the machine had been in operation.

After a number of runs had been made under first effect conditions, the steam and boiling point were changed to correspond to second effect conditions. The partly concentrated liquor produced in first effect operation was fed into the machine and concentration continued until the desired second effect density was reached. After this, thick liquor was pumped out and more liquor fed, using thin liquor if the length of operation was sufficient to use all the thick liquor produced in the previous effect. In the same way, third and fourth effect runs were made. A summary of the data for all these runs is given in Table I. After this, without cleaning, there was a return to first effect operation, using a fresh lot of thin liquor and the first three effects were run through a second time exactly as described above.

In this second set of experiments the fourth effect was run with a steam temperature of 247° F. and a boiling point of 211° F. in order to reproduce the conditions that would exist if thin liquor were fed to the second effect of a quadruple-effect evaporator, the feed passing then to the third and fourth effect, pumped from the fourth to the first, and finished to thick liquor in the first effect. It has been explained that the viscosity of the liquor is one important source of difficulty. Since viscosity decreases rapidly with increasing temperature, it is obvious that finishing with thick liquor at a high temperature should result in an increased capacity of the evaporator because of the decreased viscosity of the liquid.

In these runs concentration was carried to about 60 per cent solids. This concentration was not exceeded merely because of conditions of the work and not because the machine failed to perform. All the work was done on day shift only. When the evaporator was left with the 60 per cent solution in it overnight, the material in the pipe lines became so hard that it took considerable time the next day to thaw out these lines and get the apparatus running. So much time was lost, and the liquor was so diluted that the rest of the day's operation merely served to get back to about 60 per cent solids again. There is no way of telling from this experiment the limiting concentration that would be practical in the machine.

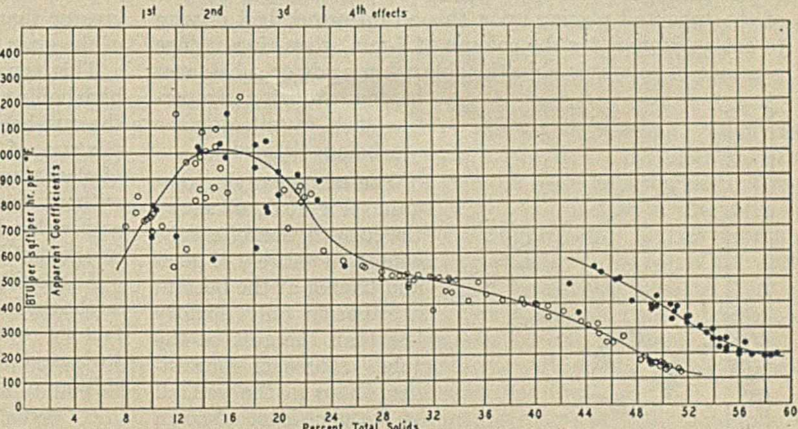

Figure 3—Heat Transfer Coefficients in Evaporating Sulfite Liquor
○—First series. ●—Second series

Results

The results of these tests are reproduced in Figure 3. There are several interesting features, but the most important one is that in the second set of runs, where the evaporator had been in operation upwards of 60 hours, the coefficients obtained are fully as high as the first time over when the evaporator was clean. After this work was completed and the evaporator dismantled, the tubes were examined. There was a very thin, black deposit which may have been nickel

Table I—Evaporation of Sulfite Liquor in Forced Circulation Evaporator (Summary of Data)

	First Effect	Second Effect	Third Effect	Fourth Effect	
Total time of operation up to end of first series	7 hours 10 min.	20 hours 00 min.	26 hours 55 min.	63 hours 05 min.	
Total time of operation up to end of second series	73 hours 55 min.	87 hours 25 min.	100 hours 20 min.	148 hours 00 min.	
Number of test runs averaged	13	24	23	60[a]	35[b]
Average per cent total solids	9.8	14.7	21.4	39.9	50.3
Average steam temperature, ° F.	230.79	214.05	192.59	175.47	246.76
Average vapor temperature, ° F.	210.67	194.10	167.25	130.94	210.92
Average temperature drop, ° F.	20.12	19.90	25.31	44.53	35.84
Average velocity, feet per second	11.5	7.9	7.1	9.4	7.6
Average pressure drop, feet H_2O	14.75	15.23	19.05	22.64	24.00
Average coefficient (B. t. u. per square foot per hour per ° F.)	734.5	989	723	346	337

[a] First series of runs, under fourth effect conditions.
[b] Second series, finishing at atmospheric pressure.

sulfide, but the surface of the tubes was smooth and metallic to the touch and nothing that can by any stretch of the imagination be called scale was present. The principal result of these experiments may therefore be stated as follows: In these tests, at the end of approximately 150 hours of operation, no scale had been formed in this evaporator. Considering the performance of ordinary evaporators on this liquid, this result is so remarkable that it stands out as the principal feature of the test.

The next most important item is obviously the very high value of the coefficients. The reason for the low values in the first effect cannot even be guessed. It could not have been due to scale formation by the raw liquor, because the second effect operation certainly would not have dissolved such scale and first effect operation the second time over checked these results. The results are more erratic in the first three effects than could be desired. This variation is undoubtedly due to irregularities in rate of feed and rate of drawing off thick liquor. The concentration in each run was based on a single determination of specific gravity and may not always have reflected the average density throughout the run. Even allowing for the wide fluctuations in the data, the curve still shows a coefficient several times as high as could be obtained in either a standard vertical or standard horizontal tube evaporator, even when clean.

Acknowledgment

The writer wishes to acknowledge his indebtedness to the Swenson Evaporator Company, who made all the arrangements for the experimental work and financed it throughout.

An All-Glass Distilling Tube without Constriction[1]

By Howard J. Lucas

California Institute of Technology, Pasadena, Calif.

THE usual distilling tube is constricted near the bottom at the very place where maximum capacity is needed. Peters and Baker[2] overcome this difficulty by putting a wire through two small holes in the wall near the bottom of the tube and placing upon this an openwork ball of wire to act as support for the column of 5-mm. glass rings. The presence of copper is objectionable when acids or substances having oxidizing properties such as nitrotoluene are being distilled.

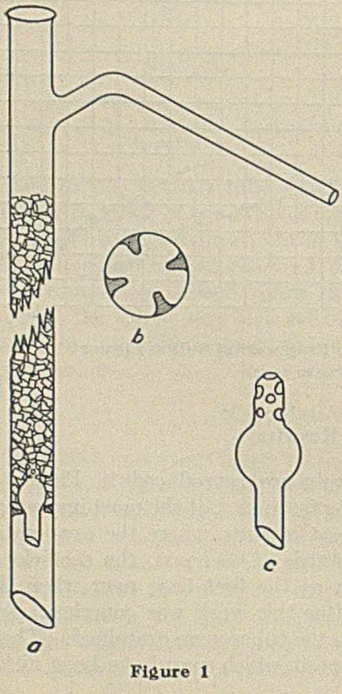

Figure 1

The accompanying diagram (Figure 1, *a*) shows the construction of a tube composed entirely of glass and having at the bottom a capacity only slightly less than the rest of the tube. Three or four indentations in the wall, all at the same level as shown in *b*, support a hollow-glass nipple, *c*. Enough holes are blown in the upper half of the nipple to take care of decreased capacity resulting from the closing of openings by the glass rings above resting against them. It is evident that the decrease in the capacity of the tube at the level of the indentations corresponds to the cross-sectional area of the indentations and of the wall of the nipple. It is probable that this decrease is not much greater than that resulting from the presence of the glass rings higher up.

This type of tube is useful where liquids of high boiling point are being distilled and where the run-back is large. The distillation of a mixture of nitrotoluenes through a column of glass rings 5 × 5 mm. can be accomplished without troublesome holdup in the column and with a fair separation of the ortho isomer in one distillation.

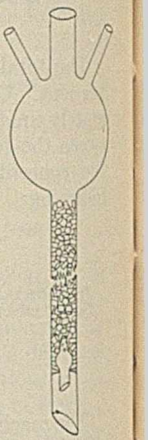

Figure 2

A modified Pim's chlorinating apparatus[3] is shown in Figure 2. This has given satisfactory results in the chlorination of toluene to benzyl chloride when filled with a 20-cm. column of glass rings 5 × 5 mm.

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[1] Received March 14, 1927.

[2] This Journal, **18**, 69 (1926).

[3] Martin, "Industrial and Manufacturing Chemistry," Vol. I, p. 366b, Crosby Lockwood and Son, London, 1915.

Celanese Corporation Doubles Capacity of Maryland Plant—The Celanese Corporation of America, formerly the American Cellulose and Chemical Manufacturing Company, Ltd., which recently changed its name and increased its capital stock by $5,500,000, plans to award contracts at once for the erection of buildings to house machinery which will double the capacity of the maximum output of the present plant at Amcelle, Md., a suburb of Cumberland, Md., at a cost of about $5,000,000. A contract has already been awarded to the Cumberland Contracting Company to build a new road to the main plant, 26 feet wide. A new brick office building will be erected and another artesian well is being drilled. It is understood that the Baltimore and Ohio Railroad will build a subway under its fill to connect two sides of the plant.

CHEMICAL EQUIPMENT SYMPOSIUM

These articles comprise in large part the material of a series of lectures on chemical equipment presented by representatives of member companies of the Association of Chemical Equipment Manufacturers, under joint sponsorship of the Association and Columbia University, Carnegie Institute of Technology, Ohio State University, College of the City of Detroit, Yale University, and Case School of Applied Science, before advanced technical students and invited industrial and technical men, at each of the educational institutions mentioned, on different dates, in January to May, 1927.

Filtration Equipment in Today's Industry

By H. J. Runyon, Jr.

United Filters Corporation, Hazleton, Pa.

When anyone mentions filters or filtration the average person thinks of water filters. However, water filters are a decidedly special type of equipment and will not be covered in this discussion. The simplest method of classifying the various types of filters is the following:

(1) Filters with loose filtering layer. This division includes sand filters for water filtration, percolating filters as found in many of the sewage filtration plants, char filters as used in sugar refineries, etc.

(2) Filters with felted or woven filter medium. This is the division generally covered by the term "industrial filters," the main subdivisions of which are: (*a*) plate and frame (or chamber) filter presses; (*b*) leaf filters, both pressure and vacuum types; and (*c*) continuous filters.

(3) Filters with rigid filter medium. This division includes porous stoneware, etc., and is a highly specialized group covering equipment for handling special highly corrosive liquids.

This discussion will be limited to the second type. Probably few people realize that equipment of this character is not only used extensively in the manufacture of chemicals, but also plays an important part in the manufacture of beet and cane sugar, starch, yeast, vegetable oils, copper, zinc, lead, gold, lubricating oils, pigment, and a host of other essential materials.

Bag Filters

Everyone is familiar with the housewife's method of making jelly from the common fruits or berries, where the mixture of pulp and juice is put into a bag and allowed to drain to produce a relatively clear juice. Records show that the Chinese made wine as far back as 2000 B. C., and undoubtedly they followed a procedure of this character. The bulk of the refined sugar produced prior to 1917 or 1918 was filtered in a manner very similar to this. At that time most of the sugar refineries used what were known as Taylor bag filters, a very limited number of which are still in use.

Each Taylor bag filter unit consisted of a chamber or room in which were suspended from the ceiling two hundred fifty or more bags or stockings, probably 5 to 6 feet long. Each stocking was tied to a short pipe running through the ceiling and the juice to be filtered ran down through this pipe from the floor above and filled the stocking, the solids being caught on the interior of the stocking and the clear liquid draining to the floor and flowing to a common discharge pipe. In a moderate-sized sugar refinery approximately twenty-four men would be required to remove these stockings or bags every 12 hours, turn them inside out, and wash them.

Pressure Filters

Today practically all the refinery liquors are handled through pressure leaf type filters, for which three or four men are required instead of the twenty-four men necessary with bag filtration. Incidently, the change from gravity-feed bag filters to pressure-feed leaf filters involved a change in the method of treating the liquid so as to avoid a gelatinous precipitate which, under pressure filtration, would quickly clog the filter medium. In order to use the pressure filters with a much lower labor cost, the industry switched over to the use of a filter aid, usually infusorial earth somewhat similar in its microscopic porous character to very finely divided pumice stone. This material, commonly known as kieselguhr, is purely mechanical in its action. A thin deposit of it on the cotton filter medium prevents the gummy matter from closing the pores of the cotton cloth and at the same time produces a very brilliant clarification of the liquid.

Filter Presses

Old records indicate that in the early days the ceramic industry of England used a modified type of bag filter, which consisted in fastening woven filter cloth across two open faces of a very shallow box. This provided two faces of filter cloth spaced apart the depth of the narrow frame of the box. A pipe or hose connection was run to the upper side of the box and the material fed into the interior of the box. This was really a semi-rigid form of bag filter, and in order to remove the solids it became necessary to remove one piece of the filter cloth so as to get at the interior of the frame.

A patent granted in England in the early part of the nineteenth century covers what is probably one of the first patented improvements in the art of filtering. Here the scheme described above was improved by the insertion of a solid plate of wood with grooved faces between each of the box-like hollow frames which had been used in the previous arrangement for separating the filter cloth. In this improvement the cloth was simply dropped over the top of the solid frame and allowed to fall down across both grooved faces of the wooden plate. The hollow frames and the solid frames were alternated in an assembly of these units and individual feed connections were made to each of the hollow frames. This is the basis of the present-day filter press.

The cumbersome hose connections to the individual frames have been eliminated in the modern filter press. Feed connections are now made to a rigid, stationary head plate, and the feed is carried along to all the frames by a series of eyes or corings in the plates and frames, which match up in the completely assembled press and form a continuous enclosed passageway connecting with all the hollow frames.

There are two main types of filter presses in general use today:

(1) Recessed-plate filter presses, where the solids are deposited in a recess in the face of the plate and no hollow frames are used in the unit, all the plates being exactly alike.

(2) Flush plate and frame type filter presses, where hollow frames to provide for the cake formation are interposed between each pair of solid plates.

The variations in the details of these designs are almost unlimited. For instance, in the recessed type plate press the feed eyes are usually located in the center of the plate, while with the flush plate and frame type press the feed eyes may be located at the side of the plate or at one of the corners. This leads to such designations as "2-eye side feed" or "2-eye corner feed" filter press.

The question of the delivery of the filtrate from the filter press leads to other specifications such as "open delivery" through filtrate shut-off cock to an open trough or "closed delivery" which is obtained by carrying the filtrate through a series of eyes forming an enclosed passageway through all the plates and frames.

Washing type filter presses are usually designated as either "single washing" or "double washing" type, depending upon whether provision is made for passing the wash water in one direction only through the cake or whether the design includes provision for washing the cake first with a flow of water in one direction and then reversing the flow and washing in the other direction.

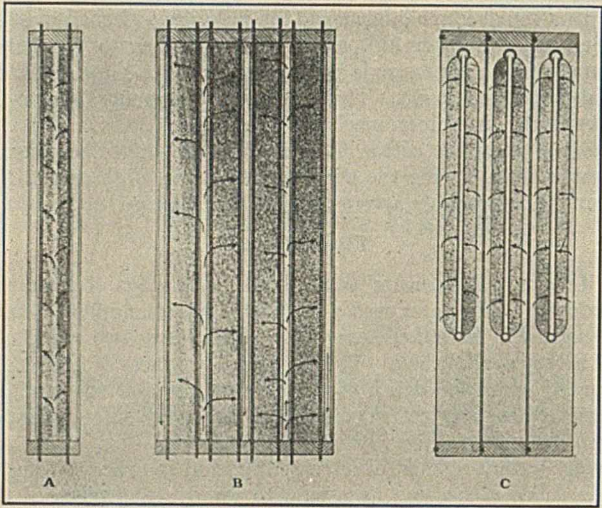


Figure 1—Relation of Flow in Filter Presses and Leaf Type Filters

A—Flow during deposit of cake in frame of filter press
B—Direction of wash water flow through cake in frame of filter press
C—Direction in flow during filtering and washing in leaf type filter

Filter presses also offer a great variety in the possible materials of construction. Wood filter presses are used extensively for the handling of acid liquors. Metal construction usually includes cast-iron plates, but where necessary Duriron, antimonial lead, or similar special metals can be employed to resist the action of corrosive liquors.

There is a considerable variation in the design of closing and locking devices for filter presses, some of the better known devices being (1) ratchet, (2) back gear, (3) capstan wheel, and (4) hydraulic. Filter presses are sometimes made with cored passageways in the plates to provide for heating with steam or cooling with brine.

It can thus be appreciated that there are more than two hundred different styles of filter presses when viewed from the various combinations of specifications mentioned above.

The rate of filtration decreases as the thickness of the cake accumulation increases. Hence it is important from the standpoint of operating efficiency to have a filter designed for the proper thickness of cake, as otherwise it might take an excessively long time to fill the frame and wash the material. On the other hand, too thin a frame means too frequent shutting down of the filter press for removing the cake accumulation.

ADVANTAGES—(1) Filter presses are simple, accessible, and can be used for filtering almost any kind of a sludge. They are therefore frequently used for new processes where ample time and study are not possible with a view to using a more highly developed type of filter. Some of the more highly developed filters are more limited in their scope with respect to the kind of material they will satisfactorily handle. The filter press is therefore more flexible in its application than some of the other types.

(2) They lend themselves to wood construction for acid or corrosive liquids.

(3) They are cheap in initial cost when considered from the standpoint of cost per square foot of filter area.

(4) They will produce a relatively hard cake if properly operated, and hence will deliver a cake with as low or lower moisture content than can be obtained with other types of equipment.

(5) They are well adapted to the handling of small-batch process work and deliver the cake in good form for tray drying.

DRAWBACKS—(1) High labor cost because of the large amount of labor required for pulling apart the plates and cleaning out the cake accumulation.

(2) High filter-cloth cost because the cloth is used to form a gasket between the plates and is thus subject to mechanical wear.

(3) Liability to leakage between the plates, which may result in loss of valuable liquid if operators are not skilful and efficient.

(4) Slightly lower washing efficiency than leaf type filters when handling cakes which are subject to shrinkage during washing. This is due to the fact that during washing the water passes through the full depth of the cake and thus causes a change in direction of liquid flow through half of the thickness of the cake. (Figure 1)

OTHER FILTRATION EQUIPMENT

The wide expansion in industrial activity and the large-scale production have made the labor cost per ton of solids handled an important consideration. On this account the last fifteen to twenty years have been marked by unusual activity in the development of other types of filter equipment. The following incentives have led to the development of these later types of filters: (1) saving in labor; (2) saving in filter cloth; (3) saving in time that material is held in process; (4) higher washing efficiency, usually with a view to saving evaporating cost at a later step in the process.

Vacuum Leaf Type Filters

The cyanide process in the mining industry led to the development of what is usually known as the Moore or Butters type filter. This is a vacuum filter consisting of a series of drainage frames covered with filter cloth and fastened to a suitable overhead carriage. A suction connection is provided to the interior of these frames, which are termed "leaves." A crane makes it possible to lower the unit of filter leaves into a tank filled with the material to be filtered. The suction on the interior of the leaves forms the accumulation of cake on the outside of the leaves and the clear filtrate is drawn away through a vacuum system. After the cake has been deposited on the leaves they are picked up by the crane and submerged in a tank of wash water to remove the solubles in the cake. The cake is discharged by carrying the unit of leaves over a suitable receptacle and then admitting compressed air to the interior of the frames, thus dislodging the cakes.

This type of filter came into general use in the cyanide process because of the large working area provided and the comparatively low labor cost required in operation.

There are several disadvantages to this type of filter. It is limited to the use of vacuum to obtain the difference in pressure and therefore, with some materials, would not show such high capacity per unit of filter area as a pressure filter. The installations are large and in some cases rather unwieldy. Flexible connections are required for taking away the filtrate. It requires skilled operation to move the units of leaves about without losing some of the cake and thus impairing the washing efficiency. There are still some Moore type filters being installed, but they have largely given way to the modern continuous vacuum filter of either the drum or leaf type.

Care must be taken in operating any leaf type filter to avoid building up too great an accumulation of cake. If the cake on adjacent leaves is allowed to accumulate to a point where the cakes merge together, a very unsatisfactory wash will be secured. This is in direct contrast to the operation of washing type filter presses where the hollow frames must be thoroughly filled with cake in order to avoid contractions in the cake and channeling during washing.

Kelly Pressure Filters

This is a pressure-type leaf filter which came into use in connection with cyanide work, beet sugar manufacture, and large-scale chemical processing. The shell of the filter is of steel-plate construction and consists essentially of a cylinder placed horizontally and provided with a movable head. The head is built as an integral part of a carriage which holds the filter leaves, and the whole movable part of the unit, including the head, carriage, and filter leaves, can be run out on a track so that the filter leaves are wholly exposed to view during the cleaning operation. This type of filter is usually limited to the handling of materials which will efficiently build up a cake of one inch or more in thickness. If a cake of this thickness cannot be built it is difficult to obtain automatic discharge of the solids. The automatic discharge is one of the features of the filter which eliminates a considerable amount of labor.

The following advantages are embodied in this type of filter:

(1) A relatively high filtering pressure can be obtained. For special work units of this kind have been designed for operating pressures as high as 250 pounds per square inch.

(2) It is possible to jacket the body of the filter with comparative ease, thus providing for heating with steam or cooling with brine.

The filter leaves run lengthwise in the cylindrical shell. Hence a complete set of leaves includes quite a variety of sizes. This lack of interchangeability of leaves and the fact that the filter is limited to the handling of material in batches are two of the important disadvantages of this type of filter.

Sweetland Pressure Filter

This filter originally came into vogue in an early design for metallurgical work, but has since been modified and found wide application in handling such materials as sugar, slow-filtering slimes, and petroleum oils after contact bleaching.

The filter body is of cast-iron cylindrical design for normal working pressures of approximately 50 pounds per square inch. The body is mounted horizontally and split along the horizontal diameter, the upper body being mounted stationary and the lower body being hinged at the back to the stationary upper body. The leaves are of circular disk construction and are therefore all of the same size for a given size of unit. This is in contrast to the Kelly filter, where the leaves are rectangular. The Sweetland filter is provided with an internal manifold pipe for playing streams of water across the surface of the filter medium, and hence has been particularly successful in handling materials involving the removal of a very small percentage of solids where a filter aid can be used to protect the cloth from gumming and to improve the clarity of the filtrate.

The Sweetland filter has met with favor in the handling of strong alkalies because of the ease with which monel metal filter cloth can be installed. Likewise the construction of the filter makes it comparatively simple to provide a lead lining and lead filtrate connections for sulfuric acid and other corrosive liquids which can be handled with lead contact. The small excess space in the filter body recommends this unit to problems where a very thorough washing of the cake must be obtained.

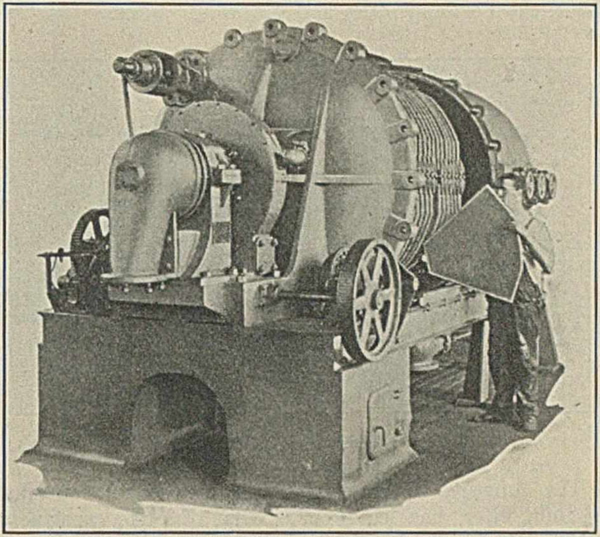


Figure 2—Sweetland Cantilever Type Filter

In operating this filter care must be taken to see that it is not overcharged with solids. Furthermore, it is usually difficult automatically to "dry" discharge cakes of less than one inch thickness. Like the Kelly filter and other leaf-type non-continuous filters, this unit is designed for the handling of material in batches.

Rotary Leaf Type Pressure Filters

Experience showed that the stationary type of pressure-leaf filter was unable to handle certain materials which had a rapid settling tendency. Materials of this kind produced tapering cakes which were thicker at the bottom than at the top, thus frequently impairing the washing efficiency. To provide a filter for handling materials of this character and also to secure a more thorough sluicing of the filter leaves than is possible with a stationary leaf filter, a rotating pressure leaf type filter was produced. At present there are two filters of this type and the filter leaves are of circular disk construction mounted on a horizontal shaft supported within a pressure tight shell. These include:

(1) The Vallez filter, which came into use several years ago and which has found considerable application in the handling of materials which can be discharged by sluicing without opening the filter body.

(2) The Sweetland cantilever type filter, which operates on the same principle as the Vallez but which includes certain advantageous mechanical structural details. The filter can be opened and the leaves exposed to view in a few minutes. It is comparatively easy to replace any leaf element without disturbing the remaining elements. A demand for improved accessibility and easier renewal of the filter cloth led to the development of the cantilever filter.

Continuous Vacuum Filters

The increase of large-scale manufacturing and the increasing rate of wages have largely been responsible for the increasing use of filters of this type. The first satisfactory commercial filter of this type was of drum design. Here the outside surface of a drum is covered with the filter medium and the lower half of the drum is submerged in an open tank containing the sludge to be filtered. The surface of the drum is broken up into individual sections which connect with individual ports in a valve mounted on the central supporting shaft of the drum. As the drum rotates each section goes through a cycle of filtering, washing, drying, and discharging, and the whole operation is continuous. There are several different makes of drum type filters, including the Oliver filter, the Portland filter, and the Mount filter.

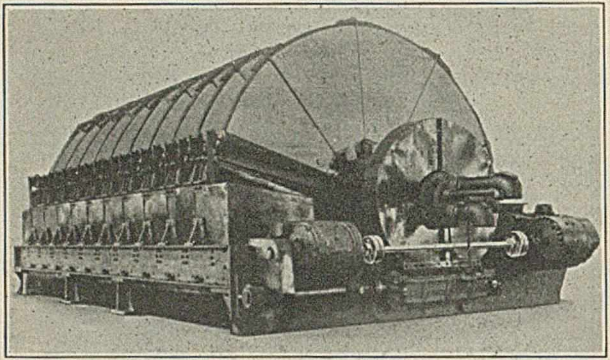


Figure 3—American Continuous Filter

The American filter, a more recent type of continuous vacuum filter, has leaves of circular disk-like construction composed of individual V-shaped units to make up the complete disk. A series of these disk-shaped leaves is supported on a horizontal shaft and the lower halves of the disks are submerged in an open tank containing the sludge to be filtered. Vacuum is applied to the various V-shaped leaf units through a rotating valve so that each unit comes through a period of filtering, washing, and drying as mentioned above for the drum filters.

Continuous vacuum filters offer the advantages of very low labor operating cost, low filter-cloth maintenance cost, high output per square foot of filter area because of continuous operation.

Their disadvantages are: (1) limitation to certain classes of material which are amenable to vacuum filtration; and (2) limitation in general practice to a feed which contains at least 20 per cent solids, thus frequently necessitating a thickener to increase the concentration of solids in the feed to the filter.

COMPARISON OF TWO GENERAL TYPES—(1) The drum type construction provides somewhat better washing where very large volumes of wash water are required per unit of filter area.

(2) The drum construction facilitates the use of certain devices such as compressor belts and rollers to secure a slightly drier cake than is possible in ordinary practice.

ADVANTAGES CLAIMED FOR DISK TYPE—(1) It requires less floor space.

(2) A damaged filter cloth can be replaced with little or no shutdown of the filter.

(3) Filter elements are interchangeable and readily removed so that the filter cloths can be easily removed for cleaning.

Continuous Vacuum Filter and Drier

One of the most interesting developments in recent years is a unit of this kind which has been placed on the market by the Filtration Engineers, Inc. This unit consists of a drum type vacuum filter with a traveling belt of comparatively open structure. This belt passes around the drum of the filter, and the solids build up in the interstices of the belt and are carried away from the surface of the drum in the belt, the latter then passing to a drier. The drier is so proportioned that by the time the belt emerges from the drier the solids are thoroughly dry and are knocked out of the belt by a vibrating mechanism. This arrangement does away with hand labor in filtering and drying the solids.

There are a number of successful installations of this device and it bids fair to find an application in industries where conditions run relatively uniform. The chief objection to this unit is that if anything goes wrong in any part of the apparatus both the filter and the drier are out of commission.

Thickeners

Dorr thickeners have found a wide application in thickening the feed to continuous vacuum filters. These units consist of a series of trays mounted inside a large open tank. The feed enters the center of the tank and the solids settle to the bottom of the tray and are raked to the center so that they gradually drop to the lowest point in the tank and are drawn out by a special diaphragm pump. The clear liquor from the top of each tray compartment is drawn off continuously.

During the last few years several types of thickeners using a filter medium have come into vogue because they offer advantages as saving in floor space for a given capacity and quicker handling of the material in process.

A Sweetland type thickener is one of the simplest in mechanical construction. Other types of thickeners using a filter medium for the separation of the solids include the Genter thickener and the Borden thickener.

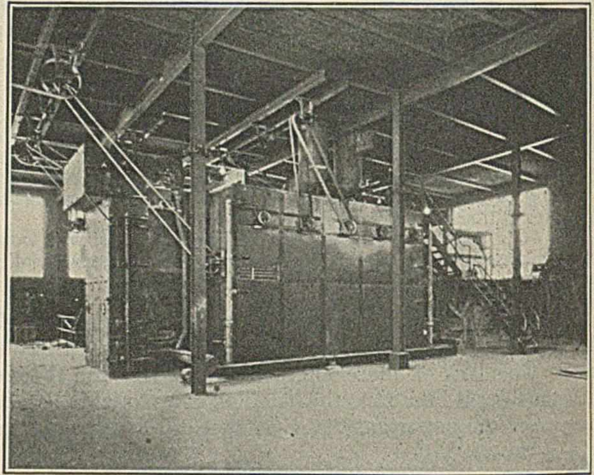


Figure 4—Continuous Vacuum Filter and Drier

Another newcomer to the thickener field is the Hardinge superthickener, which is essentially a sand bed somewhat similar to that used in a water filter. With this unit the top layer of the bed is continually removed by a set of plows, thus providing clear material which has filtered through the sand bed and a thickened accumulation of solids which has been deposited on the top of the sand bed.

Importance of Thorough Investigation of Filtration Problem

In this discussion we have briefly described some of the better known types of equipment in order to draw attention to the wide variety available and the necessity of investigating any filtration problem thoroughly to make sure of installing the type of equipment best suited to handling each particular problem.

In the past many thousands of dollars have been wasted in the purchase of filtering equipment. We know of instances where large purchases of equipment have been made without the material having been tested beforehand. This has frequently given rise to very unsatisfactory installations and waste of money. Even the same material frequently shows widely different filtering characteristics when manufactured in different plants, and it is always advisable, wherever possible, to test out a problem on a small scale with several different kinds of apparatus and to determine definitely which is most suitable for the work.

Furthermore, care should also be taken in purchasing second-hand equipment, for many manufacturers have several different designs of a given filter. Second-hand units are frequently purchased and it is later found necessary to rebuild a good part of the machine in order to adapt it to the particular work in hand. It is much cheaper to discover one's problems while working on a small scale than to put in a large installation and find that a mistake has been made.

The Fahrenwald Sizer

By Wm. C. Weber

The Dorr Company, New York, N. Y.

This company has recently taken over a new type of hydraulic classifier which, although primarily metallurgical in its applications, may be found to have very widespread and general application. By a classifier we mean a device other than screens for separating or grading particles according to size, particularly when suspended in water. Anyone who has given much thought to the development of a machine of this type is aware of the possibility of separating by using vertical currents of water of such velocity that the large particles sink and the smaller particles are carried upwards. This is termed "elutriation" or, more commonly, "hydraulic classification," as differentiated from classification by horizontal flow.

The development of the Fahrenwald sizer was an outgrowth of an investigation of table concentration undertaken by the Bureau of Mines at the instigation of the zinc-lead producers of the Coeur d'Alene district of Idaho. It is well known that a closely sized or, even better, a hydraulically classified feed gives the most favorable condition for good table concentration, and in following this to a conclusion, A. W. Fahrenwald invented the machine now under discussion.

Hydraulic classification as a means of preparing ores for tables has fallen into disuse because of the inefficiency of machines heretofore employed for this purpose. The usual procedure has been merely to dewater and deslime the grinding-mill product in some form of mechanical classifier. To appreciate thoroughly the beneficial effect of grading a feed before concentration, a discussion of the action of a pulp composed of particles of unlike sizes and specific gravities on a concentrating table is not amiss.

Stratification on Concentrating Table

As the feed is subjected to the reciprocating motion of the machine a stratification of the particles takes place. The particles are rolled and tumbled over each other, in which process the larger, light particles come in contact, supporting each other, forming interstices through which the fine and heavy particles fall, so that as the action continues the lower strata are composed of the fine, heavy particles and the upper strata of the light, coarser particles. After stratification, two forces are at work, the reciprocating motion which has effected stratification, and the force of the wash water, which is at right angles to the table motion. This second force carries the larger, lighter particles away from the finer, heavy materials, forming the lower stratum. In an ungraded feed an intermediate stratum is formed which is not positively subjected to the above action. The accompanying diagrams show how materials depose themselves on a table deck:

Figure 1. Particles of different sizes but of the same specific gravity, when treated on a table, are disposed on the deck with the very finest particles farthest from the very coarse particles. The finest particles occupy the highest position on the table deck.

Figure 2. Particles of different sizes and different specific gravities, the smaller having the greater specific gravity, take positions on the deck with the fine, heavy, mineral particles a maximum distance from the light, large ones.

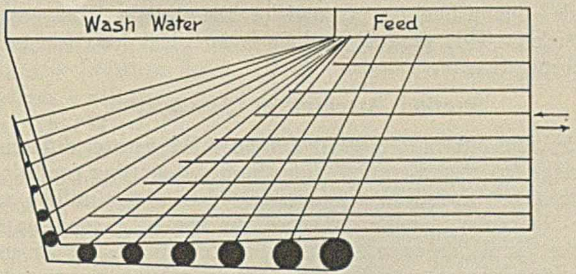
Figure 3. Particles of different sizes and specific gravities in this case, the large particles being the ones with greater specific gravity and the small particles being the ones with lesser specific gravity, do not show a marked separation—i. e., the particles tend to follow the same paths on the table deck.

Figure 4. Particles of the same size but of different specific gravities show a tendency to take different paths in passing over the deck. The tendency is due to specific gravity only, size not being a factor.

It can be seen that an ideal feed for a concentrating table is one in which the particles of fine, heavy materials are of a more or less uniform size, and light coarser materials are of another uniform size, as in Figure 2. A brief statement of the principles of hydraulic classification will illustrate how this is exactly the type of product produced, especially under hindered settling conditions.

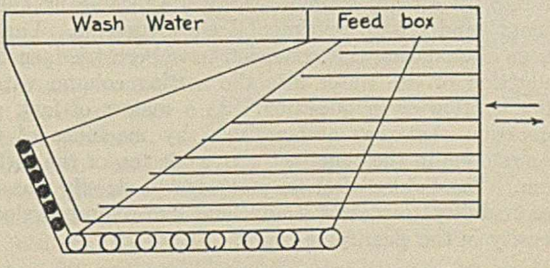
Principles of Hydraulic Classification

The force of gravity causing a particle to fall in a liquid is opposed by the resistance offered by that liquid. The ratio of surface to weight is greater for small particles than for



Particles of same sp. gr. but varying in size

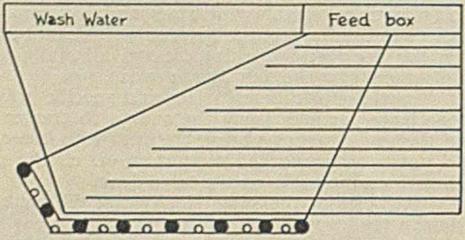
Figure 1



Particles of different sizes and sp. gr. the smaller having the greater sp. gr.

Figure 2

large ones; hence, the larger particles fall at a faster rate. A large particle having the same settling rate as a smaller particle must therefore be of lower specific gravity. The ratio of diameters of particles of unlike specific gravities having the same settling rates is known as their "free settling ratio." The free settling ratio is affected by the density of the surrounding medium. Consequently, as the density of the surrounding medium increases the free settling ratio increases. Mr. Fahrenwald's experiments demonstrated that a dense pulp composed of fine solids suspended in water has the same effect on the settlement of the particles composing it as a liquid medium of the same density. Therefore, the free settling ratio of particles settling in such a medium is greater, hence the difference in size of particles of unlike specific gravity will be greater when graded by a machine utilizing this property. This condition is known as "hindered settling classification." Particles kept in a crowded but fluid suspension by an uprising stream of water are said to be in "teeter." Such a teeter pulp has a specific sand-water gravity which is greater than that of water alone. Particles of different specific gravities developing the same full teeter density have, as in free settling, different diameters. This relation of diameters is termed the "hindered settling ratio" of the particles. Thus, if a feed composed of mixed solids is fed into a pocket in which there is a rising stream of water of uniform velocity, so adjusted as to keep the heaviest particles in teeter, particles of less mass will be carried away, while the particles remaining will be of two kinds—one of fine, heavy particles, the other of light, coarse particles. This graded product is an ideal feed for table concentration.



Particles of different size and sp. gr. the larger having the greater sp. gr.

Figure 3

Previous Attempts at Classification

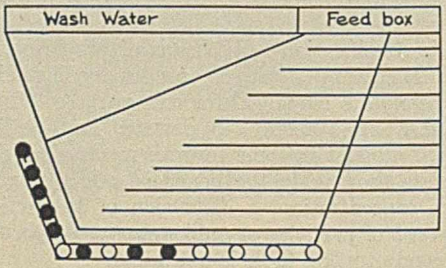
Previous efforts to take advantage of this greater difference in size of particles graded under hindered settling conditions have met with indifferent success. Most of the million and one hydraulic classifiers involve the use of a cone-shaped pocket similar in cross section to a filter funnel. It consists of a rectangular or cylindrical sorting column, surmounted by a conical vessel. Sands accumulate on the sides of the cone until there is a sufficient amount to cause them to slide down into the sorting column. These are technically known as "clots" and set up detrimental eddy currents. Various methods of obviating this condition have been tried, such as introduction of the water into the sorting column with a swirling motion or in pulsation. As a matter of fact, any classification that was accomplished by machines of this type was done in the zone just above the top of the sorting column. The failure of these machines to classify was due to the inability to maintain anything like uniform velocity or density in the classifying zones.

Description of Fahrenwald Sizer

The Fahrenwald sizer has overcome these difficulties as shown in Figure 5, and incorporates the essentials of a good hindered settling classifier. The pocket of the Fahrenwald sizer is rectangular in shape, which design allows an uprising stream of water of uniform velocity, thus insuring the prime requisite of hydraulic classification. The pocket is divided into two compartments by a constriction plate. The upper is termed the "grading compartment," the lower the "hydraulic pressure compartment." The lower compartment receives the water which passes through perforations in the constriction plate, this plate functioning to supply the water uniformly to the grading compartment.

The use of a so-called constriction plate is novel and one of the secrets of the success of this machine. It consists of a horizontal perforated metal plate having a number of small-diameter holes spaced on about 2-inch centers. The per cent opening is small and is calculated to give an appreciable constriction or pressure drop through the plate, thereby assuring a uniform distribution of the hydraulic water in spite of any density inequalities of the pulp in the pocket. Channeling and eddying are 100 per cent eliminated. Water from a constant-head tank is fed to the hydraulic pressure chamber. The volume of flow is controlled by a valve of the pinchcock type, which has been found particularly adapted for supplying a uniform flow. As can be seen, particular care has been taken in design in order to obtain a uniform flow of uniform velocity.

The Fahrenwald sizer consists of five main elements (Figure 5): a settling chamber, *A;* a group of classifying pockets, *B;* a perforated constriction plate, *C;* a group of hydraulic pressure chambers, *D;* and a group of automatic sand-discharge mechanisms, *E*. The settling chamber is V-shaped over the first five pockets, and conical over the sixth or desliming pocket. The feed is introduced into a shallow pocket equipped with a constriction plate, its function being merely to put the feed in a liquid condition and ease it into the first classifying pocket without undue disturbance. Two overflows are provided, one along the side of the settling chamber, *E*, for the length of the first five pockets, another in the form of a weir at the cone end of the chamber. The weir has an adjustable overflow lip which may be adjusted to vary the pulp level and thereby regulate the flow into the side launder.



Particles of same size but of different sp. gr.

Figure 4

The classifying chamber has vertical side walls continuing downward from the V sides of the settling chamber and is divided into the desired number of pockets by the suitable spacing of vertical partitions, *b*, thus forming rectangular pockets. The front side of each pocket is equipped with a glass window (Figure 6) to enable the operator to observe and adjust the grading of the material. The windows are indispensable for intelligent adjustment of the machine.

The constriction plate, *C*, divides the pocket into a grading chamber, *B*, and a hydraulic pressure chamber, *D*.

The hydraulic pressure chamber is that portion of the pocket below the constriction plate. It is provided with an inlet for the hydraulic water (Figure 6) and a bleeder or drain plug for the removal of any coarse sands that may pass through the constriction plate. This runs a small stream all the time. The discharge pipe, 14, of the automatic sand-discharge mechanism passes through the pressure compartment.

The hydraulic header (Figure 6) is a metal box on the outside of the settling chamber, the side of the chamber forming one side of the header. Branching from the header are individual pipes and valves going to the respective hydraulic pressure chambers. The valves of the pinchcock type regulate the flow of water to the hydraulic pressure chambers.

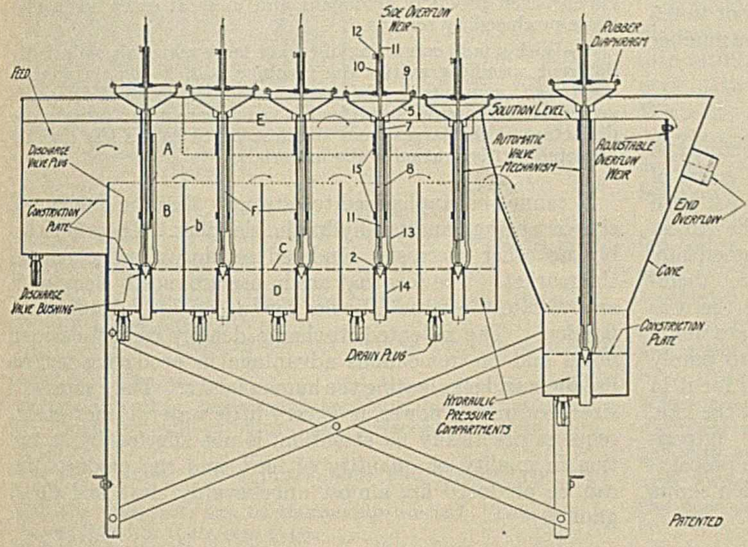


Figure 5—Fahrenwald Sizer

Water is admitted to the header from a constant-head tank, placed from 6 to 10 feet above the pulp level in the sizer, and equipped with an overflow pipe so that an amount of water slightly in excess of that required by the machine may be overflowed, thus maintaining a constant pressure.

The constant density or discharge control mechanisms are complete, individual units supported upon the constriction plates and held in vertical positions through holes in the constriction and bottom plates. They operate on the principle that a column of a dense material, teeter pulp, will support a higher column of a less dense material, water. Each consists of a discharge pipe, 14, and two sleeves, 15, welded to three supporting rods, 13. A movable pipe, 8, which contains the water column, is mounted in the sleeves, terminates a few inches above the discharge pipe, and is adjustably held in place by being threaded through the upper sleeve. A dish-shaped, hollow diaphragm chamber, 5, is attached to the upper end of this water-column pipe. A thin rubber diaphragm, 9, is stretched across the top of the diaphragm chamber. A small, vertical pipe, 10, is supported at the center of the diaphragm and engages a thin rod valve stem, 11, which passes down through the small pipe, diaphragm, and large pipe and carries on its lower end a tool-steel conical plug, 2, which fits into a conical seat in the upper end of the discharge pipe, 14. As the pulp in the classifying compartment builds up—i. e., grows denser—a higher column of water is supported in the water-column pipe, until the water flows into the diaphragm chamber, then into the small pipe, and pushes up on the rubber diaphragm to lift the valve plug, allowing some of the sands to discharge. As solids from the feed are continually building up the pulp bed, the discharge of graded sands becomes continuous and entirely automatic.

Operation of Machine

The pulp flows through the upper part of the classifier as it would through an enlarged launder. The coarse sand settles down to the bottom of the flaring settling chamber, where it comes under the influence of the sorting action of the rising column of water. The amount of water admitted to the first classifying pocket is adjusted to keep the coarsest and heaviest particles just in suspension, or what is called "full teeter." A dense, clean, liquid sand bed nearly the depth of the classifying pocket quickly builds up as the feed comes in, and is held at this density and approximate depth by the discharge mechanism, which is automatically operated by any changes in depth or density of the teeter bed. The sorting action of the first pocket then becomes very selective or exclusive, and only particles of each mineral present, of a small range in size, find a friendly environment in it, and all others are gently ushered along to the second pocket in series. The amount of water required by the second pocket to give just "full teeter" of the coarsest and heaviest particles reaching it is adjusted and the second pocket like the first soon develops its own teeter bed of definite density, which is somewhat less than that in the first pocket. The depth of bed and its density are automatically controlled. Thus we may have any desired number of classifying pockets in series, each having its own water requirement and each being automatically controlled and thereby effecting a number of classifications, the first product coarse and the very last fine sand with all gradations between these two. The maintenance of fluid sand-water beds of constant depth and density is the secret of the high-grade classification accomplished by this machine.

Accomplishments

The following examples are indicative of results obtained from the Fahrenwald sizer at over forty plants:

In one case the Fahrenwald sizer was installed at a metallurgical plant in the Middle West. Data were taken before and after installation. Previous to the installation of the Fahrenwald sizer the mill in question classified its table feed by means of a drag in closed circuit with a ball mill, the classifier overflow going to the concentrating tables. A Fahrenwald sizer was installed to classify the overflow from the drag before going to the tables. This change resulted in an increase of the table capacity of 100 per cent and a reduction of the metallic content of the tailings from 0.3 to 0.21 per cent, and materially raised the grade of concentrate produced.

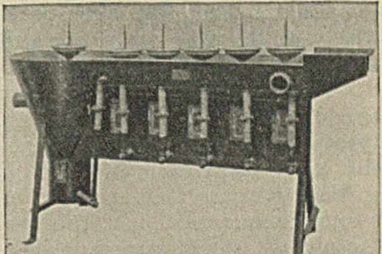


Figure 6—Fahrenwald Sizer (Photo

One of the first sizers was installed at a plant in the Coeur d'Alene district of Idaho, where gravity concentration had been employed for a number of years using screens to size the feed for the tables. The sizes to the tables were −20 mesh + 60, −60 + 100, and −100. Under these conditions the tables pulled out the clean galena very well, made a clean concentrate and no middlings, in fact showed no stratification of middlings whatsoever. To look at the tables one would think there were no middlings in the feed. The tailings ran about 2 per cent lead, the initial feed about 8 to 10 per cent. A six-spigot Fahrenwald sizer was installed. Each of the first five spigots was sent to one table, the sixth spigot was divided between two tables and the overflow, which was −200 mesh, was thickened and split between three slime tables. It was evident at once that, while before no middlings were apparent on the table, they now had a beautiful stratification. The first stratum was a clean galena product assaying 82 to 84 per cent lead. The second was a streak of middlings varying in size according to the percentage in the feed, and lastly, a streak of clean tailings assaying between 0.4 and 0.5 per cent lead. The middlings were reground to −200 mesh. Reducing the tailings from 2 per cent to 0.5 per cent or less, and at the same time decreasing the number of tables required, represented a tremendous saving.

Scope of Application

Although the remarks in this paper have been confined to the field of grading concentrating table feeds, the scope of the sizer is by no means limited to this use. Stress has been laid on this particular field because it is, to date, the largest single application in which the machine has been commercially demonstrated. However, as operators familiarize themselves with the device it is becoming apparent that the uses for which the Fahrenwald sizer is peculiarly fitted are many and widely diversified. Although its application to purely chemical processes may be few, there is a wide field for it in the treatment of non-metallics, sand, abrasives, and the like, which are closely akin to the chemical industry. Experiments are now under way on a modified type for the preparation of fine sizes of anthracite coal. This application shows considerable promise.

The Fahrenwald sizer acts as a classifier, a sizer, or a concentrator, depending entirely on the type of feed it is given and the nature of the products. To illustrate:

1—With a pulp consisting of two or more materials of distinctly different specific gravities, the machine will, if given an unsized feed, produce a series of very closely classified products. That is, each material will be graded to size, but each spigot product will consist of a mixture of the materials associated according to their hindered settling ratios. As previously brought out, such products are ideal as table feed, or where the specific gravities are widely different, the materials may subsequently be separated by screening.

2—With a pulp consisting of particles of uniform specific gravity it will, if given an unsized feed, produce a series of very closely sized products analogous and in most cases better than those produced by screens.

3—With a pulp consisting of two or more materials of distinctly different specific gravities the machine will, if given a properly sized feed, concentrate the particles according to their specific gravity. A properly sized feed is one wherein the ratios of the diameters of the largest and smallest particles are less than the hindered settling ratios of the materials.

It cannot be emphasized too strongly that the Fahrenwald sizer is not just another hydraulic classifier. There is probably no other successful hindered settling classifier now on the market. The few that are in use are mostly home-made and violate the essential rules for successful hydraulic classification. The patented discharge density control device is novel and of tremendous advantage in producing uniform products and eliminating the human factor. The Fahrenwald sizer requires no power, uses very little water, is inexpensive, requires practically no attention, is not affected by fluctuation in quality or quantity of feed, and the products that can be produced are almost unbelievably clean and closely graded.

Filter Presses—Standard Types

By John H. Clark, Jr.

T. Shriver & Company, Harrison, N. J.

THERE are very few branches of chemical manufacture which do not have the problem of filtration, and of the various types of equipment used to accomplish filtration the filter press is probably the most widely used, most easily operated, and most adaptable to a varied assortment of problems.

A large proportion of the men responsible for the selection of equipment realize the advantages of adhering to standard types of filter press. Many engineers, however, consider that their particular problem requires a filter press of a special type. Of these, some can be quickly convinced that standard equipment is satisfactory. Others become antagonistic if any attempt is made to convince them. Such men can always have exactly what they want, but they surely pay for it. Then there are problems which really require special filter presses.

We have made square, circular, triangular, and rectangular presses in sizes from 7 inches square up to 4 by 6 feet. There are various standard ways of feeding, discharging the filtrate, closing, etc. We have made four to five hundred types of filter presses, each distinct from all others in some important respect. It would seem that a buyer could satisfy his requirements from an assortment of five hundred; but it is surprising how often this is not true.

In several instances buyers have insisted that we furnish certain working parts of their own special design when it was perfectly clear that our standard design permitted much quicker operation. In such cases we draw up new designs, make the patterns, and then as a rule never use the patterns again unless the customer re-orders.

The prospective buyer may be a new man on the job. He wants to prove to his new employer that he is productive of ideas, so he decides on some change to be made in a certain filter press. If we cannot convince him of the inadvisability of making a change contrary to our standard practice, we make up special patterns and he pays for them. If we cannot first sell a standard type, we will design a press of any size or shape, whether it is elliptical, parabolic, 4 inches square, or 6 feet square.

This is no attempt to belittle the new ideas that engineers may have about the particular line of equipment which we manufacture. They give us many good ideas and we welcome them. In fact, we encourage our customers to do this and ask them if we can make modifications that will simplify their filtration problems. This is rather a plea to buyers that they consider standard types of equipment without prejudice.

The advantages and disadvantages of the various standard types are not always fully realized. These will now be briefly summarized.

Recessed Plate *vs.* Flush Plate and Frame

Shall a filter press be recessed plate or a flush plate and frame type? In the former the press cake is formed between two recessed plates. In other words, the pyramid or drainage surface is not flush with the joint surface. No frames are used with this type. In the flush plate and frame type both plates and frames are used, and the drainage surface is flush with the joint surface. The press cake is formed within the frames.

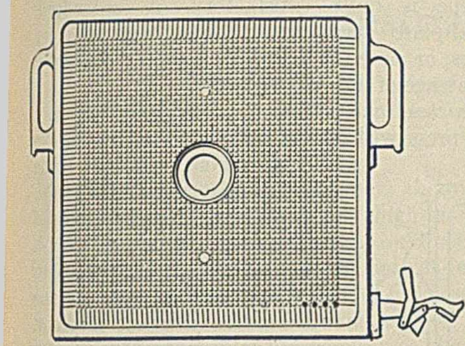


Figure 1—Recessed Plate, Center Feed, Open Delivery

The advantages of the recessed type over the flush plate and frame type are:

(1) Ten to twenty-five per cent lower cost, the difference being least in the larger sizes.
(2) It is shorter and lighter per unit of filtering area and holding capacity.
(3) The feed channel is large and there is no danger of stoppage and resulting plate breakage due to unequal pressures.
(4) There are half as many joint surfaces to be kept tight.

The advantages of the flush plate and frame type are:

(1) The press cake can be thoroughly washed. This cannot be accomplished in the recess type.
(2) A flush plate is lighter than a recessed plate and therefore easier to handle.
(3) The press cake can be made uniformly solid. There is usually a soft core around the feed channel of a recessed plate.
(4) Frames of any reasonable thickness can be used.
(5) The filter cloth is not subject to severe strain as on a recessed plate.
(6) Filter paper or fine-meshed wire screens can be used as a filtering medium.

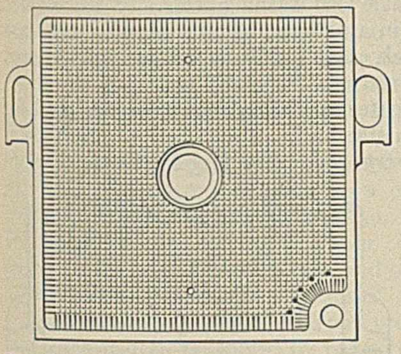


Figure 2—Recessed Plate, Center Feed, Closed Delivery

Location of Feed

Should the press be center-fed, fed through an eye in the joint surface, or through a lug outside the joint surface?

A center feed is necessarily limited to a recessed type of plate. As previously mentioned, it allows an unrestricted feed with little danger of plugging. The feed can be at any point in the recessed portion of the plate, but we standardize on the center of the plate and do not find it necessary to locate it otherwise. Holes must be properly located in the cloths, which are made tight at the centers of the plates, either by clip nuts or sewing.

A feed outside the joint surface can be through lugs at any point. It can be applied to the plate and frame press only. We standardize on side lugs, about one-third the height of the plate or frame from the top. These lugs then act also as the supports for the plates and frames. This design makes it unnecessary to cut holes in the filter cloth and the clothing of the press is a simple operation. It is only necessary to cut the cloths to length and fold them over each plate. Rubber collars or cloth pockets are used to make the lug joint surfaces tight.

A feed through an eye in the joint surface can be located at any point of that surface. We, however, use the corners only. For this type of feed it is necessary to locate a hole properly in the cloths, but the use of rubber collars is obviated. The cost is very slightly less than with outside lugs.

Open *vs.* Closed Delivery

Shall the press be open or closed delivery? For an open delivery press some means is provided for discharging the filtrate from each plate by a cast-on bibb, a screw or flanged cock, either one- or two-way, or a quick-action flap cock. When the filtrate from any one plate runs cloudy in an open delivery press, that particular plate can be quickly located and the cock on that plate closed, unless a cast-on bibb has been used.

In a closed delivery press the filtrate from each plate is led either to an eye in the joint surface or an outside lug, and delivered out through the head of the press. This method is particularly adapted to volatile liquids. Furthermore, it enables the filtrate to be delivered at a level above the press without additional pumping equipment. However, if the filtrate from any one plate begins to run cloudy, this plate can be located only by opening the press. This difficulty can be avoided by using a gage glass and cock on the side of each plate, running the filtrate first through this and then back to the closed channel. This feature raises the cost considerably.

Washing *vs.* Non-Washing

Whether the filter press shall be a washing or non-washing type is determined by the requirements of the problem. The wash is delivered to the filter press either by eyes or side lugs, and the remarks as to feed apply equally as well here. The washing feature can be added to the recessed plate type, but this type can never compete with the flush plate and frame type in this respect.

How Shall the Press Be Closed?

Ratchet, gear and pinion, and hydraulic are the three usual methods of closing. As a rule, a ratchet closing device is sufficient up to and including a 30-inch press. It is advisable to use a gear and pinion closing on the 36-inch size and larger. It adds about $40 to the cost, but is well worth it. The use of hydraulic closing will depend on the filtration cycle, and the number of presses to which it might be applied. A 36-inch press can be closed or opened in 30 seconds with hydraulic closing, whereas a gear and pinion will require 10 to 20 minutes. It can easily be determined whether the additional cost is advisable.

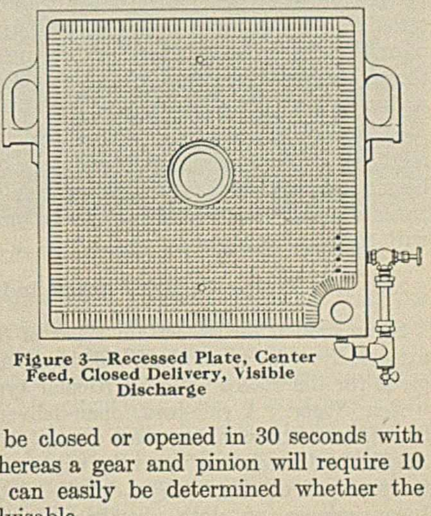


Figure 3—Recessed Plate, Center Feed, Closed Delivery, Visible Discharge

Other Considerations in Determining Type of Press

In the determination of the best type, there are still a few more points to be considered.

Shall the frames be open or of the so-called solid type? The required holding capacity of the press will determine this. If the amount of the solids to be removed is very small, the frames should be cast with a solid web. The holding capacity of the press can thereby be reduced so that the amount of unfiltered liquid remaining in the press at the end of the filtration cycle is exceedingly small.

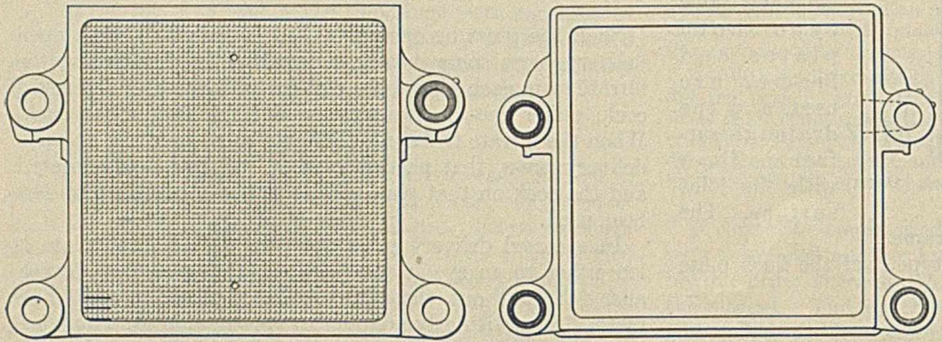


Figure 4 Figure 5

Flush Plate and Frame, Side Feed, Closed Delivery, Washing Type

Shall the plates be cored so that they may be steam-heated or brine-cooled during the filtration? Determination of this question should not be subject to guess work as cored plates add considerably to the cost.

What material may be used for the plates and frames? Special alloys quickly increase the cost of a filter press. Wood plates and frames can be used up to about 70–80° C., depending on the material to be filtered. It should be remembered that the joint surfaces on wood plates and frames are wider. A larger size is therefore required to give the same filtering area as on a metal plate. The cost per square foot of filtering area of a press with wood plates and frames is, however, about the same as that for one with cast-iron plates and frames.

No attempt will be made here to discuss the methods of determining the proper size of press and number of chambers. This should be no matter of guess work. It is surprising how many inquiries are received for a filter press to produce so many gallons, no mention at all being made of the characteristics of the material to be filtered. Apparently crankcase oil can be pumped through a filter press as quickly as distilled water.

Most any combinations of the various methods of feed, wash, and delivery can be made in standard types, so that conditions of nearly every problem can be met with standard equipment.

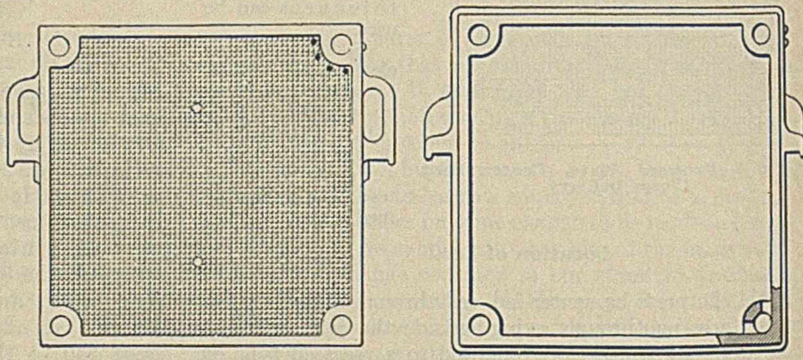


Figure 6 Figure 7

Flush Plate and Frame, Eye Feed, Closed Delivery, Washing Type

Presses Used in Various Industries

Some industries use certain types of filter presses almost exclusively. A few of these will be mentioned and reasons given for the choice of the particular types.

Raw Sugar. A side-feed, open-delivery, flush plate and frame, cast-iron washing press is used in nearly every case. A side feed is chosen to avoid wastage of filter cloth due to improper cutting of eyes in the cloth by cheap labor. Inconvenience of cloth shrinkage is also avoided. The selection of a washing type is of course imperative. The plate and frame type gives the most satisfactory washing. Open delivery is necessary owing to the danger of one or more chambers running cloudy.

Clay. This is purely a dewatering proposition, so that the cheapest type is quite satisfactory. A center-feed, cast-iron recessed-plate press with either open delivery with cast-on bibbs, or closed delivery is chosen. The center feed allows the passage of any large lumps.

Lacquers, Varnishes, and Enamels. The selection is a plate and frame press with closed delivery through an eye and feed through an eye. The plates are cast with solid webs. Closed delivery is used because of volatile constituents. Flush plates are necessary so that paper or fine-mesh wire screens may be used as the filtering medium. Feed and delivery are through eyes to avoid the use of rubber collars which might be affected by solvents. Solid frames are used to give a small holding capacity.

Fruit juices are handled either in wood or aluminum presses. The flush plate and frame type is most desirable as thicker press cakes can then be formed.

Wood presses are used for *cider and vinegar,* a recessed plate for cider and a flush plate for vinegar. Thicker press cakes can be formed with vinegar when using a filtration aid so that the flush plate is desirable.

Dry and pulp *colors* usually require either a center or side feed cast-iron press. If the user does not believe that washing can be accomplished in a filter press, a center feed type is used; otherwise a side feed washing press.

Shellac is handled in a plate and frame press so as to use paper or to form thick cakes by use of a filter aid. Closed delivery is usually preferred.

Yeast requires a center feed cast-iron press designed for pressures higher than standard.

The *dyestuff* industry runs very largely to wood plate and frame presses of the washing type with open delivery.

Waxes require steam-heated plates.

In some cases several different types will be found in use for exactly the same purpose.

Conclusion

In closing, we wish again to emphasize the advantage in not assuming that your particular filtration problem is different—somebody else has probably done about the same thing in a standard type of filter press. You can do it, too, and you can save money by doing it. And saving a few dollars will make more of a hit than the doubtful cleverness of special designs.

Industrial Heating by Oil Circulation

By Alexander B. McKechnie

Parks-Cramer Co., Boston, Mass.

During the last thirty years there have been many attempts to construct a high-temperature heating system in which a liquid would act as a transmitter of heat and which would, in principle at least, be similar to the well-known hot water heater. These attempts were brought about because the industries were demanding higher temperatures in their process work and the only available method was either high-pressure steam or direct fire.

It will be readily understood that many difficult problems are encountered when steam above 125 pounds is applied to ordinary heat-consuming vessels of either the cast integral or the welded steel jacket type, and that any direct fire methods are usually accompanied by hazard, ill effects on the product, and inefficiency. It was supposed by the builders of the earlier systems that all that was necessary to solve the problem was to place any medium with a high boiling point into some kind of a system arranged for heating and circulating. In fact, several attempts were made in which no pump at all was used, depending entirely on thermal circulation.

All these systems were very short-lived as they ceased to operate owing either to fouling by carbon which deposited rapidly, or to burning out of the heaters themselves. It was quite natural for the designers to suppose that all their troubles lay in the circulating fluid, and because they were using the best that the market produced it was probably decided that a practical solution of their problems was impossible.

There is no question that the same difficulties would be met today by anyone building up a circulating oil system with no experience in this connection. In fact, in the development of the particular system discussed here there seemed to be no end of problems, and on the solution of one others of even greater difficulty arose.

By consistently attacking each new problem as it came up—and some had to be solved by actually testing parts to destruction—a satisfactory performing system has been developed.

Advantages

Heat transmission by hot oil embodies the desirable features and eliminates the objections of other methods for obtaining high temperatures. The quantity of heat delivered is under control at all times, and product temperatures up to 550° F. are reached without difficulty.

The pressure on the entire system is practically negligible, making it particularly adaptable to vessels with cast integral jackets, usually built to withstand pressures of about 100 pounds, and to the jackets of glass-enameled steel tanks, which are built only for pressures up to 75 pounds and are used extensively in the manufacture of chemicals and food products. This point is readily understood when we consider that 100 pounds of steam represents only 338° F.

Distribution of heat is uniform over the entire surface of the vessel and the entire mass is treated instantly and alike, the temperature being sufficiently high to perform the work but without damaging the product.

The temperature can be controlled within close limits either manually or by thermostatic devices. This is of vital importance in delicate reactions where temperature variations in the heating medium are not permissible. Charts from recording thermometers show a temperature difference of from about 3° to 7° F. in the circulating oil when it is thermostatically controlled.

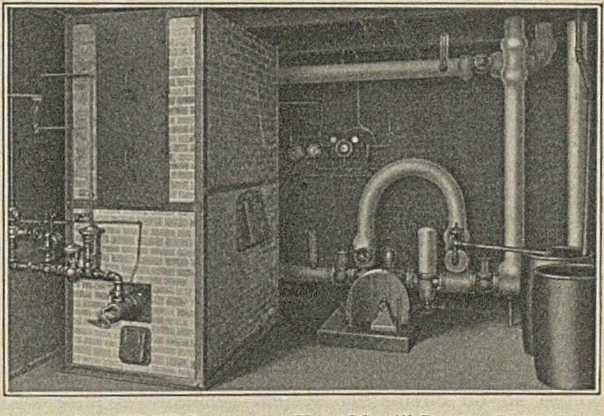
The fire hazard is removed as there is no flame in contact with the vessels. The absorber furnace, the only place where flame exists, is isolated from the manufacturing equipment, and where conditions make it necessary the entire heating plant can be installed in a separate building.

Design of System

In the design of a system of this kind, there are five main factors, each one of which requires most careful study.

Design of Heater or Absorber—The absorber, like any other heat exchanger, must be designed for maximum efficiency consistent with long life and freedom from trouble. It must be readily accessible for inspection or repair. The furnace must be built to withstand the high temperatures met in work of this kind and be thoroughly insulated to prevent undue radiation losses.

Such points as the length and size of tubes, the velocity of the circulating oil, and proximity of the fire to the tubes require careful study.



Standard 400,000 B. t. u. per Hour Merrill Process System

Circulating Pump—It is generally believed that the circulating pump should be of the positive displacement rotary type to insure a known and non-pulsating flow. The necessity for these features is readily understood as the temperature drop in the circulating oil of a system of given capacity is inversely proportional to the rate of flow of the circulating oil. A small temperature drop is desirable as it means a more uniform temperature over the entire surface of the vessel being heated.

Type of System—Experience has taught the superiority of the closed system—that is, one in which the hot oil does not come in contact with the atmosphere. This point is vital, as the oil would rapidly oxidize and soon become too viscous to pump freely, resulting in a decreased flow and burning out of the absorber tubes due to carbon deposit. Provision must be made, however, for expansion of the oil. The circulating oils generally used have a coefficient of expansion of about 0.000486, which means approximately a 25 per cent volumetric increase in 500° F. rise. An expansion tank located on the end of a dead or stagnant line attached at the proper place in the system takes care of this very satisfactorily. It also serves as a liquid seal and insures the exclusion of air. The expansion tank, being vented to the atmosphere, does not permit the building up of high pressure. A number of tests have shown the oil in the expansion tank to be about 300 degrees lower than the oil in circulation.

Circulating Oil—It is very important that the circulating oil used for this service be carefully selected. It must have a high flash point and be free from all impurities. Viscosity and specific heat are also of importance. A number of tests show that the specific heat increases with temperature on a straight line, its value being 0.68 at 550° F.

Although the circulating oil is one of the important factors entering into a successful system, it must not be supposed that the whole operation depends upon it. For instance, the proper circulating oil will not cure the ills of a poorly designed system, and a perfectly designed system with a poor oil could only bring failure. Success can only be obtained by using the right kind of circulating fluid in a system of the correct design.

Construction of Pipe Lines—Even though the design of transmitting lines for the circulating fluid would at first appear to be a simple matter, they are, nevertheless, one of the most difficult and expensive features in a system of this kind. Ample provision must be made at all points for expansion, which amounts approximately to $^1/_{32}$ inch per linear foot. As a hot oil of this nature is an exceedingly fugitive material, all castings and pipe joints must be so designed that there is no possibility of leakage. A pipe line constructed in the same manner as for steam would be merely a source of expense and trouble. It is practically impossible to use threaded joints above 2 inches, and thus far sheet packings have proved to be useless for the flanges. As the pressure is comparatively small—from 10 to 20 pounds per square inch—standard weight steel piping is satisfactory. There is no corrosion as the oil actually preserves the pipe. Steel flanges, screwed and welded onto the pipe, prevent leakage at that point, and specially designed metal gaskets take care of the flanges. It is advisable to avoid joints as much as possible, so pipe bends and offsets are substituted for fittings. These parts also reduce friction and vibration caused by column inertia.

Fuel

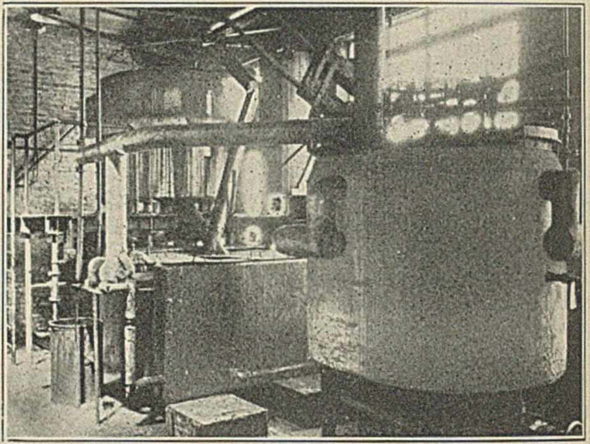
Compounds requiring temperatures that make it necessary to use an oil circulating system generally require also a uniform temperature in the heat applied. For this reason fluid types of fuel are used, the most satisfactory being oil, gas, or electricity. It is probable, however, in the absence of either of these kinds of fuel that the absorber could be coal-fired and with proper attention maintain reasonably close temperature regulation.

When electricity is used as the primary source of heat, it is applied through specially designed, high-resistance, electric-heating elements. These elements must be so installed that all chance for overheating of either the element itself or the oil in contact with it is removed. The thermal efficiency of the absorber is very close to 100 per cent and, where the cost of current is low enough to justify its use, this method of heating is ideal.

Applications

Installations have been made in a great many chemical plants for high-temperature heating and evaporating, distilling, subliming, and refluxing.

In connection with the high-temperature heating of certain vegetable oils for deodorizing, some of the most successful installations have been made. The vegetable oil in batches ranging from 5000 to 30,000 pounds is raised to 450° or 500° F. Wide application has been found in the manufacture of electrical equipment such as transformer and other coil impregnation, molded electrical products, wire insulation, etc. In the asphalt-consuming industries, asphalt shingles, saturated roofing, and many forms of coated paper are being produced.



Battery of Enameled Jacketed Tanks for High-Temperature Heating

In all this work the material to be heated can be maintained within very close temperature limits owing to the simplicity of heat regulation at the absorber. Owing to the high uniform temperatures that can be carried in the circulating oil, the equipment can be operated for the maximum hourly production and a product of the highest quality and uniformity is assured.

A plant manufacturing rubber-covered electric wire formerly operated on steam and could not maintain above 280° F. in eleven dipping and polishing kettles. They were using 125 pounds pressure steam. Today the oil system operates at 14 pounds pressure and their required temperature of 325° F. in tanks is uniformly maintained. The production was increased about 50 per cent and the quality vastly improved.

A plant manufacturing hard wax products has the heating plant isolated in a separate building outside the plant and circulates the oil at about 525° F. through 4-inch piping to the third floor of the manufacturing building. There it is passed through jackets of a number of glass-enameled vessels and returns at 490° F. for reheating. This plant formerly operated on direct-fire gas. The intense heat damaged the glass enamel with which these kettles were coated and also discolored this compound to a brownish shade. Owing to the overheating of some parts of this product because of poor heat distribution, a loss of some of the more volatile constituents was unavoidable, thus impairing the quality. The material today comes from the kettles finished and is snow-white in color. The system has been operating for about ten years.

Another concern, manufacturing a popular food product by boiling it in a vegetable oil, has a system of this type and circulates the hot oil through the jackets of a battery of eight kettles. The vegetable oil is maintained without difficulty at the desired temperature. Gas is used for heating the circulating oil in the absorber tubes. Three gas burners are attached to the furnace and the entire system is extremely simple.

In connection with a great many of these industries it is necessary to convey over long distances materials that are in a solid state unless they are maintained at fairly high temperature. For this work a system of jacketed piping, fittings, and cocks is used. The product passes through the center pipe and this center pipe, by means of the jacket, is completely surrounded with the circulating oil at the proper temperature. These jacketed lines are so constructed that there is no chance for leakage of one fluid to the other.

Capacities

These systems are built in a number of different sizes and there are systems today ranging from 100,000 to 2,800,000 B. t. u. per hour. There is no known limit to the size of these absorbers. Where a greater quantity of heat is required than can be delivered by one absorber, two or more machines can be connected in battery similar to steam boiler practice; in fact, a great many installations have been made this way.

Stoneware as a Chemical Engineering Material

By Percy C. Kingsbury

General Ceramics Company, New York, N. Y.

In the transfer of a chemical process from the laboratory to the plant so many new factors are introduced that a laboratory success often proves to be an industrial failure. Frequently these misfortunes are due to the selection of the wrong material for the construction of the industrial plant. Usually the laboratory experiments are carried out in glass or porcelain, and these materials would be ideal for large-scale production if it were possible to manufacture chemical plant equipment from them at a reasonable price and with sufficient mechanical strength to withstand ordinary factory abuse. Unfortunately, however, the use of these ideal materials is limited by the sizes and shapes that the manufacturer can produce, by their fragility, and sometimes also by the expense.

In seeking a suitable structural material for a new plant the engineer, especially if his experience has been largely outside the chemical field, is apt to look to the metals and alloys that can be made up into large shapes and that have considerable mechanical strength. It is usual to justify the selection of a particular metal or alloy by laboratory tests indicating the loss in weight of the material over a certain period of time. Often, however, after the plant has been in operation a short time, it is found that in the laboratory tests the actual conditions were masked by the formation of a protective coating which in the plant is removed almost as fast as it is formed. Often also electrolytic conditions occur in the plant that are absent in the laboratory and greatly enhance the rate of corrosion. Even if the corrosion is inconsiderable it may prove objectionable in many ways. The metal of the vessel may entirely change or even inhibit the reaction, or a slight corrosion may so contaminate the product as to make it worthless or at least impair its value materially. This is a vital consideration in the manufacture of foodstuffs and pharmaceuticals and may also be of great importance in the manufacture of dyestuffs and intermediates.

Notwithstanding these drawbacks, the metals and alloys have very obvious advantages as structural materials for chemical plant. In the effort to use them to the fullest possible extent an entirely new technical literature has developed during the past decade covering the action of various corrosive agents on metals and alloys, and the problem is now exercising not only the chemical industry but technical associations in every branch of engineering. In using the large mass of such data now available, however, it is important to bear in mind that the presence of quite small quantities of other chemical products, sometimes unsuspected, may entirely change the conditions as regards corrosion. Another important fact is that, however small the corrosion may be, it is continuous and cumulative and that when used under such conditions the ultimate failure of metal equipment is inevitable.

The use of clay and other silicate products for chemical plant removes the corrosion problem entirely and enables us to secure on an industrial scale conditions parallel to those under which the process was worked out, also in silicate products, in the laboratory. As equipment made of clay is usually cheaper than similar equipment of metal or metallic alloys, it is now the usual practice to use it wherever possible.

Excluding the immense field of refractories and certain special ceramic products of limited application, the various silicate products used for chemical processing are glass, fused silica, enameled iron, and chemical stoneware, and of these the most important is stoneware.

Properties of Stoneware

Chemical stoneware is the most durable of all clay products. It is extremely hard and dense, and steel will strike a spark from it just as it does from flint. It is an electric insulator and insulators made of a special grade of stoneware have been used for experimental purposes at a potential of 600,000 volts. It resists the action of all acids and other corrosive materials encountered in industrial work. The only exceptions are those materials which also attack glass—that is, hydrofluoric acid and hot, strong caustic alkalies, which also have a slight surface action on this ware just as they have on glass.

Chemical Composition of Average Chemical Ware

	Per cent
Silica (SiO_2)	73.23
Alumina (Al_2O_3)	22.27
Iron (Fe_2O_3)	0.58
Lime (CaO)	0.58
Magnesia (MgO)	Trace
Potash (K_2O)	2.02
Soda (Na_2O)	1.42
Loss on ignition	0.06
	100.16

It is essentially an aluminum silicate partly combined and partly mixed with other silicates.

Physically, stoneware is an aggregation of more or less refractory particles of ceramic material in various stages of fusion, bonded together by means of a vitrifying clay, usually with the addition of a flux. The physical characteristics of such a material can obviously be modified between very wide limits by varying the size of the particles and the nature and proportion of the grog, the clay, and the flux. Thus stoneware covers a range of ceramic products which at one extreme are as coarse in texture and as porous as fire brick, and at the other extreme are as fine and as dense as porcelain. When manufactured for chemical purposes they are all resistant to corrosion, but the more porous bodies are more resistant to sudden changes in temperature. Consequently, when the ware has to withstand extremes in temperature, as in pipe lines for carrying off the hydrochloric acid gas from salt-cake furnaces or in the supports for the basins in a sulfuric acid cascade concentrator, a porous ware is selected. Where a non-porous material is required, as in the electrolytic refining of precious metals, a porcelain-like ware is furnished. Between these two extremes it is possible to develop a ceramic material to fulfil the requirements of most chemical operations.

The evaluation of the principal physical characteristics of chemical ware is necessary in order to determine the usefulness as well as the limitations of this product as an engineering material:

Tensile strength	1000 to 2500 lbs. per sq. in.
Compressive strength	25,000 to 80,000 lbs. per sq. in.
Modulus of elasticity	6,000,000 to 10,000,000 lbs. per sq. in.
Thermal conductivity (B. t. u.)	0.6 to 0.9
Specific heat	0.185 to 0.190
Specific gravity	2.06 to 2.36
Coefficient of expansion (° F.)	0.0000023 to 0.0000027

The tensile strength is high compared with other clay products and the next few years may show some very remarkable advances in this respect. It is, of course, low as compared with most metals. The compressive strength is high and this should be borne in mind in designing chemical-ware equipment. The thermal expansion is low, being about that of ordinary glass and much lower than the metals. The thermal conductivity is good compared with other ceramic products, though naturally very much lower than the metals.

Glaze

Chemical ware is usually glazed to give it a smooth, attractive finish. The only satisfactory glaze for this purpose is salt glaze, which is formed by throwing common salt into the kiln as the maximum temperature of firing is reached. The salt volatilizes and combines with the aluminum silicate of the ware, forming a sodium aluminum silicate, dense fumes of hydrochloric acid gas passing out through the stack.

It should be emphasized that the glaze is merely to improve the appearance and finish of the ware, as occasionally stoneware is sold for chemical purposes in which it is attempted to overcome the shortcomings of the ware by coating it with a heavy glaze of fusible clay applied by means of a brush or by spraying or dipping. This ware has the same objection as enameled iron in that the slightest break in the continuity of the coat, such as a small scratch or pinhole, allows the corrosive material to penetrate beneath the glaze which soon begins to peel off as it is merely held by adhesion to the body. Such glazes are liable to crack or craze when subjected to change in temperature, as there may be a difference between the thermal expansion of the glaze and of the body. Salt glaze, on the other hand, cannot craze or peel as it is intermolecularly combined with the body.

Equipment Now in Use

The practicability of chemical ware as an engineering material can best be demonstrated by considering some of the equipment that is already in service.

Perhaps the most impressive development in this field is the manufacture of high-speed machinery from chemical ware. Exhaust fans and blowers are made for handling such corrosive gases as hydrochloric acid, chlorine, nitric acid and oxides of nitrogen, sulfur dioxide, hydrogen sulfide, in which all parts coming in contact with the gas are made of this ware. These machines are furnished in capacities up to 6000 cubic feet per minute or more, the operating speed being 1000 r. p. m. for the larger sizes to 2000 r. p. m. for the smaller sizes. The impellers of these machines are made entirely of chemical ware without any reënforcement; consequently there is no possibility of corrosion. There are several of these machines in use today that have been in continuous service for fifteen years or more. An ample margin of safety is assured by testing each impeller at 50 per cent above its rated speed before shipment. We have, in fact, never succeeded in bursting one of these clay impellers in spite of the fact that in attempting to test one of them to destruction we ran it up to a peripheral speed of 21,200 linear feet per minute.

High-speed centrifugal pumps are similarly made from chemical ware for handling such corrosive liquids as sulfuric, muriatic, nitric, and acetic acids, fruit juices, vinegar, chlorinated brine, tin tetrachloride, etc. These pumps and, in fact, chemical-ware equipment in general are ideal for handling food products as they can be kept as clean as a china dish. The pumps are at present made in capacities from about 200 to 350 gallons per minute. The demand for them has been so great that we are at present working on an entirely new line of centrifugal pumps with capacities from 60 to 800 gallons per minute that can be used for lifts up to 100 feet.

Plunger pumps are also made of stoneware for handling corrosive liquids at pressures up to 30 pounds per square inch. With some modifications in the design these pumps are used for the evacuation and compression of corrosive gases.

Many chemical engineers prefer to use compressed air for moving acids and other corrosive liquids. All the various devices for moving liquids by compressed air are somewhat inefficient, but they have the advantage of having no moving parts and being simple in construction. They require the attention of an operator at regular intervals, but an automatic device is made in which these operations are carried out by means of a floating ball valve. This automatic acid elevator will operate year after year with absolutely no attention and in some plants this assurance of constant operation and absence of expense for upkeep is considered as ample justification for a somewhat higher cost of operation as compared with the use of pumps.

In addition to the devices that have been described, the shapes furnished by the chemical-ware manufacturer comprise the usual line of containers, tanks, piping, valves, etc., and in addition such chemical equipment as condensers, scrubbing towers, rectifying columns, kettles of all kinds, absorbers, filters, ejectors, agitators, etc. In general, it may be said that it is possible to duplicate in chemical ware any equipment that can be made in metal, with due allowance, of course, for the difference in physical properties of the two materials.

The standard material that has been described represents not more than perhaps 30 per cent of the products of the stoneware manufacturer. Most of the equipment manufactured is to special design and this material lends itself excellently to special work of this nature, as the ware is molded out of soft clay and can therefore be worked up by hand into almost any desired shape at no great expense.

Development of Chemical Stoneware

The first primitive experiments in chemistry were made in clay vessels and today the same material forms the backbone of industrial chemical apparatus. As an industry the manufacture of chemical plant equipment from clay is about one hundred years old, stoneware for chemical purposes having been made in Philadelphia as early as 1816, while the first factory devoted exclusively to the manufacture of chemical ware was established in Germany in 1836.

At first the chemical manufacturer had to adapt his equipment to the shapes the potter was able to make without regard to their efficiency but the chemical-ware manufacturer of today is able to meet most of the demands that modern chemical industry makes on his product.

The users of chemical equipment are therefore urged not only to study the advances made in the metallurgical field, but also to acquaint themselves with and to take full advantage of the progress made in the ceramic industry. They would thereby eliminate the corrosion problem entirely, with its hazard, its contamination of product and expense for upkeep and repair, and they may secure at a considerable saving in initial cost chemical equipment that, with the most ordinary care, is more permanent than their most substantial buildings.

Oxy-Acetylene Welding in Chemical Plant Construction

By G. O. Carter and W. B. Miller

The Linde Air Products Co., and Union Carbide & Carbon Research Laboratories, Inc., New York, N. Y.

THE broad subject of oxy-acetylene welding in the chemical industries has received considerable attention during the past two years. Most of the articles have been of a primary nature, discussing the fundamentals of correct welding procedure and applying particularly to low-carbon steel. It cannot be expected that the chemical engineer will also be a welding engineer. However, he should know enough of the process and its possibilities to enable him to carry on his work efficiently. At present many metals are at the disposal of the chemist and new alloys are being frequently brought out having special properties. Whatever the metal is, the skill of the welders should be checked by asking them to make test welds in the metal under consideration and then testing these welds. Any new construction work should be properly designed, laid out, executed, and tested. In other words, a knowledge of what may be termed "procedure control" is assumed to be in the minds of the engineers and supervisors. Procedure control in oxy-acetylene welding consists of the proper application of the process to correct materials. The essentials of proper application to all processes of fabrication may be summed up as follows:

(1) Proper design by capable engineers who understand welding.
(2) Selection of the proper materials—i. e., plate and rod.
(3) Testing of welders.
(4) Efficient supervision by a shop foreman who understands welding.
(5) Proper inspection during construction by the purchaser.
(6) Careful final testing and stamping thereon of the working pressure and other necessary data.

Probably 98 per cent of all welders are working with steel or cast iron. Many assume, therefore, that it is easier to weld steel and cast iron than to weld the other metals so frequently used in chemical equipment. As a matter of fact, steel is not so easy a material as cast iron to weld properly, and usually requires more skill than for welding lead, bronze, brass, aluminum, nickel, and copper, all of which can be joined most satisfactorily by oxy-acetylene welding. A welder, of course, must have practice before he can satisfactorily weld any special metal, and a steel welder must practice on the new metal just as he did when learning to weld steel. Regardless of the metal, the same steps should be used in checking the welding—i. e., the idea of procedure control is applicable to the welding of any material. The workman should qualify in welding the particular metal used, which should be of approximately the same thickness as that used in the equipment he is called upon to make. Next, the materials of construction should be suitable for welding, and the filler metal should also be of proper quality.

Many types of apparatus can be fabricated by oxy-acetylene welding, usually without the use of elaborate blueprints, with a corresponding saving in time and money. Following is a brief list of apparatus which have been fabricated in this manner—pressure and vacuum reaction tanks, condensers with closely spaced tubes having considerably higher capacity per unit, stills, agitators, pipe lines, plain or jacketed, having no flanges and thus allowing for easy insulation, driers, kilns, etc. Such apparatus may be made of steel, copper, aluminum, nickel, monel metal, or other suitable metals or alloys.

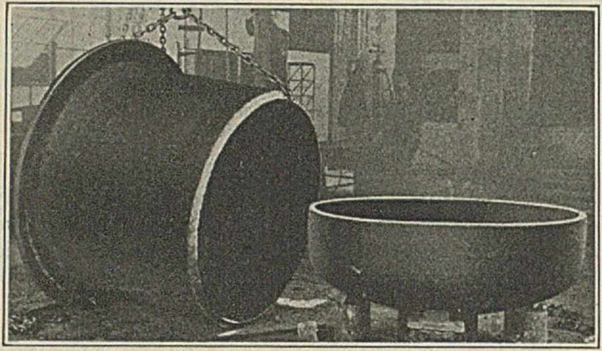
Study of Construction Materials Necessary

When choosing a particular metal for a piece of apparatus its properties must be carefully considered, for the oxy-acetylene flame is so hot that it brings about reactions equivalent to those that occur during the manufacture of the material. Any impurities, therefore, that become active at high temperatures may result in welds of inferior quality.

For example, commercial copper usually contains appreciable quantities of cuprous oxide disseminated throughout the metal. However, such copper is troublesome in welding, for at temperatures just below the melting point the oxide is rejected to the grain boundaries either as such or as a eutectic. These films of oxide or eutectic result in low-strength material of low ductility. On the other hand, copper which has been thoroughly deoxidized with silicon and welded with rods containing silicon does not experience this trouble and yields welds with superior physical properties.

Even low-carbon steel has sometimes been found to contain an excessive amount of non-metallic inclusions, such as sulfides, oxides, and silicates, which at times collect at the junction of weld metal and plate, resulting in potential planes of weakness. A fusion test and a quick microscopic examination will usually locate such defective material. Defective steel often sparks and boils excessively when melted. Fabricators have found low-carbon steel of firebox or flange quality to be excellent material for welded construction.

Aluminum which will roll into sheets can hardly have any impurities that will be troublesome under the flame, and it is recognized by experienced welders that aluminum is an extremely satisfactory metal to weld. However, for obvious reasons one cannot expect to develop in a weld the strength of a cold-rolled aluminum sheet or a duralumin sheet in which the strength is obtained by rolling and heat treatment. Furthermore, special provisions must be made to prevent the collapse of the article while welding because aluminum maintains its form and color without change until the melting point is almost reached, when it suddenly collapses. It is also weak when hot and it is therefore desirable to support it properly during welding.



Corroded Cast-Iron Kettle Bottom Replaced

There is such a large variety of brasses and bronzes that it is difficult to name any particular composition as a type. As a general rule, the presence of lead is troublesome and causes hot shortness, but if its percentage is kept low the material will weld satisfactorily.

When welding brasses containing large percentages of zinc, the zinc volatilizes and comes off as a white vapor at the welding temperature. Zinc fumes frequently nauseate welders, but trouble from this source can be usually avoided by proper ventilation. Masks can be worn, if necessary. Men can offset the effect of the zinc fumes by drinking sweet milk at intervals, as is done in smelters.

The knowledge gained from a careful consideration of the various properties of a metal or alloy often causes one to depart from usual welding procedures or practices. Brasses, when molten, dissolve readily gases which are rejected on solidification and at times result in a porous condition. Instead of the customary neutral flame, good results may be obtained by using a flame with a slight excess of oxygen. Probably the more rapid oxidation or combustion of the reducing gases tends to prevent their absorption by the molten metal. With nickel, the best results are obtained by using a flame with a slight excess of acetylene. A study of the metallurgy and metallography of nickel shows this to be a rational procedure.

Lead is one of the easiest metals to weld, and has been so joined for lining chemical equipment for fifty years or more. The welding of lead is commonly spoken as of "lead-burning."

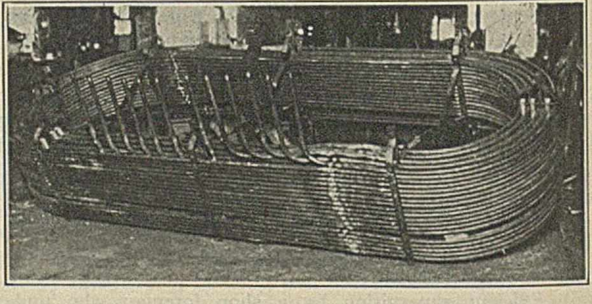
The corrosion-resisting alloys are often troublesome, not on account of their welding, but because of a changed condition of the metal adjacent to the weld. This may be called a welding problem, but is just as much a problem for anyone who is flanging such alloys or is in any way heating the metal to temperatures above the critical range. Certain alloys will, undoubtedly, always give trouble under the effects of high temperatures because of grain growth, which cannot be broken up by annealing. It therefore behooves the purchaser and fabricator to learn everything possible about the dependability of a fabricated structure rather than judge the suitability of a material entirely by its corrosion resistance. If one is not familiar with the suitability of a material for welding, the information can usually be obtained either from the manufacturer of that material or from the service departments of the large producers of welding gases.

Another material used in chemical construction that must be handled very carefully in welding is high-silicon iron. This material can be and has been very successfully welded, but it is so hot-short that it is liable to fly to pieces after a good weld has been made and before it has completely cooled.

From the foregoing it is quite apparent that the material of construction must be carefully studied. It is also evident that proper preparations must be made for welding each different metal. Aluminum, for instance, must sometimes be held in a jig or otherwise supported to prevent collapsing. High-silicon irons must be very carefully preheated and annealed. In some cases the use of flux is necessary to render fusible the oxide formed during welding. Special materials in sheet form sometimes buckle and warp unless clamped and handled so as to take care of the expansion and contraction properly.

Welding Operation

The actual welding operation is usually a very simple one provided the proper precautions and preliminary steps have been taken. As a rule a neutral flame is used, and the material should be fused and built up in a single operation wherever possible. With special materials remelting is generally objectionable. Suitable welding rods are now available for steel and practically all common nonferrous metals and many special alloys.



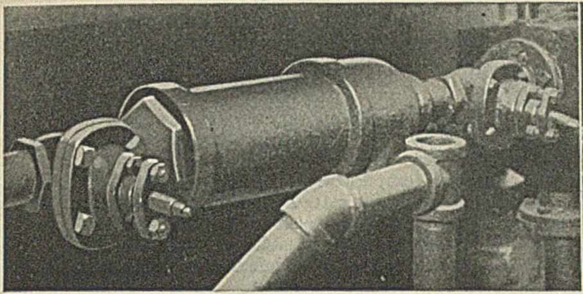
Copper Coil Containing 3000 Feet of Welded Tubing

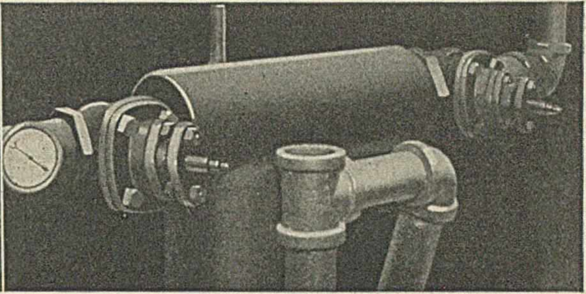
As a final step a thorough test should be given all work to prove that the joints have proper quality, particularly in apparatus involving elevated pressures, combustible gases, poison gases, etc.

Advantages of Welded Joints

In a short space it has been endeavored to show that oxy-acetylene welding can be successfully applied to the many special materials the chemical engineer has found suitable for his various processes, and he should be alive to the possibilities of the oxy-acetylene welding process. Welded joints offer many advantages over riveted or screwed joints. They are stronger and are an insurance against loss of gases or liquids through leaky joints, with the elimination of unsightly apparatus caused through seepage, etc.

Welded pipe lines are smooth inside, offering no obstruction to flow, and are easily insulated on the outside at a minimum cost, there being no flanges to cover. The welded pipe line can be made in any shape to suit the engineer, fittings of any type and angle being easily fabricated.


Separators Often Used in Oil Refineries


Same Arrangement Made of Welded Pipe

Lastly, oxy-acetylene welded apparatus is safe. We know it is because welded apparatus in our own works has been working under 3000 pounds pressure for eight years.

It is therefore evident that the applications of the oxy-acetylene process in a modern industrial plant are almost without limit for welding not only iron and steel but also the less common metals and alloys. All that is necessary is for the men in charge of operation, maintenance, and new construction to have a clear understanding of the possibilities of the process.

It is not surprising, too, that in an industrial art which has grown with such rapidity in the past few years the workmen have not been able to advance their knowledge and skill accordingly. To correct this situation and to instruct the shop foremen as well as the welders, some of the leading companies producing oxygen and acetylene maintain large forces of competent engineers and skilled welders who are available on request for expert advice. The calling of a service man may also result in accomplishing difficult repairs with great savings in time and cost.

Original Frederking Apparatus

By S. O. Solt

Bethlehem Foundry & Machine Company, Bethlehem, Pa.

THE object of this paper is to give a brief description and present the possibilities of Original Frederking apparatus, also to show what factors must be studied to determine whether it can advantageously replace existing jacketed or direct-fired equipment for any particular process. An actual study of any process involves operating and performance data, which are beyond the scope of this discussion.

The name "Original Frederking" is applied to all cast-iron vessels, of any form or size, having a series of steel-tubing coils cast in the walls according to methods originally used in Germany by the Frederking Brothers and perfected in 1904. In the manufacture of this equipment attention must be given to coil construction, because of difficulties which are encountered, and the surface of the tubes must be specially treated before the assembled coils are placed in the mold. Foundry practice, especially methods of molding and pouring must be carefully studied for each casting. For the past twenty years the chemical industry of Germany has been using apparatus of this construction, and it has been found advantageous for so many processes that several foundries have taken up its manufacture.

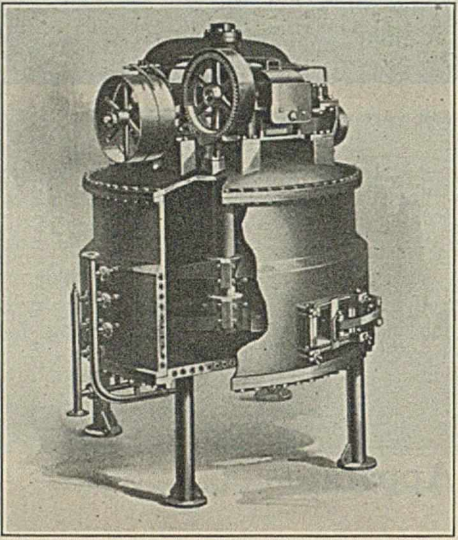
Heating Medium

We will consider only the use of either saturated steam or hot water as a heating medium. The former is the more common heating medium, and it is essential that the prospective user bear in mind that the cast-iron tubes are fully capable of withstanding high pressures. The tubes which conduct the heating medium are arranged in a series of individual coils and connected in parallel to supply and discharge headers. Experience has demonstrated that to give maximum efficiency or rate of heat transfer a coil must not be too long. Moreover for any given surface the transfer rate, under the same operating conditions, will be increased when there are a number of live-steam inlets distributed over the surface. The surface temperature of the vessel is practically uniform since the drop in temperature through each coil is comparatively low and there is a tendency to equalize through the cast-iron wall. The fact that the tubes are designed to withstand high pressure offers an opportunity for increasing the production from a given unit of apparatus, especially when the process is one of drying, distilling, or evaporating, which may be accelerated by the use of high-pressure steam, thus increasing the over-all temperature difference.

Steam Heating and Cooling Operations

In the chemical industries many processes involve the use of large, jacketed, vertical stills or horizontal cylinders for steam pressures ranging from 100 to 200 pounds per square inch, and such equipment usually develops leaky joints, causing a loss of steam as well as maintenance expense in attempting repairs or to give the area around the apparatus a more sightly appearance. These conditions are absolutely eliminated by the use of Original Frederking apparatus. Operations of such character often include cooling at some stages, and this is likewise accomplished to advantage by the use of the cast-in coil equipment. When a mass is to be cooled or a reaction develops heat at a rapid rate so that there is danger of overheating the material, Original Frederking apparatus proves itself very efficient, since by making the proper connections to the headers a quick reversal from heating to cooling, or vice versa, may be accomplished.

There are also special cases in which this equipment is very effective where cooling only is desired, and it may replace jacketed kettles. In the latter the large area through the jacket permits only a very low velocity of the cooling medium over the surface, while in the Original Frederking construction it is circulated through the tubes at high velocity, and it is well known that velocity of flow is an important factor in determining the coefficient of heat transmission. This is also true to a certain extent if coils are inserted in a kettle, but for such construction it is difficult to divide the heating surface efficiently, and sometimes cast iron resists the corrosive action of the material better than steel. Frequently, when making a study for the application of Original Frederking apparatus for steam heating and cooling operations, other special advantages present themselves.



Vacuum Still for Steam Heating

Apparatus Is Moisture-Proof

In the manufacture of some chemicals it is essential that all moisture due to possible steam leakage be excluded, since only small quantities entering the interior of the vessel will deteriorate the product, or even in some cases there may be danger of explosion. For such processes the porosity of jacketed cast-iron vessels will eventually prove objectionable, especially after even slight corrosion has attacked the layer in the inside surface. This condition cannot develop in an Original Frederking vessel and the equipment has been adapted for such processes.

Adaptable to Changes in Pressure

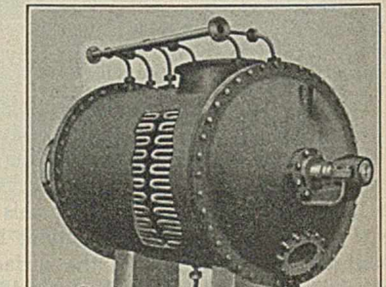
In the ever changing demands of product or process, it frequently becomes desirable to use a certain heat-transfer apparatus for a different purpose than that for which it was originally designed. The new operation may require a working pressure much higher than the previous one and jacketed equipment must be redesigned or, if this is not possible, new equipment purchased. However, a unit of Original Frederking apparatus with steam as heating medium is adaptable to any change with respect to operating pressure.

High-Temperature Processes

When the working temperatures are beyond the range of available steam, and uniformity or control of temperature is desirable, the Original Frederking apparatus connected to a Bethlehem hot water system meets the requirements. With this arrangement temperatures up to at least 660° F. may be attained in the material or mass, with the following advantages over direct-fired equipment:

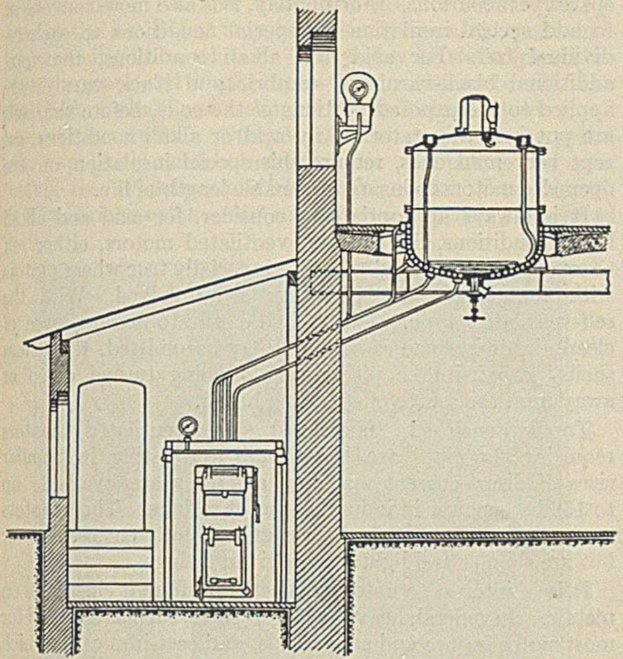
1—Uniformity of temperature over the entire interior surface of the vessel, and the elimination of any hot spots where material may be overheated.
2—Ease of temperature control.
3—Fire hazard eliminated when treating inflammable material since the furnace or heater may be located in a building separate and apart from the vessel.
4—Increase of thermal efficiency, which assures a saving of fuel.
5—Arrangements for discharging the contents are usually greatly simplified.
6—More rapid rate of heat transfer.
7—By using a special method of vessel construction, these installations may also be used for alternate heating and cooling.
8—Extremely low maintenance cost.
9—Increased life of stills or pans.

These hot water installations operate without a circulating pump or other mechanical device and, when properly adjusted, need no other attention than that necessary to the furnace or heater. Such plants have been in successful operation in the German chemical industry for twenty years, and many are being built today as new applications are developed. The pressure in the system is high, corresponding to the temperature, and this causes some prospective users to feel that the installations are impractical from the standpoint of explosion danger. The real danger of damage by explosion in any system containing hot water and steam under pressure is the total energy content, and this is very large in steam boilers, owing to the great amount of water. The quantity of water in the hot water system, when ready for operation, is comparatively small, and therefore no violent explosion or series of explosions is possible, even if rupture occurs. The largest Bethlehem hot water system will contain, when ready for operation, less than 225 pounds of water, while a 250-horsepower boiler will have from 12,000 to 20,000 pounds. The ratio of the amount of energy per pound of water for the hot water system at its maximum pressure, compared with a boiler operating at 235 pounds per square inch, is about 5 to 1; hence the total energy present is only 6 to 10 per cent, or less, of that in a boiler as outlined above.



Steam-Heated Horizontal Still Arranged for Alternate Heating and Cooling

These data show that it is not unusual to find systems with a greater amount of stored energy than that of a hot water system. The entire system is designed with a liberal factor of safety, and the use of distilled water prevents incrustation, since the same water continually circulates in the system. This last fact also accounts for the high efficiency of the system, since all the heat is expended in the processing vessel or by radiation, there being no other loss,



Typical Elevation, Bethlehem Hot Water System, with Original Frederking Vessel

for the reason that the heating medium never leaves the system.

With recent developments of handling gases under high pressure due to the development of such processes as nitrogen fixation, it is not considered beyond the ability of engineers to design equipment safe for high pressure. Therefore, a hot water system with a reasonable factor of safety should not be considered so much of a hazard as a steam boiler plant since the total energy content of the former is much less.

Applications

Original Frederking apparatus, heated with steam or hot water, may be used in processes involving the manufacture of the following products:

Acetic acid—Vacuum distillation with steam
Formic acid—Vacuum distillation with steam
Salicylic acid—Vacuum distillation with steam
Continuous sulfonation of oils—Cooling process
Synthetic camphor—Steam heating
Dyestuffs—Hot water heating, particularly those processes requiring temperature control; also applications of steam heating
Concentration of caustic lye—Vacuum evaporation with hot water as heating medium
Distillation of fatty acids—Vacuum distillation with hot water as heating medium
Varnishes and lacquers—Hot water heating
Hardening animal oils—Hot water heating
Sublimation of benzoic acid—Hot water heating

This is only a partial list of European uses. Up to this time a limited number of applications have been attempted in the United States, and in practically every instance the equipment has been considered successful.

The use of superheated steam as heating medium has not been discussed since its application is economical only under favorable plant conditions, but it is of interest to note that Original Frederking apparatus is so constructed that it presents an efficient means for using superheated steam.

The methods of manufacture used for all castings produced by this company are protected by United States patents.

Electrical Equipment in the Chemical Industry and in Chemical Processes

By R. H. Rogers

General Electric Company, Schenectady, N. Y.

THE manufacture of chemicals and the utilization of chemicals in manufacturing present fields for special consideration in regard to electrical equipment. Most of the motor and control applications in industry are not subjected to particularly detrimental conditions and therefore in the interests of economy are not armed against foes that will never be met. The nature of chemical manufacture and use is such that in many cases ordinary electrical equipment might either be harmed or cause harm; hence we will analyze characteristic conditions and characteristic procedure.

The mechanical equipment involved is great in both variety and quantity and the majority of it requires electric motor drive and control which are often operated in conditions detrimental to long life and successful service. These menaces common to chemical production and chemical processes may be catalogued in general family groups:

A—Liquids such as acidulated or alkali water, oils, solvents. These liquids may quickly or by accumulative effect over a long interval spray or drip upon or into electrical equipment or even flood parts or entire units.

B—Fumes and vapors. These may be of solvent nature, corrosive, steamy, or inflammable. They may thoroughly wet all parts of the electrical equipment or in the case of explosive vapors they may be set off by unguarded sparks or flashes from the equipment itself.

C—Dusts. While seemingly of benign nature, dusts under certain circumstances and given time can work havoc with electrical equipment, especially if the dust is conductive or, worse, magnetic, such as the impalpable dust of cast iron. Abrasive dusts are obviously bad and explosive dusts, which are now believed to include almost everything metal, mineral, or organic, have particularly to be guarded against.

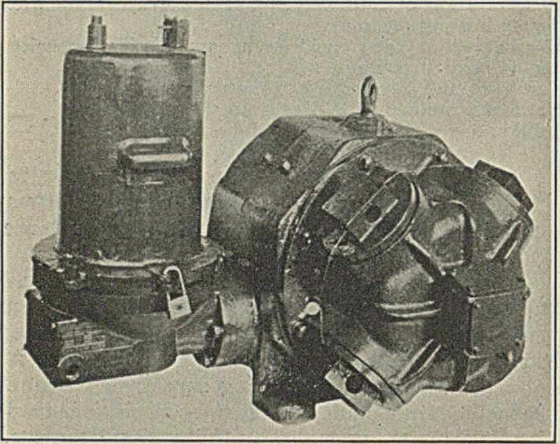
D—High temperature. So many of the unit processes involve heat in greater or less degree it is inevitable that attendant electrical apparatus will often be subjected to temperature much higher than the classical standard of 40° C.

The effects of these conditions and the methods of coping with them will be discussed in the order of this outline. It must be remembered that it is practically impossible to make apparatus "proof" against any particular condition. It can be made highly "resistant" to such a condition. The aim is to prolong the life of the apparatus, by the use of special insulation and construction, to what may be considered a reasonable length of life for the specific conditions.

Apparatus where Liquids Are Encountered

Acids and Alkalies—Where liquids are liable to spray, drip, or splash directly on the motor, as is often the case with direct-connected pump outfits, the low-voltage, totally enclosed motor with special insulation is undoubtedly best, unless heavy fumes are also present. However, there are sometimes certain factors, such as space requirements, that demand the smaller frame, open or partially open types. Every effort should be made to protect the motor windings against direct contact of liquids. The larger motors can sometimes economically be placed at a distance from the application. Often baffles or protective casings or covers can be provided by the user.

Special insulation is required in most cases. The black varnishes and black-varnished cambric used in most insulation processes are asphaltum-base products and are not affected to any extent by any acids or alkalies. These liquids may be considered about the same as water in their method of attack on windings. That is, if the insulation were in perfect condition, with the windings completely sealed, there would be no failures from liquids coming in contact. But it is practically impossible to maintain a perfect seal, owing to vibration of the motor, almost imperceptible movements of the coils, etc., and the liquid finds minute holes to enter and reach the copper. Creepage to ground and between phases leads to ultimate failure. Liquids that are strongly corrosive attack the cotton covering of the wire and are often conductive, and are therefore quicker than water in causing shorts and grounds.



Class BM 5-Horsepower "Permissible" Motor and Control for Use in Extra Hazardous Locations Such as Gaseous Mines

Small, partially closed-slot induction motors utilize random wound coils with no space between the coil end projections. This type of construction gives better operating characteristics in the small sizes and, more to the point, lends itself admirably to the compound type of insulation, which can be applied to this kind of winding more effectively than can any other types of insulation.

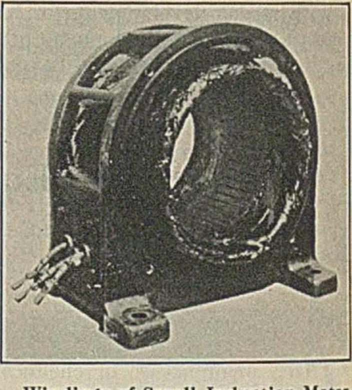
The best standard lines of induction motors utilize this black asphaltum compound insulation in all small and medium motor sizes. A new and improved method of applying the compound—namely, dipping the windings into the hot compound—has been developed and is gradually being adopted. Standard motors so treated may be relied upon to withstand unusual acid and alkali conditions, but where very severe conditions are to be met by open or partially open motors, extra precautions, such as special wedges, extra compound, special arrangement of the wires in the slots, etc., which are not warranted or necessary in the general run of motors, may be used.

Larger induction motors utilize open stator slots and form-wound molded coils. The advantages of compound insulation are not so great with this construction and there are some disadvantages, one of the most important being that the compound on these motors would close the ventilating spaces between coils. Fortunately, it is also more convenient to add special insulation for special conditions to each individual coil. For acid and alkali conditions, therefore, additional black-varnished cambric and black varnish are applied to the exposed portions of the coils, before the coils are put into the stator. Any acid or alkali conditions, except very mild ones, require this special insulation on the open-slot motors to insure reasonable length of life.

It is always appropriate to consider, for acid and alkali liquid conditions, the enclosed ventilated motors, either self or separately ventilated. This is especially true where motors with commutators or slip-rings are involved. With the self-ventilated type, pipes may be run to some source of clean air, or in some cases pipes may be omitted, the "clam shells" or air-intake pieces simply being turned down or away from the source of splashing liquid.

Totally enclosed "fan-cooled" (self-ventilated) motors requiring no pipes are being built for listing in popular sizes of direct-current machines and they are available up to 150 horsepower in induction-motor ratings. These motors have all the advantages of the regular totally enclosed motor but are smaller and lighter for a given rating.

It is of interest to note the effects of different chemicals on metals. In general, heavy cast-iron parts, such as are used for most motor frames and end-shields, and cast-iron cases which can be furnished for most small control devices, withstand acids and alkalies better than any other metal. Sheet metal parts and castings may be protected by liberal and frequent applications of paints, such as red lead and black varnish, or special protecting paints.

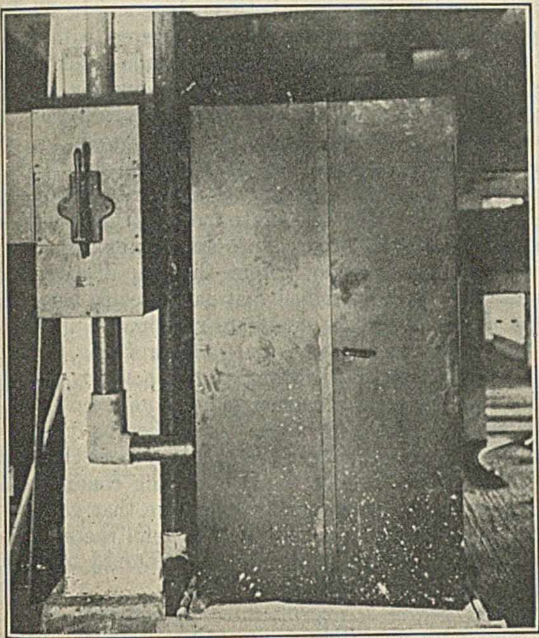


Windings of Small Induction Motor Completely Sealed with Compound to Exclude Magnetic and Conducting Particles, Acid and Alkali Fumes, Water, or Steam

Windings will last longer when frequently cleaned and brushed or sprayed with black varnish. A winding may often be saved, after flooding or splashing with liquid, by rinsing out with water to remove the acid or alkali liquid, then heating slowly by passing current at very low voltage through the winding. When the insulation resistance is brought up to a high value after the moisture is driven out, several coats of black varnish should be applied.

Control Apparatus. It is quite often easy and advisable to locate the control devices where they will not be subjected to acids and alkalies. Where such conditions cannot be avoided, by proper enclosures or location, special features can be supplied. Devices can be secured that are furnished with (*a*) all steel parts cadmium-plated (or double cadmium-plated if conditions are extreme); (*b*) bearings of bronze or brass; (*c*) cast-iron cases or welded steel cases with red lead and acid-resisting varnish treatment and provided with gasketed joints (for extreme conditions, cases may be made of brass); (*d*) exposed contacts may be protected by coatings of vaseline. As an alternative, oil-immersed apparatus may be used.

OILS—The foregoing applies somewhat to extreme oil conditions, although obviously the corrosive effects are not present. Oils are obnoxious and harmful, mainly for two reasons: First, black varnishes and compounds are somewhat soluble in oil and where any great amount of oil is present the insulation may be seriously impaired, the winding becoming "oil-soaked." The yellow or clear linseed-oil-base varnishes and cambrics are more resistant to oils than the black asphaltum-base products and are used where oil is to be encountered. Often the yellow varnishes are applied over the black-varnish insulation for the purpose of protecting the insulation underneath from oils. Secondly, oil on any surface catches dirt and dust, and if this happens to be conductive, creepage paths are formed to ground and between coils, which soon may result in breakdowns.



Automatic Compensator for Controlling 200-Horsepower Motor

All parts are tightly enclosed to prevent arcs from setting off the inflammable dust.

Fumes and Vapors

Corrosive—The remarks concerning acids and alkalies in general apply where corrosive fumes are encountered. Windings are protected by the same compounds as are used for liquids. However, where heavy acid fumes are present, totally enclosed motors are not suitable as acid gradually collects inside the case due to breathing. Enclosed motors with piped ventilation are indicated for such cases.

Much can be done to improve operating conditions for electrical apparatus by adequate ventilating systems to carry off destructive fumes.

Solvent—Solvent fumes or vapors, such as benzene, carbon bisulfide, etc., will readily attack black varnishes and cambrics, and therefore for such vapors coils must be finished with yellow-varnished cambric and yellow varnishes. Compound insulation is likewise protected by treatments of yellow varnish.

Explosive—Highly inflammable liquids, vapors, and fumes are often present where electrical machinery is to be installed. The plant layout may be such that the fire and life hazards involved by use of motors and control in the gaseous area are not great and standard, open squirrel-cage motors are considered safe enough. The gas may only in rare cases surround the motor and control, and the chances of sparks from a shorted coil or rotor rubbing on the stator of a well-cared-for motor are very remote.

Where the hazards to life and property are great the safest installation obviously is one in which the electrical equipment is in a spearate well-ventilated room.

When conditions warrant the placing of electrical equipment in the gaseous or danger zone, the ordinary totally enclosed motor should not be used. Ordinary enclosing features of the standard lines of motors and control of any manufacturer are not gas-tight, are not strong enough to withstand the pressures involved in an internal explosion, and are not constructed so that they will prevent the flame of an internal explosion from igniting the gas surrounding the motor or control.

The safest type of motor for use in explosive atmospheres is a motor with enclosing features such as are recognized by the Board of Fire Underwriters and the Bureau of Mines. These features include:

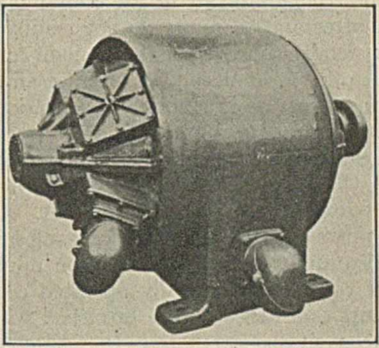
(*a*) Enclosures of material strong enough to withstand pressures of an internal explosion. (These may easily exceed 100 pounds per square inch.)

(*b*) All joints carefully machined and sufficiently wide to cool the outrushing flame of an internal explosion. For certain parts threaded joints are preferred.

Several types of motors have already been developed along these lines and some have been approved, after prolonged testing, by the Bureau of Mines and the Underwriters' Laboratories.

The Underwriters' Laboratories' approval of the case construction motors was really a blanket approval, inasmuch as any single-phase, polyphase, or direct-current motor up to a size equivalent to the 15-horsepower, 1800-r. p. m., enclosed squirrel-cage induction motor can be built in the "case" construction shown. The safety feature of this construction is embodied in the design of the enclosing case. The mechanical features of the motor inside the case are those of the open motor of the standard lines.

While every effort is made to design such motors for maximum safety, no guarantee can be made or implied that they will be "explosion-proof" under all conditions. Since a manufacturer has no control over the maintenance and operation of such equipment after it is sold, no such guarantee can be given and the term "explosion-proof" should not be used.



75-Horsepower Wound Rotor Induction Motor Totally Enclosed for Safe Operation in Oil Refineries and Similar Places

The design of motors larger than can be made in the case construction are totally enclosed fan-cooled with a double-shell stator frame. Cooling air passes between the inner and outer shells. This feature permits larger ratings than does the ordinary enclosing features.

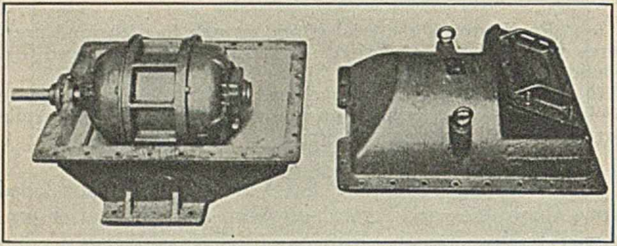
Enclosed ventilated motors may be used in explosive atmospheres with comparative safety, provided tight intake and exhaust pipes carrying fresh air are used and a supply of air is constantly maintained.

Where the hazards are not so great, open squirrel-cage motors may often be used. If the application requires a wound rotor motor or a synchronous motor, these types can be made practically as safe as the squirrel-cage motor by the use of enclosing features for the collector rings designed along the lines of Board of Fire Underwriters' motors.

Control devices that cause exposed sparking obviously cannot be used in explosive atmospheres. It becomes necessary to (*a*) locate the control in a separate well ventilated room, (*b*) enclose all contact-making parts in Board of Fire Underwriters' enclosures, or (*c*) immerse all contacts in oil and exercise great care to see that proper oil levels are maintained and that the oil is in proper condition. Many control devices of the oil immersed type have been developed.

Control apparatus for use in corrosive fumes should in general be built like that discussed in connection with acids and alkalies.

STEAM—There are many applications where apparatus is exposed to excessive steam, frequently acidulated steam. Condensation on windings and metal parts results in a condition similar to splashing and flooding previously discussed.



Case of Class BU Motor Opened to Show Construction

Motor has to be provided with a longer than standard shaft. No stuffing box is used but the long space about the shaft cools the exploded gas so that no fire comes through.

Dusts

Certain dusts, especially grain and coal dusts, also aluminum and bronze dusts, are easily ignited and propagate flame readily, requiring only a small flame for a start. Others require a source of heat of large size for ignition, but burn readily, while there are still other dusts that do not readily form clouds in air or are contaminated with incombustible matter and therefore do not readily propagate flame. It is generally conceded that two main conditions must be present in order that dust may produce an explosion: (1) fine, dry dust must be in a state of suspension in an atmosphere containing the proper amount of oxygen; (2) a source of sufficient heat must be brought into contact with the dust.

Obviously, electrical apparatus must be designed so that no exposed sparking is present. Generally speaking, the apparatus recommended for explosive gas conditions would also apply here. An exception might be made in the case of certain magnetically operated control devices, which for dust conditions can be furnished with cases tight enough to keep out dusts.

Conducting and abrasive dusts may be quite injurious, especially to insulated windings, collector rings, commutators, and bearings. Aided by any slight vibration, these dusts, such as graphite, coal, coke, carbon, iron, bauxite, etc., rapidly work their way through most insulations and form creepage paths to ground and between coils, quickly resulting in failure.

Compound insulation, which covers all coil ends and seals the slots of small motors, will successfully resist these dusts. Extra tape and varnish treatments on larger motor coils are practically always required. The special purpose to be accomplished by special varnish treatments for dust conditions is to procure a smooth glossy surface with no breaks or rough spots for the dusts to act upon. The clear or yellow varnishes are best for producing such surfaces, and are therefore used for windings that will encounter dust.

Rotors of wound rotor machines can be given extra dippings in varnish, the spaces between bars can be filled with compound, and connections can be covered with caps, to prevent dusts causing short circuits in the rotor windings. Often the slip rings of wound-rotor induction motors or synchronous motors can be enclosed, further adding to the resistance to dust conditions. For very severe conditions, however, motors other than the squirrel-cage induction motor must usually be either totally enclosed, enclosed-ventilated, or placed in a separate room. It may even prove economical from the maintenance standpoint to enclose the squirrel-cage motors, too, rather than to dismantle them frequently to dig out the dust that has collected between and around the coils. Some dusts are so abrasive that the insulation rapidly wears away due to the rubbing of the dust particles as they are carried through the motor by the normal ventilation. In such cases enclosed motors are preferable.

The motor bearings on all new sleeve bearing type motors are tightly housed and have plenty of oil to last for months without attention. Under good operating conditions, after properly oiling such motors, making sure that all plugs are in tightly, there should be no need to refill the oil wells for several months. More harm is usually done by too frequent inspection and oiling in dusty conditions.

Standard *control devices* mounted in cast-iron or welded-steel cases with dust-tight joints will successfully withstand abrasive or conductive dust conditions.

High Ambient Temperatures

Electrical apparatus is occasionally required to operate in ambient temperatures greater than 40° C. For this condition motor windings are usually insulated with Class B (A. I. E. E. Standards) insulation, which consists of asbestos, mica, and like materials. Motors can be built to operate at temperatures as high as the oil in the bearing housings can withstand.

Standard control devices can usually be used in high temperatures by using resistance in series with voltage coils and by derating the current-carrying parts.

Conclusion

From this outline of hazards and safeguards it becomes clear that at least an appreciable portion of electrical equipment intended to drive chemical equipment must be carefully scrutinized. This should be done for two purposes—to keep unsuitable equipment out of hazardous locations, and to insure the use of proper equipment where the hazards cannot be abated or avoided.

Germany's Exports of Potash Decrease—The Department of Commerce announces that sales of products of the German Potash Syndicate in foreign countries declined during the early part of this year, while domestic sales increased. The decreased demands of American fertilizer manufacturers are said in Germany to have been responsible for the decline in the export business of the syndicate.

In January and February of this year the Potash Syndicate sold abroad 75,000 tons of raw kainite as compared with 80,805 tons in the corresponding period of 1926.

Italy Permits Free Entry of Perfume Ingredients—Information has been received from the American Commercial Attaché at Rome that benzaldehyde and benzyl chloride when imported for the manufacture of synthetic perfumes are exempt from Italian duty. American manufacturers of synthetic organic chemicals should not hesitate to make use of this cabled information, especially as American coal-tar dyes are competing in the world's market successfully. Our exports of coal-tar products grouped as "Other Intermediates" in 1924 were 1,557,429 pounds, and in 1925, 1,727,467 pounds.

Chemical Warfare Service Boll Weevil Investigation[1]

Progress Report

By H. W. Walker and J. E. Mills

CHEMICAL DIVISION, CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL, MD.[2]

OVER one thousand possible poisons and poisonous mixtures have been tested against the cotton boll weevil for their relative toxicity.[3] Calcium arsenate was used as a standard, and controls using unpoisoned cotton were run in all cases. The materials were first run both as dusts and molasses mixtures in preliminary tumbler tests. Those materials showing any definite toxicity were re-run several times in tumbler tests, and if they continued to compare favorably with calcium arsenate were re-run in cage tests in the field. Observations were made during these tumbler and cage tests as to the nature and extent of injury to the cotton plant, as well as the daily and total weevil mortality. Also, plant toxicity tests were run on field cotton and the injury carefully noted. Over 150,000 boll weevils have been used in this work.

The following substances showed in tumbler tests a toxicity about equal to, or greater than, calcium arsenate:

(*a*) Compounds showing weevil toxicity about equal to, or greater than, calcium arsenate and causing little or no plant injury:

Sodium fluosilicate
Barium fluosilicate
Special calcium arsenate (containing about 24 per cent As_2O_5)
Barium fluoride
Cryolite
Potassium fluosilicate
Sodium ferrofluoride
Barium arsenate
Magnesium arsenate
Zinc arsenate
Lead arsenate

Zinc arsenite
Calcium methyl arsonate
Barium methyl arsonate
Lead methyl arsonate
Magnesium methyl arsonate
Calcium ethyl arsonate
Calcium phenyl arsonate
Lead benzyl arsonate
Magnesium phenyl arsonate
Lead fluoride
Barium fluochloride

(*b*) Compounds showing weevil toxicity about equal to, or greater than, calcium arsenate but causing definite plant injury:

Arsenic trioxide
Arsenic pentoxide
Arsenic trisulfide
Arsenic pentasulfide
London purple
Paris green
Copper arsenate
Ferric arsenate
Mercuric arsenate
Sodium arsenate
Calcium arsenite
Copper arsenite
Ferric arsenite
Lead arsenite
Magnesium arsenite (AsO_3)
Magnesium arsenite (AsO_2)
Mercuric arsenite
Sodium arsenite
Chlorovinyl arsenious oxide
Methyl arsenious oxide

Phenyl arsenious oxide
Diphenyl arsenious sulfide
Methyl arsenious sulfide
Trimethyl arsine sulfide
Sodium methyl arsonate
Copper fluoride
Sodium fluoride
Strontium fluoride
Calcium cyanide
Mercuric cyanide
Sodium cyanide
Barium salicylate
Magnesium salicylate
Barium benzoate
Calcium benzoate
Lead tetraethyl
p-Dichlorobenzene
Trichlorophenol
Methylene blue
Malachite green

Of these substances, those mentioned in the first list showed little or no plant toxicity. The more soluble poisons shown in the second list were invariably toxic to the cotton plant. The arsonates of calcium, magnesium, barium, and lead showed little or no plant toxicity when properly prepared and purified, but it is not probable that these materials could be prepared commercially to compete with calcium arsenate at this time or in the near future.

When questions of cost and effectiveness were considered, only the first five substances on the list seemed to offer commercial possibilities at the present time. These substances were therefore thoroughly tested in cage tests.

Extensive experiments were carried out with some of the more soluble poisons, such as arsenic trioxide adsorbed on various absorbents. Coal dust proved to be the best absorbent tried, and even as low as one per cent of arsenic trioxide adsorbed on coal dust gave a very definite toxicity to the weevil and was not toxic to the cotton plant. None of the soluble poisons thus tried was, however, so effective as calcium arsenate when percentages were used that did not injure the plant. It is possible that such adsorbed soluble poisons might find a use against certain leaf-feeding insects.

Some compounds, such as diphenylamine arsenious oxide, of known high toxicity, when tried as dusts against the boll weevil, showed almost no effect. It is thought that such materials are insoluble in the digestive juices of the weevil.

The materials or mixtures tested were made at Edgewood Arsenal or were secured from stock or from commercial sources. All dusts were ground to minus 200 mesh.

Cotton

The cotton used for tumbler, cage, and field tests during 1924 and 1925 was on the grounds of the Georgia Experiment Station or in the immediate vicinity. There was never sufficient infestation of the cotton set aside for field tests in 1925 to cause economic damage, owing to the extremely hot, dry weather that season. Greenhouse cotton was available at the Georgia Experiment Station during both these years, enabling tests to continue late into the fall as long as the supply of storage weevils held out. The cotton used at Clemson College during 1924 was on the college grounds.

Examination of over 6000 acres of cotton in widely varying parts of Georgia during 1926 showed a total average infestation of less than 0.5 per cent, and consequently the field tests planned for Georgia had to be transferred to Florida.

The cotton used in the cage tests and for breeding weevils in Florida was on the college campus at Gainesville and in the State Plant Board field there. The cotton used in the large-cage tests was that from the regular planting and at the time these cage tests were initiated (August 16, 1926) this cotton was between 3 and 4 feet high. The large cages were 4 feet square by 4 feet high. The cotton used in the small-cage tests was late cotton and averaged between 1 and 2 feet high when used for test. The small cages were about 2 feet square by 3 feet high, and it is believed that these tests were more representative than those with the large cages.

The cotton used for the 1926 field tests in Florida had an average infestation of 40.8 per cent when poisoning was started. This cotton was by no means ideal for these tests, the stand being very irregular and the cotton in general poor, but it did have weevil infestation.

Cotton grown in the greenhouse at Edgewood Arsenal has

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[1] Received March 28, 1927. Published by permission of the Chief, Chemical Warfare Service.

[2] The following men were actively engaged in carrying out the experimental work in the field: H. W. Walker, H. S. McQuaid, G. A. Sachs, B. Gehauf, J. G. Hartnett, D. Ehrenfeld, L. A. Forrest, W. A. Shands, R. G. Pridmore, J. F. Touchstone, and V. I. Greer. In addition F. M. Pralatowski, R. D. Kulp, and T. F. McCabe were employed at Edgewood Arsenal, besides which the personnel of the Analytical, Engineering, and Organic Departments of the Chemical Division, Chemical Warfare Service, assisted at various times.

[3] A complete report of the Chemical Warfare Service Boll Weevil Investigation will be published at a later date.

TABLE I - TOXICITY OF CERTAIN COMPOUNDS COMPARED WITH CALCIUM ARSENATE - CAGE TESTS 1926.

	Compound Tested	No. of Cages*	Grams Poison per Cage	Apparent Density Poison	Total No. of Weevils	Daily Mortality					Per-cent Dead	Percent Relative Toxicity
						1	2	3	4	5		
1	CaAs	14 L	2.58		425	10	48	65	63	30	48.5	
	Na_2SiF_6 - P	12 L	5.67		364	63	63	58	41	37	72.0	148.5
	CaAs	26 S	1.39	1.00	384	17	52	60	46	60	61.2	
	Na_2SiF_6 - P	21 S	3.03	2.80	284	52	63	34	17	42	88.4	144.5
2	CaAs	11 L	2.65		331	10	26	43	32	22	40.4	
	Na_2SiF_6 - W	10 L	6.65		297	28	59	36	27	33	61.6	152.5
	CaAs	30 S	1.50		438	10	54	64	52	69	56.9	
	Na_2SiF_6 - W	24 S	2.86	1.87	355	71	76	46	24	60	78.0	137.1
3	CaAs	2 L	2.15		56	4	8	14	10	x	64.2	
	Na_2SiF_6 - JL	2 L	4.65		55	2	14	11	4	x	56.4	87.8
	CaAs	18 S	1.29		266	13	44	49	39	34	67.3	
	Na_2SiF_6 - JL	15 S	2.26	2.28	222	55	53	21	19	24	77.5	115.1
4	CaAs	5 S	1.14		76	8	13	19	6	5	67.1	
	Na_2SiF_6 - JEL	4 S	1.75	1.67	48	11	8	9	3	2	68.8	102.5
5	CaAs	19 L	3.05		551	18	79	85	82	40	55.1	
	Na_2SiF_6 - EA	26 L	3.26		840	67	134	112	99	59	56.1	101.8
	CaAs	22 S	1.33		323	17	46	55	46	43	64.1	
	Na_2SiF_6 - EA	36 S	1.17	0.9	525	117	114	83	39	60	78.7	122.8
6	CaAs	12 L	2.32		342	10	30	55	42	35	50.3	
	$BaSiF_6$ - G	11 L	8.08		329	24	48	62	27	35	59.6	118.5
	CaAs	26 S	1.39		384	17	52	60	46	60	61.2	
	$BaSiF_6$ - G	22 S	3.29	2.65	319	76	57	39	30	47	78.1	127.5
7	CaAs	23 L	2.64		679	20	92	100	98	64	55.1	
	$BaSiF_6$ - EA	23 L	3.71		673	62	79	74	58	54	46.5	84.5
	CaAs	22 S	1.33		323	17	46	55	46	43	64.1	
	$BaSiF_6$ - EA	21 S	1.91	1.40	291	55	78	49	25	28	80.7	125.6
8	CaAs	18 L	2.86		537	13	73	95	80	59	59.8	
	CaAs - EA-1	18 L	3.43		518	15	38	81	75	63	51.0	85.3
	CaAs	29 S	1.45		421	18	60	67	57	55	61.0	
	CaAs - EA-1	27 S	1.61	1.25	381	25	57	60	58	63	69.1	113.2
9	CaAs	17 L	2.96		508	12	72	90	78	50	59.4	59.6
	CaAs - EA-2	17 L	3.10		493	13	40	37	48	56	35.4	
	CaAs	17 S	1.25		250	14	36	41	39	30	64.0	
	CaAs - EA-2	16 S	1.29	0.86	239	8	24	19	22	43	48.5	75.8

The control mortality (weevils on unpoisoned cotton) in these tests was less than 10% in all cases.

* L = large cages, S = small cages.

Compounds Tested

1. Na_2SiF_6—P: Sodium fluosilicate, pure, over 98 per cent Na_2SiF_6
2. Na_2SiF_6—W: Sodium fluosilicate, Wiarda, about 94 per cent Na_2SiF_6
3. Na_2SiF_6—JL: Sodium fluosilicate, Jungmann, "Light"—about 78 per cent Na_2SiF_6
4. Na_2SiF_6—JEL: Sodium fluosilicate, Jungmann, "Extra Light"—about 60 per cent Na_2SiF_6
5. Na_2SiF_6—EA: Sodium fluosilicate, Edgewood Arsenal, about 80 per cent Na_2SiF_6
6. $BaSiF_6$—G: Barium fluosilicate, Grasselli, over 98 per cent $BaSiF_6$
7. $BaSiF_6$—EA: Barium fluosilicate, Edgewood Arsenal, about 90 per cent $BaSiF_6$
8. CaAs—EA-1: Calcium arsenate, Edgewood Arsenal, about 24 per cent As_2O_5
9. CaAs—EA-2: Calcium arsenate, Edgewood Arsenal, about 10 per cent As_2O_5

been available for preliminary plant toxicity tests for the past two years.

Boll Weevils

The weevils used during 1924 were field weevils obtained in the immediate vicinity of the Georgia Experiment Station. The average mortality of the controls (weevils on unpoisoned cotton) and blanks (no poison and no food) in all these tests was 6.4 and 8.0 per cent, respectively. This work did not start until August, 1924, and weather conditions were not unduly severe.

Seventeen thousand weevils were put in cold storage at the Georgia Experiment Station during September and used as needed, thus enabling the work to continue until December 15, 1924. Of these, 31.8 per cent were alive and sufficiently active for use. Of these weevils, 13,000 were field weevils, and 4000 were obtained from nearby cotton gins. It is worthy of notice that only 12.5 per cent of the gin weevils were available when needed, as against 40.6 per cent of the field weevils. This may have been due to the rough usage which the weevils received during the ginning of the cotton, or it may have been due to the fact that they were deprived of food for several days prior to their enforced hibernation. The per cent mortality of the controls in the case of gin weevils used in tests was not noticeably greater than in the case of field weevils.

Those weevils used in the work at Clemson College were field weevils obtained in that immediate vicinity. There, also, the control mortality was negligible.

In order to obtain an early supply during 1925, weevils were bred from infested squares at Gainesville, Fla., and shipped as needed to Experiment, Ga. Over 95,000 infested squares were used in this work, and the total number of weevils so obtained was over 37,000 or 39.2 per cent. This work has been completely described elsewhere.[4] In addition to these weevils bred from infested squares, about 100,000 were obtained from the field later in the season.

[4] Gehauf, *J. Econ. Entomol.*, **19**, 593 (1926).

On account of the extremely hot, dry weather throughout the Piedmont Section during the 1925 season, the mortality among the controls in some tumbler and cage tests was extremely high, and many tests had to be thrown out on this account. This does not apply to the cage tests run at Gainesville, Fla., during this season.

Calcium Arsenate

Most of the calcium arsenate used in the check tests for 1924 and 1925 was obtained through the Georgia Experiment Station and was the standard material approved by the State of Georgia, which undertook the distribution of large quantities to the cotton planters throughout the state.

This material contained 0.40 per cent soluble arsenic as As_2O_5, 41.52 per cent total arsenic as As_2O_5, and 32.5 per cent calcium, and had an apparent density compared to water of 0.35.

The dusting properties of this calcium arsenate were very good. Comparisons of various standard brands—including Corona, Niagara Sprayer, and Grasselli—gave remarkably uniform results.

For the 1926 work Niagara Sprayer and Grasselli calcium arsenates, which met all the requirements of the U. S. Department of Agriculture, were used. Some of these samples had a higher content of water-soluble arsenic (As_2O_5 = 0.68 per cent) than the Georgia material, but this seemed to make no appreciable difference in the toxicity. Our interpretation of the reason for this will be discussed later.

Sodium Fluosilicate

Commercial fluosilicate analyzing about 95 per cent, or over, Na_2SiF_6 showed a distinctly higher weevil toxicity than calcium arsenate. This material also showed some plant toxicity, but not enough to prevent its possible use as a field poison. Marcovitch,[5] about the same time that these first tests were run and entirely independently of this investigation, showed that the fluosilicates were extremely effective against the Mexican bean beetle. He also did some preliminary work on their effect against the boll weevil. However, the density of commercial brands is such as to require 3.9 pounds to cover the same area 1 pound of calcium arsenate will cover, and although there are so-called "light" and "extra light" brands on the market, their respective densities are still above that of calcium arsenate, and the total percentage of sodium fluosilicate is about 78 per cent in the case of the "light" and about 60 per cent in the case of the "extra light." Our comparative toxicity results with these materials indicate that while the "light" sodium fluosilicate appears to be at least as toxic to the weevil as calcium arsenate, the "extra light" is somewhat less toxic than calcium arsenate. Both these materials are less toxic to the plant than the ordinary sodium fluosilicates, and it is believed that either of them can be used on field cotton without any economic damage. It would seem that sodium fluosilicate should contain at least 75 to 80 per cent Na_2SiF_6 to retain its comparative effectiveness.

Commercial sodium fluosilicate is manufactured by adding fluosilicic acid to a solution of sodium chloride. A considerable quantity of the fluosilicic acid of commerce is obtained as a by-product from the phosphate industry. Ordinary phosphate rock generally contains, in addition to phosphate, some fluorspar (CaF_2) and silica (SiO_2). When sulfuric acid reacts on these substances, silicon tetrafluoride (SiF_4) is formed.

$$H_2SO_4 + CaF_2 = 2\,HF + CaSO_4$$
$$4\,HF + SiO_2 = SiF_4 + 2H_2O$$

Commercial fluosilicic acid is obtained by reaction of the silicon tetrafluoride fumes with water.

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

It was found that if, instead of water, a solution of sodium carbonate were used, a gel was obtained which on subsequent drying produced a light sodium fluosilicate containing about 80 per cent Na_2SiF_6.[6]

$$3\,SiF_4 + 2Na_2CO_3 = 2\,Na_2SiF_6 + SiO_2 + 2CO_2$$

One sample batch analyzed 79.5 per cent Na_2SiF_6, 0.74 per cent NaF, 19.61 per cent SiO_2, and 0.15 per cent H_2O, and had an apparent density (H_2O = 1) of 0.26.

It was found that a composition having practically the same physical characteristics could be made by treating a mixture of sodium silicate and sodium carbonate with aqueous fluosilicic acid (35 per cent H_2SiF_6). The product made in this way had an apparent specific gravity of from 0.30 to 0.36, and contained about 20 per cent SiO_2. There was no difference in the weevil toxicities of the materials, whether made from SiF_4 or H_2SiF_6, provided they had the same content of Na_2SiF_6.

About 100 pounds of this material were made and used in cage and field plot tests during 1926.

Barium Fluosilicate

The commercial fluosilicate used was purchased from the Grasselli Chemical Company, and had a relative apparent density compared to calcium arsenate of about 2.65. It showed practically no plant toxicity, and analyzed about 98 per cent $BaSiF_6$.

A light barium fluosilicate was prepared at Edgewood Arsenal in the same manner as the light sodium fluosilicate by passing silicon fluoride into a barium hydroxide solution and drying the gel thus formed.

Some of the batches made on a small laboratory scale had an apparent density as low as 0.8 (calcium arsenate = 1), but the material prepared for field work averaged about 1.40 and analyzed about 88 per cent $BaSiF_6$, 0.5 per cent BaF_2, 10 to 11 per cent SiO_2, and less than 0.1 per cent H_2O. There is no doubt that this material could be prepared commercially with as low a density as calcium arsenate.

Calcium Arsenate Containing Less than 40 Per Cent As_2O_5

Different mixtures and combinations of lime, limestone, or precipitated chalk with arsenic trioxide or arsenic pentoxide were investigated in 1924 regarding their respective toxicities against the boll weevil and also the cotton plant. Varying percentages of the arsenious and arsenic oxides were used and different methods of effecting the combination were tried. From the data obtained in these tests it was indicated that considerably less arsenic than that contained in commercial calcium arsenate (commercial calcium arsenate contains at least 40 per cent As_2O_5) was equally as effective as the commercial calcium arsenate if properly prepared, and did not injure the plant. It was also suspected that, under the proper conditions, arsenic trioxide could be combined with lime or precipitated chalk in any desired proportions, and at the same time the arsenic could be converted to the pentavalent state without the use of any oxidizing agent other than air or oxygen. Since this work was initiated, several patents[7] have issued on the conversion of arsenic trioxide and lime to calcium arsenate, but so far as is known no use has been made of calcium carbonate. While an excess of lime tends to form basic calcium arsenates which are less soluble in the weevil's digestive tract and therefore less toxic than normal calcium arsenate [$Ca_3(AsO_4)_2$], this difficulty may be overcome by using precipitated chalk or limestone, leaving the excess calcium in the more inert form of calcium

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[5] University of Tennessee, Agr. Expt. Sta., *Bull.* **131**.

[6] Gehauf and Walker, U. S. Patent 1,617,708 (February 15, 1927).

[7] U. S. Patents, Lloyd and Kennedy, 1,517,516 (December 2, 1924); Cullen, 1,532,577 (April 7, 1925); Taylor, 1,612,233 (December 28, 1926).

carbonate. It was the attempt of our experiments to produce particles of calcium arsenate dust containing an excess of calcium carbonate, most of this excess constituting the cores of the particles while the outer surfaces approached the formula $Ca_3(AsO_4)_2$.

After considerable experimental work it was found that mixtures of precipitated chalk and white arsenic in any desired percentage could be combined to form calcium arsenate by heating in the presence of excess air at 650° C. The complete data on these experiments will be published in the near future. Almost complete conversion of the arsenic to the pentavalent state is obtained and the loss of arsenic is about 20 per cent of the original arsenic. Practically no lime is formed at this temperature for the length of time required to convert the arsenic to the pentavalent state (15 minutes to 1 hour). The arsenic lost could be recovered on a commercial scale.

The following is a typical laboratory run for approximately 20 per cent As_2O_5 calcium arsenate:

Original mixture As_2O_3	3 grams
$CaCO_3$	12 grams
Temperature	650° C.
Time heated	1 hour
Trivalent arsenic as As_2O_3	0.16 per cent
Total arsenic as As_2O_5	24.9 per cent
Total loss of arsenic (on original As) as As_2O_5	7.2 per cent

With the coöperation of the Mechanical Division, Edgewood Arsenal, about 500 pounds of this material were prepared on a semiplant scale in batches of about 50 pounds each. The average analysis for this material was as follows:

Moisture	0.23 per cent
Density (calcium arsenate = 1)	1.25
Trivalent arsenic as As_2O_3	0.20 per cent
Total arsenic as As_2O_5	24.25 per cent
Water-soluble arsenic as As_2O_5	0.68 per cent

This product was used in cage tests and field plot tests for 1926.

In the same manner about 300 pounds of material containing about 10 per cent As_2O_5 were prepared. As shown by the accompanying toxicity results, it is indicated that this product, while possessing definite weevil toxicity, is not so effective as calcium arsenate. The average analysis of this material was as follows:

Moisture	0.09 per cent
Density (calcium arsenate = 1)	0.864
Total arsenic as As_2O_3	9.97 per cent
Trivalent arsenic as As_2O_5	0.18 per cent
Water-soluble arsenic as As_2O_5	0.24 per cent

Cryolite

Commercial cryolite was about as toxic against the boll weevil as calcium arsenate and also was practically non-toxic to the plant, but its apparent specific gravity is about 1.13 ($H_2O = 1$) and it requires approximately 3.34 pounds to cover the same area as one pound of calcium arsenate. The material used in these tests was the natural cryolite purchased from the Pennsylvania Salt Manufacturing Company. On account of the relatively high density of cryolite, its expense per unit of area dusted is considerably higher than that of calcium arsenate, and as no economical way of lightening it was apparent, it was abandoned for large-scale field tests. It is understood that the value of this material is about 3.5 cents per pound (the selling price is about 7 cents per pound)[8] and should the price of calcium arsenate be increased for any reason, or should cryolite be obtainable as a by-product from some industry in a considerably lighter form, it offers a possible substitute for calcium arsenate.

Barium Fluoride

Barium fluoride, while proving definitely toxic to the weevil and non-toxic to the cotton plant, did not seem to be quite so toxic to the weevil in cage tests as calcium arsenate. It is open to the same objections regarding its comparative covering power as cryolite and the commercial fluosilicates. The relative apparent density to calcium arsenate is about 2.73. As no economical method of lightening this material was apparent, it was abandoned for large-scale field tests, although it is a possible substitute for calcium arsenate should a cheap method of making a lighter barium fluoride be found, or should the price of calcium arsenate increase sufficiently to warrant its use. It is possible that a mixture of barium fluoride and colloidal silica could be obtained which would have the desired characteristics, but in view of the relative toxicities of barium fluoride and barium fluosilicate, such a mixture would probably have no advantage over the light barium fluosilicate.

Use of Soluble Poisons on Absorbents as Dusts

Relatively small percentages of thirteen soluble poisons were absorbed on twenty-eight different cheap vehicles and the various mixtures tested for both weevil and plant toxicity.

The absorbents alone, without the addition of soluble poisons, were non-toxic to the cotton plant in all cases, and none of them showed any appreciable weevil toxicity with the exception of barium carbonate.

Of the soluble toxics, when impregnated on absorbents, only the following showed any appreciable weevil toxicity in the maximum percentages used: arsenic trioxide, arsenic pentoxide, sodium arsenate, sodium arsenite, methyl arsenious oxide, chlorinated oil, and lead tetraethyl.

Lead tetraethyl showed definite weevil toxicity on silica-gel, but very low toxicity on coal dust. It was also definitely toxic to the cotton plant, and because of the extremely insidious nature of lead tetraethyl and the consequent danger to personnel, there does not seem much hope of making practical use of it as a boll weevil poison.

Chlorinated oil[9] was the only other absorbed poison, not an arsenical, which showed some definite toxicity to the weevil, although it was not so effective as calcium arsenate. The material did not injure the plant. Not much more than 3 per cent may be used on absorbents as larger amounts tend to make the material gummy and sticky, and detract from its dusting properties. Additional experiments with this material are worth while.

Of all the various inert absorbents for soluble poisons, finely powdered coal dust seemed to possess the most desirable features, including good adherence to the plant, even when the plant was dry, and also adherence to the weevil. In other words, the coal dust stuck well to the plant and yet was readily picked up by the weevil when it came in contact with the dust. Coal dust also dusted readily and gave good dust clouds from the present-type dusting machines. Hard-coal dust seemed to dust slightly better than soft-coal dust. Coal dust, when impregnated with various poisons, seemed to prevent plant injury to a greater extent than any of the other vehicles except activated charcoal and wood charcoal, both of which are much more expensive than the coal dust. Also, coal dust so impregnated with a soluble poison seemed to be able to release the toxic fairly readily when taken internally by the weevil.

Trivalent arsenic on coal dust proved definitely more toxic than the pentavalent. The limit of arsenic trioxide from the standpoint of plant toxicity was about 1 per cent, which mixture, while proving definitely toxic to the weevil, was not so toxic as calcium arsenate. When about 3 per cent of some inhibiting agent, such as olive oil, cottonseed oil, etc., was added to the coal dust, 2 per cent arsenic trioxide was used without much plant injury, but the weevil toxicity was

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[8] Davis, *Bur. Mines, Mineral Resources 1925*, Vol. II, Pt. 2, p. 7.

[9] McQuaid and Mitchell, U. S. Patent 1,492,391 (April 29, 1924).

still lower than with calcium arsenate. The difference in the degree of toxicity was more marked in the case of field cage tests than in tumbler tests. Methyl arsenious oxide was certainly no more toxic in the same percentages than arsenic trioxide, which seems contrary to our general ideas concerning the relative toxicity of organic and inorganic arsenicals, the more so when we consider that the methyl arsenious oxide is relatively soluble in water. However, the methyl arsenious oxide was more injurious to the cotton plant than the same percentages of arsenic trioxide.

In cage tests, 4 per cent of arsenic trioxide on coal dust without any inhibiting oil, killed the plant in from 3 to 5 days, and showed only from 40 to 50 per cent of the weevil toxicity of calcium arsenate.

Discussion of Use of Poisons as Dusts

How a Boll Weevil Is Poisoned—In 1924 it was suspected that the weevil did not obtain the bulk of its poison through feeding or drinking the poisoned dew, but by more or less accidentally picking up the particles of dust on its moist snout and subsequently ingesting the same. The fact that this occurs was proved experimentally by allowing weevils to remain on filter paper dusted with calcium arsenate and comparing the mortality with that of weevils allowed to feed on cotton dusted with calcium arsenate. A control consisting of weevils on undusted filter paper was run. The mortalities of the two dust tests were very nearly equal. E. F. Grossman independently proved that weevils were poisoned after walking across a glass plate dusted with calcium arsenate. There is no doubt that the weevil is also poisoned to some extent by drinking poisoned dew.

Dusting Properties—This more or less accidental poisoning of the weevil emphasizes the importance of uniform surface distribution of the dust and also limits the stickiness of the dust, as it must not stick so tightly to the plant that it cannot be readily picked up by the weevil. Most commercial calcium arsenates seem to possess this nice adjustment to a very marked degree. At the present time the light fluosilicates, as made at Edgewood Arsenal, do not adhere to the plant so well as calcium arsenate, but they are much more free-flowing and dust better than calcium arsenate, and there is no question but that their sticking properties, so far as the cotton plant is concerned, can be increased to the desired point by the addition, during their preparation, of small amounts of adhesives, such as casein, agar-agar, glue, etc. The specially prepared calcium arsenates containing less than 40 per cent arsenic as As_2O_5 can be made so as to possess essentially the same physical characteristics as commercial calcium arsenate. It must be remembered that the preparation of the light fluosilicates on a semiplant scale was a rush job and, consequently, all the minor refinements could not be used as these materials were needed in the field immediately. On a laboratory scale, batches of these materials were repeatedly made which always had a lower apparent density than calcium arsenate and which showed no plant injury at all to greenhouse cotton. Some of the minor injury shown in the cage tests was probably due to small amounts of free hydrofluoric acid remaining in the powdered material.

The difference in the relative toxicities of the materials in the large and the small-cage tests was probably due to the better adherence of the calcium arsenate in the large cages. The amount of the other materials which actually stayed on the plant could be much better controlled in the small cages. The increased effectiveness of all poisons in the smaller cages was due to the fact that the plant occupied more of the space in the cage and there were fewer weevils on the sides of the cages and a greater percentage on the plant. For this reason it is believed the small-cage tests are a fairer approximation of field conditions than the large-cage tests, although it is also believed that the mortality of all poisons on a field scale would be greater than in cage tests as the weevils would have to be on the dusted cotton plants all of the time and their chances of picking up some of the dust would therefore be increased.

Toxicity to Higher Animals—The following are some figures determined by the Medical Research Division of Edgewood Arsenal on comparative toxicities of sodium fluosilicate and barium fluoride to calcium arsenate when administered by mouth. The complete data for these experiments will be published in the near future by the Medical Research Division.

Ratio Lethal Dosages

$$\frac{\text{Calcium arsenate}}{Na_2SiF_6} = \frac{1}{2.5}\ \text{(rabbits)} = \frac{1}{4}\ \text{(dogs)}$$

$$\frac{\text{Calcium arsenate}}{BaF_2} = \frac{1}{4}\ \text{(rabbits)} = \frac{1}{14}\ \text{(dogs)}$$

Replacement of Arsenic in Calcium Arsenate by Carbon Dioxide—It is probable that calcium arsenate owes some of its effectiveness as a boll weevil poison to the fact that the carbon dioxide of the air continuously replaces some of the AsO_4 radical, thus liberating water-soluble arsenic more or less continuously. This was shown experimentally by making successive determinations of water-soluble arsenic (according to Association of Official Agricultural Chemists' Methods 30 and 31) and allowing the calcium arsenate to stand exposed to the air for 48 hours between determinations. The results of these determinations follow:

Detn.	Soluble Arsenic as As_2O_5 Per cent	Detn.	Soluble Arsenic as As_2O_5 Per cent
1	0.06	6	0.72
2	1.35	7	0.69
3	0.80	8	0.69
4	0.90	9	0.64
5	1.00		

Second Runs—In the field it is possible that ultimately a coating of calcium carbonate would be formed on the outer surface of the particle, thus rendering the arsenic more or less inaccessible to the weevil when ingested by it. Accordingly, so-called "second runs" were made on a number of compounds by placing weevils on plants that had been dusted 5 days previously. The relative deterioration of some of the poisons compared with that of calcium arsenate is summarized in Table II.

In all cases the fluosilicates were considerably more toxic than the second-run calcium arsenate; in fact, most of them appeared equally as toxic as the first-run calcium arsenate, in spite of the fact that considerably more calcium arsenate was visible on the plants at the end of the run (10 days) than any of the other poisons. The cages were covered, which prevented excessive loss of poison by wind and rain, although such loss was probably greater in the large cages than in the small ones. This means that in the field, if there is no rain or excessive wind, the fluosilicates would approximate their maximum effectiveness longer than calcium arsenate. It should be noted that the 24 per cent As_2O_5 calcium arsenate second runs seemed at least equally as effective as the commercial calcium arsenate second runs.

Quick-Killing Properties—It will be noted in the first-run toxicities (Table I) that all the fluosilicates killed a greater percentage of weevils in the first 48 hours than did calcium arsenate. This is of especial importance in localities where there are sudden rains during the season that dusting is necessary, as the fluosilicates will probably get in some of their effects even if allowed to remain on the plant only a short time.

TABLE II - RELATIVE DETERIORATION OF POISONS - CAGE TESTS - 1926

Compound	No. of Cages*	Grams Poison Per Cage	Apparent Density of Poison	Total No. of Weevils	Daily Mortality: 1	2	3	4	5	Percent Dead	Percent Rel. Toxicity: CaAs (New)	CaAs (Run #2)
1 CaAs	1 L	3.2		37	3	8	3	2	1	46.0		
CaAs - Run #2	1 L	2.5		31	1	6	2	2	1	35.5	77.2	
Na_2SiF_6 - P - Run #2	1 L	4.2		31	0	7	4	3	3	55.0	119.5	155.0
CaAs	15 S	1.40		204	18	31	37	17	25	62.8		
CaAs - Run #2	15 S	1.38		217	11	25	30	17	32	53.0	84.4	
Na_2SiF_6 - P - Run #2	14 S	2.69	2.80	195	41	45	23	14	19	72.8	116.0	137.4
2 CaAs	9 S	1.37		120	8	22	20	11	18	65.8		
CaAs - Run #2	10 S	1.50		142	7	21	19	14	22	57.4	87.2	
Na_2SiF_6 - W - Run #2	9 S	3.73	1.87	127	14	30	19	20	20	81.1	123.1	141.2
3 CaAs	12 S	1.31		166	17	21	26	13	21	59.0		
CaAs - Run #2	13 S	1.22		188	11	21	27	13	24	51.0	86.4	
Na_2SiF_6 - JL - Run #2	10 S	2.26	2.28	143	19	22	8	14	17	55.9	94.8	109.6
4 CaAs	6 S	1.42		84	10	9	17	6	7	58.4		
CaAs - Run #2	5 S	1.14		75	4	4	11	3	10	42.7	73.1	
Na_2SiF_6 - JEL - Run #2	4 S	1.75	1.67	55	11	7	1	1	3	41.8	71.6	97.9
5 CaAs	4 L	3.43		135	3	10	8	10	13	32.6		
CaAs - Run #2	6 L	3.98		184	5	12	9	7	12	24.5	75.2	
Na_2SiF_6 - EA - Run #2	7 L	3.23		214	9	18	10	11	21	32.3	99.1	131.8
CaAs	15 S	1.39		204	18	31	37	17	25	62.8		
CaAs - Run #2	15 S	1.38		217	11	25	30	17	32	53.0	84.4	
Na_2SiF_6 - EA - Run #2	25 S	1.15	0.9	347	53	43	30	35	44	59.1	94.1	111.5
6 CaAs	2 L	2.65		61	2	2	11	10	16	67.2		
CaAs - Run #2	2 L	2.80		60	1	3	4	6	13	45.0	67.0	
$BaSiF_6$ -G - Run #2	2 L	10.35		54	2	6	5	3	10	48.2	71.7	107.0
CaAs	15 S	1.39		204	18	31	37	17	25	62.8		
CaAs - Run #2	15 S	1.38		217	11	25	30	17	32	53.0	84.4	
$BaSiF_6$ - G - Run #2	14 S	3.88	2.65	201	34	43	23	19	22	70.1	111.6	132.2
7 CaAs	6 L	3.13		196	5	12	19	20	29	43.4		
CaAs - Run #2	8 L	3.69		244	6	15	13	13	25	29.5	68.0	
$BaSiF_6$ - EA - Run #2	8 L	4.48		243	12	24	32	14	26	44.5	102.5	150.8
CaAs	15 S	1.39		204	18	31	37	17	25	62.8		
CaAs - Run #2	15 S	1.38		217	11	25	30	17	32	53.0	84.4	
$BaSiF_6$ -EA - Run #2	15 S	1.56	1.40	216	47	37	17	19	23	66.2	105.4	124.9
8 CaAs	3 L	2.70		98	5	17	13	14	12	62.3		
CaAs - Run #2	6 L	4.80		173	5	10	9	10	17	29.5	47.3	
CaAs - EA-1 - Run #2	6 L	4.88		165	8	8	6	10	28	36.4	58.4	123.3
CaAs	18 S	1.32		249	20	40	44	19	31	61.9		
CaAs - Run #2	16 S	1.40		228	11	27	35	18	34	54.8	88.5	
CaAs - EA-1 - Run #2	16 S	1.85	1.25	235	18	22	20	35	44	59.2	95.6	108.0
9 CaAs	2 L	2.65		69	4	9	9	9	8	56.5		
CaAs - Run #2	5 L	4.14		151	3	9	9	8	15	29.1	51.5	
CaAs - EA-2 - Run #2	5 L	3.46		142	1	1	9	6	25	29.6	52.4	101.6
CaAs	11 S	1.42		151	14	27	34	14	14	68.2		
CaAs - Run #2	10 S	1.26		147	6	14	24	13	23	54.4	79.8	
CaAs - EA-2 - Run #2	11 S	1.25	0.86	162	6	20	15	19	20	49.4	72.4	90.8

(For explanation of compounds tested, see footnotes to Table I.)

PLANT INJURY—While there is no question that all the fluosilicates were more toxic to the cotton plant than calcium arsenate, the special fluosilicates prepared at Edgewood in no case showed a positive harmful burn. This fact is emphasized by the large-scale one-acre plot tests in which no sign of plant damage was visible, although thirteen dustings were made in 25 days and conditions were most favorable for obtaining definite plant injury. That what injury there was in cage tests did not grow more severe with time was shown by the plant toxicity observations made during the second runs. Also, as previously mentioned, laboratory batches of sodium and barium fluosilicates made at Edgewood Arsenal showed no plant toxicity to greenhouse cotton.

Use of Sweetened Mixtures

In the preliminary tumbler tests all the toxic substances tried as dusts were also tried as molasses mixtures. Calcium arsenate in molasses was used as a check. Except in the case of cryolite the molasses mixtures of the materials seemed about equally as effective as the dusts. In the case of cryolite the molasses mixture was considerably less effective than the dust.

The relative effectiveness of calcium arsenate dust to calcium arsenate–molasses mixture in tumbler tests for 1924 is summarized for all the checks:

	CALCIUM ARSENATE DUST	CALCIUM ARSENATE–MOLASSES MIXTURE
Number of tests	47	28
Total weevils	1246	522
Per cent total dead	66	74
Per cent dead and groggy	77	75

The calcium arsenate–molasses mixtures consisted of 7 grams of calcium arsenate, 20 cc. of molasses, and 80 cc. of water, which is about equivalent to a so-called 8:2:5 mixture (8 gallons of water, 2 gallons of molasses, 5 pounds of calcium arsenate) as used for spraying at the Georgia Experiment Station. The other poisons run as molasses mixtures were in the same proportions.

In order to determine how the molasses mixture poisoned the weevil, tests were made with filtered molasses from a calcium arsenate mixture after standing 3 hours, 1 day, 2 days, and 3 days, respectively, and the toxicity of these filtered solutions was compared with that of freshly prepared suspensions of calcium arsenate in molasses. In all cases the filtered solutions showed definite weevil mortality, although not so great as the calcium arsenate–molasses mixtures. The fact that the calcium arsenate–molasses mixtures so closely approximate the calcium arsenate dust checks in mortality shows that the toxicity of the poisoned solution is augmented by the actual particles of the dust suspended therein.

Tumbler tests of mixtures of calcium arsenate with various sweetening agents, including honey, cane sugar, maple sugar, molasses, saccharin, and glucose, indicated their order of effectiveness to be as shown. For the honey, cane sugar, maple sugar, and glucose the proportions were 7 grams of calcium arsenate, 10 grams of sweetening agent, and 90 grams of water.

The calcium arsenate–molasses mixture was the standard 7 grams of calcium arsenate, 20 cc. of molasses, 80 cc. of water, and the saccharin was 100 cc. of saturated solution of the same to which 7 grams of calcium arsenate were added.

These results do not necessarily mean that any of these substances possessed definite attraction, but simply indicate that when the weevil came in contact with a honey–calcium arsenate mixture it possibly ate or drank more. The first three mixtures were as effective as the calcium arsenate dust checks.

Under field conditions it seems to have been demonstrated that the main value of sirup–calcium arsenate mixtures lies in their use when the cotton is small, and particularly when the weevils are feeding upon the terminal buds of the plant. The Chemical Warfare Service has not yet been able to investigate the important problem of using poisons most effectively in this manner, although preliminary tests indicate that barium and sodium fluosilicates are at least as effective in sirup mixtures as calcium arsenate.

Field Plot Tests

The field plot tests laid out at the Georgia Experiment Station and in its immediate vicinity during 1925 were a total loss because the extreme drought throughout the entire Piedmont Section during that season held down the infestation to such a degree that there was no advantage in poisoning.

The cotton for the field plot tests in Florida was located about 15 miles from the Florida Experiment Station. Because of the poor stand and the variability of the cotton in the different plots no comparison of the relative effectiveness of the poisons was possible, although the yields from all the poisoned plots were considerably higher than those from the controls, in spite of rainy weather and an average initial infestation of 40.8 per cent. In no case in these field tests did the application of the fluosilicates cause any plant damage.

In addition to the tests conducted in Florida, materials were sent to J. D. Riley, at Summerville, S. C., and J. B. Robinson, Auburn, Ala., for tests. Owing to damage caused by excessive rains at Summerville, the cotton was destroyed in batches over the field and no yields were obtainable. The infestation records seemed to indicate that all the poisons—calcium arsenate, special calcium arsenate (24 per cent As_2O_5), sodium fluosilicate, and barium fluosilicate—held back the infestation as compared with the check plots, but no direct comparison of the poisons is possible. Practically the same results were obtained at Alabama, with the further assurance from Mr. Robinson that none of the materials showed any plant toxicity.

Gases as Poisons

Weevils seemed to stand concentrations of gas entirely out of line with the known poisonous effect of the gas used. Suspecting that this was due to the ability of the weevil to live without breathing the gas, weevils were found to survive after about 17 hours' exposure in pure carbon dioxide and hydrogen, respectively, and four out of seven weevils recovered after approximately 17 hours' submersion in water. This confirmed the view that weevils can live some time without breathing oxygen and therefore low concentrations of gas were used in an endeavor to poison the weevil without causing it to suspend animation or to stop breathing. It was found that the boll weevil could be killed by a relatively small concentration of poisonous gas on longer exposures.

In the field it would be practically impossible to maintain low concentrations of volatile gas for long periods of time, and there is little hope of poisoning the boll weevil by the use of volatile gases as such.

Approximate Toxic Concentrations for the Boll Weevil

GAS	CONCENTRATION	TIME	TOXIC DOSAGE PER WEEVIL
	Mg. per liter	*Minutes*	*Mg.*
Hydrocyanic acid	0.11	60	0.00036
Chloropicrin	11.4	60	0.0038
Hydrogen sulfide	0.30	60	0.0001
Arsine	2.5	60	0.00075
Nicotine	5.0	30	0.00075
Allyl *iso*-thiocyanate[a]	0.1	120	0.000066

[a] Results are probably much too low.

The toxic dosage per weevil was estimated from the toxic concentrations and times of exposure given, using the value 0.33 cc. as the amount of air breathed by a boll weevil in one hour.

Estimation of Amount of Air Breathed by a Boll Weevil

Forty-one weevils were found to eliminate 0.01739 gram of carbon dioxide in 19 hours. This is equivalent to 0.011 cc. (at 0° C. and 760 mm.) carbon dioxide per weevil per hour, and assuming an air–carbon dioxide ratio of 30, which is a questionable assumption, it is estimated that a boll weevil breathes 0.33 cc. of air per hour.

Analyses of Boll Weevils for Arsenic

Although many analyses on thousands of weevils were made, the amount of arsenic necessary to kill a boll weevil still remains somewhat uncertain. All analyses made during 1924 were high because a small amount of arsenic was obtained from the flasks used for digestion. Even when arsenic-free glass was used, there was considerable variation in the results. The determination requires the very limit of accuracy given by the modified Gutzeit test.[10]

Probably small particles of the arsenical used in the test frequently adhered to the weevil in spite of all care taken to remove such particles, and this adhering arsenic doubtless aided in producing erratic and high results.

The best interpretation that can be given to all the results obtained is to assume that they lead to the following indications:

	CALCD. AS As
	Mg.
Arsenic required to kill weevil	0.00013
Arsenic in weevils poisoned with coal dust-soluble arsenic mixtures	0.00035-0.00093
Average arsenic found in weevils poisoned with calcium arsenate	0.00204

It is believed that the minimum lethal dose of 0.00013 mg. is somewhat too high, as this average dosage is approximately 10 mg. arsenic per kilogram of body weight. The dosage

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[10] Scott, "Standard Methods of Chemical Analysis," Vol. I, p. 46 (1922); U. S. P., X, p. 428.

for man is about 2.7 mg. per kilogram. The Department of Agriculture[11] gives figures leading to minimum lethal dosages for the honeybee and silkworm of 5 mg. and 2 mg. per kilogram, respectively.

When relatively insoluble arsenicals, such as calcium arsenate, are used, it seems fairly certain that not more than one-tenth of the total arsenic ingested is effective in poisoning the weevil, probably because of the insolubility of the calcium arsenate particles in the weevil's system.

Possible Attractants for the Weevil

VAPORS OR GASES—The Chemical Warfare Service made no extended tests upon agents which might prove attractive to the boll weevil, as it was known that the Department of Agriculture was exerting every effort possible along this line. However, some substances were tested to increase our knowledge along these lines. In no case was any compound found to which the weevil was definitely and unmistakably attracted.

FLAVORS—It was thought that if calcium arsenate could be made more pleasing to the weevil's taste the weevil might ingest more of the poison, thus increasing the effectiveness of the calcium arsenate. Accordingly, about 0.25 per cent of various essential oils and some few other chemicals, respectively, were added to calcium arsenate. While there was some indication that such small amounts of aniline and one or two other substances added to calcium arsenate were each more effective than the calcium arsenate alone, no conclusive results were obtained.

Estimation of Amount of Water Drunk by Weevils

Tests in which boll weevils were allowed to drink poisoned solutions showed that on an average a solution containing 0.02 per cent anhydrous sodium arsenate would kill a weevil in 24 hours. Solutions containing 0.00087 per cent arsenic trioxide and 0.01 per cent arsenic pentoxide, respectively, will kill a weevil in 24 hours. If it requires 0.00013 mg. of arsenic to kill a weevil, the above figures would indicate that a weevil must drink 0.02 cc. per day.

It should be noted that solutions of 0.01 per cent arsenic pentoxide sprayed daily on the cotton plant with an atomizing spray until the leaves were thoroughly wet, but just short of dripping, showed very slight injury the first day and continued slight injury until the sixth day, when the injury was more positive. Solutions of arsenic trioxide in this strength killed the cotton plant.

Possible Repellents for the Boll Weevil

Although no work was carried out with this particular object in view, it was noticed in making tumbler tests with various materials that the following possibly showed some repellent action to the weevil: anthracene, benzanilide, diethylene disulfide, and chlorinated oil.

Possible Irritants for the Weevil

When the most powerful known irritants to man were tried against the weevil in the hope they might make it fly, they caused practically no signs of irritation or excitement. While some few other substances less irritating to man did seem to increase the weevil's activity under the conditions of test, in no case was the increased activity sufficient to be considered of economic importance. None of the substances tested was successful in making the weevil fly.

General Summary and Conclusions

1—Commercial sodium fluosilicate is more toxic to the boll weevil than commercial calcium arsenate on a volume basis, but on account of the greater apparent density of the fluosilicates it requires from 2 to 4 pounds of them to cover effectively the same area that one pound of commercial calcium arsenate will cover. These commercial fluosilicates show some injury to the cotton plant. So-called "light" and "extra light" commercial materials containing less sodium fluosilicate are still too dense from the standpoint of covering power, and their effectiveness is decreased with the lowering of the Na_2SiF_6 content. Also, the plant injury is decreased. When the Na_2SiF_6 content is reduced much below 80 per cent, the material is not so effective as calcium arsenate.

2—A special fluosilicate made at Edgewood Arsenal containing about 80 per cent Na_2SiF_6 and 20 per cent SiO_2 is at least as effective on a pound per pound basis as calcium arsenate, and the plant injury caused by it is of low economic importance.

3—Barium fluosilicate made in the same way as the sodium fluosilicate, containing about 90 per cent $BaSiF_6$ and 10 per cent SiO_2, is about as effective on a pound per pound basis as calcium arsenate and causes no appreciable plant injury. The toxicity of the barium fluosilicates in general is somewhat less than that of the sodium fluosilicates.

4—When the dust is applied to the plants 5 days before the weevils are introduced, both the sodium and barium fluosilicates cause at least as great weevil mortality as freshly dusted calcium arsenate. Calcium arsenate applied 5 days prior to the introduction of weevils in the cage causes appreciably lower mortality than freshly dusted calcium arsenate. In these tests the cages were covered to prevent rain from washing the dust off the plants.

5—Specially prepared calcium arsenate containing only 24 per cent arsenic as As_2O_5, the arsenic being contained mainly in the coating of each particle, is equally as effective as commercial calcium arsenate and was non-toxic to the plant in these tests. Calcium arsenate similarly prepared, containing only 10 per cent As_2O_5, was less effective than commercial calcium arsenate.

6—Calcium arsenate may be prepared to contain any desired percentage of arsenic as As_2O_5 by heating the requisite amount of As_2O_3 with precipitated chalk in the presence of air at a temperature of about 650° C. for one hour or less.

7—Barium fluoride and cryolite are at best only slightly less effective than calcium arsenate on a volume for volume basis and cause no appreciable plant injury. They require an increased poundage per acre over calcium arsenate, however, and no economical means of adapting their physical properties to overcome this has yet been devised.

8—While small percentages of As_2O_3 adsorbed on coal dust showed definite weevil toxicity and practically no plant injury, they were not so effective as calcium arsenate. When these percentages were increased they caused definite plant injury without raising the weevil toxicity to a point equal to that of calcium arsenate. Four per cent of arsenic trioxide on coal dust killed the plant. Arsenic trioxide is definitely more toxic to both the plant and the weevil then arsenic pentoxide.

9—Very insoluble organic arsenicals of known high general toxicity, such as diphenylamine chloroarsine, diphenylamine arsenious oxide, diphenyl arsenious oxide, etc., were at best only slightly toxic to the boll weevil, owing probably to their low solubility.

10—Preliminary tests indicate that the fluosilicates in molasses mixtures are at least as toxic to the boll weevil as calcium arsenate in molasses mixtures. It is further indicated in tumbler tests that molasses mixtures of calcium arsenate are about as toxic to the weevil as calcium arsenate dust. There are some indications that a calcium arsenate-

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[11] U. S. Dept. Agr., *Bull.* **1147.**

honey mixture is superior to a calcium arsenate-molasses mixture containing the same amount of calcium arsenate.

11—Unfavorable weather and crop conditions made it impossible to make trustworthy comparisons of the relative effectiveness of the fluosilicates, the special calcium arsenate, and commercial calcium arsenate from the one-acre plot tests made to date. All these materials showed definite weevil control and there was no plant injury apparent on field cotton in any case. It is hoped to establish the relative effectiveness of these materials during the present year.

12—There is little hope of poisoning the boll weevil in the field by the use of volatile gases.

13—The following are various estimates pertaining to the weevil:

Average weight of a boll weevil (does not include undersized weevils)	15.0 mg.
Amount of air breathed by a boll weevil per hour	0.33 cc.
Minimum arsenic required to kill a boll weevil	0.00013 mg.[a]
Average arsenic content found in weevils killed with calcium arsenate	0.002 mg.
Amount of water a weevil drinks per day	0.02 cc.

[a] Possibly too high.

14—No substances were found which definitely attracted or repelled the boll weevil. No substances were found which irritated the weevil sufficiently to make it fly.

15—In carrying out the directions of the Association of Southern Agricultural Workers and the Department of Agriculture for boll weevil control, the following suggestion is made: When the initial weevil infestation is below twenty weevils per acre or when it is, or has been, reduced to local infestation, the fight should be continued against the individual weevils both by local poisoning and by picking up the fallen punctured squares locally, as necessary, to insure the most complete control possible. Advanced cotton and badly infested cotton should receive special attention in order to prevent multiplication of the weevils in these local spots and later infestation of the entire crop. Success in the fight against overwintered weevils will give complete security against any large amount of weevil damage.

Acknowledgment

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Lime for the Glass Industry[1]

By **Edwin P. Arthur**

Department of Chemical Engineering, The Ohio State University, Columbus, Ohio

LESS than 2 per cent of the total lime production of the United States is consumed in the manufacture of glass.[2] Nevertheless, many lime producers find the glass trade attractive. The demand is less subject to fluctuations than building construction. The business, even though small in amount, is especially welcome during dull seasons.

For approximate calculations it is permissible to assume that glass will contain 10 per cent lime. Thus, if a glass factory produces 50 tons of glass per day, the lime requirement will be about 5 tons per day or one minimum carload per week. Somewhat more than 10 per cent lime is used in flat glass and generally less in hollow ware.

Soda ash is largely used to furnish the alkali for ordinary soda-lime glass. Thirty per cent of the soda ash produced in the United States is used in the glass business, amounting in 1925 to 520,000 tons.[3]

Estimating average glass to contain 15 per cent of Na_2O, the total production of glass is indicated as 2 million tons

$$\frac{Na_2O}{Na_2CO_3} : \frac{62}{106} : \frac{304,000}{520,000} ; \frac{304,000}{0.15} = 203 \times 10^4 \text{ tons glass}$$

with a consequent lime requirement of 200,000 tons annually. Since present consumption of lime is less than 75,000 tons, it may be seen at once that considerably less than half the glass is made from burned lime, the raw ground stone being used instead. (Allowance is not made for special glasses which require soda ash but no lime.) Burned lime is generally more expensive than raw limestone as a raw material for glass-making per ton of available material delivered for melting.[4] But since the raw material cost of glassware is often only 10 to 20 per cent of the total, a small improvement in quality by use of burned lime would more than offset its increased cost. Apparently no definite information on the relative merits of lime and limestone is available in the literature. It has been stated[5] that plate glass made with lime is as good but no better than that made from raw stone.

When raw stone of excellent quality from the same deposit is substituted for burned lime in the manufacture of window glass, no appreciable difference in operation has been noticed either in fuel requirements or in quality of glass produced. It is, of course, obviously unfair to make comparison of lime and stone of entirely different character, as, for example, a burned dolomite and high-calcium limestone. There is, however, much to recommend burned lime. It is subject to more careful inspection than raw stone. It will generally be more uniform chemically and less contaminated with incidental impurities. A batch mixed with lime occupies less space per unit weight and consequently more material can be held in the melting area of a large tank furnace.

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[1] Received May 2, 1927.

[2] Willis, *Chem. & Met. Eng.*, **33**, 753 (1926), quotes Bureau of Mines, "Lime in 1924," figures for lime sold by producers to glass works as 1.8 per cent of the total or 72,822 tons.

[3] *Chem. & Met. Eng.*, **33**, 49 (1926).

[4] Arthur, *J. Am. Cer. Soc.*, **8**, 125 (1925).

[5] Adams, *Glass Ind.*, **8**, 2 (1927).

Even though no more or better glass is delivered by a furnace using a burned-lime batch, nevertheless, the fact that the batch can be held closer to the "back end" of the furnace affords a welcome factor of safety to the glass maker, especially if the furnace is operating near capacity.

Chemically the most important item is iron content because of the green color which iron imparts to glass. First-class lime for glass-making should contain less than 0.2 per cent iron oxide.[6]

The question of iron content is becoming increasingly important. Glass sand is being produced containing 0.02 per cent Fe_2O_3. In a glass which is 75 per cent SiO_2 and 10 per cent CaO-MgO, sand furnishes less iron to the glass than lime if the lime contains more than 0.15 per cent Fe_2O_3. The table ware and hollow ware branches of the industry are forced to seek low-iron sources of lime in order to make the brilliant water-white glass demanded. It is said that some market is being found for precipitated calcium carbonate of low iron content at substantially higher prices than lime.

Lime for the glass trade should be slightly overburned. Off-color lime which might be unsuitable for building purposes would be quite acceptable for glass-making. Overburned lime does not hydrate so readily—a decided advantage in shipment and storage. Lime in the open storage bin of a glass factory on a river bank has been found to absorb as much as 9 per cent H_2O in 10 days. If reserve stocks of lime at a glass works can be kept in air-tight steel drums, using each shipment of lime as received, a uniform batch can be assured.

Little or no effort has been made by lime producers to furnish glass makers with a product adapted mechanically to the process of glass manufacture. The ordinary finishing lime is so finely ground that it is difficult to handle in mixing and conveying machinery. Lime dust blown from batch in the furnace has a tendency to clog furnace flues and regenerators. It would appear desirable for lime producers to make a companion product for the "dense dustless" soda ash now in universal use. Tailings, screenings, and rejects from an air separator might be recovered as an ideal product for glass-making.

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[6] Williams, *Bur. Standards, Circ.* **118**.

Lime for the Absorption of Chlorine in Paper Mill "Bleach Liquor" Practice[1]

By A. H. Hooker, Sr.

Hooker Electrochemical Co., Niagara Falls, N. Y.

In selecting a lime for the absorption of chlorine we consider the production of either dry "bleaching powder" or liquid bleach. By far the largest use for these two products is in the paper mills. Until quite recently chlorine was nearly always purchased by the paper mills in the form of bleaching powder; consequently, the lime used to absorb the chlorine was purchased and hydrated by the manufacturer of chlorine. A very radical change has taken place, however, and the use of bleaching powder has been rapidly displaced by the use of liquid chlorine and the purchase by the paper mills of hydrated lime, in 50-pound bags, or burned lime hydrated at the mill and the absorption of chlorine in a milk-of-lime suspension. The ultimate aim in the paper mill, whether using bleaching powder or liquid chlorine and milk of lime, is to obtain the chlorine in the form of a solution of calcium hypochlorite plus calcium chloride, together with a small amount of free soluble lime and in a clean solution. Such solutions are invariably prepared by decantation and generally with a return counter wash so as to obtain all the values possible from the sludge. One must understand this operation clearly before he can decide on the qualities of the lime most suited to his use.

Preparation of Bleach Solution from Bleaching Powder

Let us consider first the preparation of a typical bleach solution from bleaching powder. This lime must first be hydrated in a mechanical hydrator. It is then spread in layers a few inches thick on the floor of a bleaching chamber or handled in a mechanical bleach machine. Chlorine is absorbed to a point where there will be present about 38 per cent of total chlorine and 62 per cent of hydrated lime, excess moisture, and impurities. Not more than 80 per cent of the actual lime present is combined with the chlorine, an excess of about 20 per cent being required to "stabilize" the bleach. When this bleach is received by the consumer it must be dissolved and made into clear solution for use. Such bleach solutions usually contain from 21 to 42 grams of available chlorine per liter, 21 grams equal one-half pound of 35 per cent bleach per gallon.

Let us take a typical solution containing in its finished state about 0.8 pound of 35 per cent bleach per gallon, equal to 33.6 grams of available chlorine per liter. Assuming that we have two tanks each 10 feet deep and 10 feet square equipped with agitators, these tanks will have a capacity of 1000 cubic feet, or 7500 gallons, each and can be operated on the counter-wash system. A drum of bleach will weigh about 750 pounds. One drum will therefore correspond to 0.1 pound of bleach per gallon. If we add six drums of bleach at about 25° C. (77° F.), mix this bleach for about 15 minutes, and allow it to settle, we will find that with a good quality of bleach we have at the end of 2 hours 30.5 per cent of sludge, 3 hours 21.6, 4 hours 19, 5 hours 17, 10 hours 13 per cent, or 1.3 feet of actual sludge. If we mixed this bleach with colder water or if it was made with lime which did not settle so well, the volumes of sludge over this same period of time would be materially increased. The same would be equally true, of course, if we added more bleaching powder. With the same quality of bleach and the same amount added but with a difference of mixing it at 15° C. (59° F.) we would have at the end of 2 hours 47 per cent of sludge, 3 hours 35.75, 4 hours 29, 5 hours 22.25, and 10 hours 18.75 per cent of sludge. This is the actual sludge in the tank. In addition to this, in decanting the clear liquor, there is always left a certain amount above the sludge, 4 inches equal to 3.3 per cent on a 10-foot tank, which must be added to the above sludges. We would

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[1] Presented under the title "Importance of the Proper Lime in the Use of Liquid Chlorine for Bleaching and Sterilization" as a part of the Lime Symposium before the Division of Industrial and Engineering Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

thus have at the end of 5 hours about 20 per cent residue left in one case and about 28.5 per cent in the other.

If we were so operating our tanks as to make one batch every 24 hours in each of the tanks giving two counter-washings, we would have a settling time of 5$^1/_4$ hours for the strong liquor that is used for storage, 4$^1/_2$ hours for the first wash which is returned as a make-up to mix with the bleaching powder, and 6 hours for the second wash which is returned to mix with the sludge obtained from the first strong liquor, or an available average of about 5 hours' settling time. Counter-washing in this way, the amount lost in the sludge is, of course, proportional to the residual sludge. A 2 per cent loss would correspond to about 23 per cent of sludge and a 4 per cent loss to about 28 per cent of sludge. It will thus be seen that the amount of loss is practically doubled by the difference between these two typical settlings, while increasing the sludge to 35 per cent would mean a 10 per cent loss. It will be seen, therefore, that in the manufacture of bleach it is extremely important to the consumer that the lime used should have excellent settling qualities, also that it should be mixed with water at a proper temperature to bring out the true value of the settling quality.

Another word of caution is that excessive agitation of the bleaching powder produces poor settling, all other conditions being equal. The mixing of bleach by circulation through a centrifugal pump is injurious to the settling of that bleach.

Preparation of Liquid Bleach Solution from Liquid Chlorine

Turning now to the preparation of liquid bleach solutions from liquid chlorine in the paper mill, we find that the same general rules will apply—that if chlorine is added to an agitated tank containing milk of lime it will be absorbed and produce a solution practically identical with that obtained from bleaching powder. As the addition of chlorine to lime evolved heat, we will have a temperature rise of about 1° C. for each 3 grams of chlorine added per liter or 0.6° F. (0.3° C.) per gram; consequently, if we are preparing a solution containing 30 grams per liter of added chlorine the temperature will be increased about 10° C. (18° F.). Starting with water at 15° C. (59° F.), we would end with a solution of 25° C. (77° F.). Starting with water in the summer time, which might be 25° C. (77° F.), we would end with a solution at 35° C. (95° F.). This is the upper limit but still safe for solutions of this strength and, of course, this added heat materially improves the settling if it is not carried to the point of decomposition.

In passing chlorine into a suspension of milk of lime, if we have a poor settling lime, we may obtain on the first chlorination as much sludge as would be obtained from an equal strength of bleaching powder settled at the same temperature. In that event only one batch could be made before washing the residual sludge with three counter-washes and the tankage capacity would not be increased over that obtainable with a good bleaching powder, in spite of the fact that only about 10 per cent of excessive lime was used to insure the stability of the solution instead of 20 per cent with bleach. If, on the other hand, we use a quality of lime which would have made good settling bleach, taking advantage of the temperature used in making the solution and of the fact that, while a 10 per cent excess of lime is required for the first batch, each successive batch will require only enough added lime to correspond to the chlorine added, we can build up at least four batches before there is any occasion to wash the sludge. If we do this and prepare a solution containing 33.6 grams of available chlorine, equal to 0.8 pound of 35 per cent bleach per gallon, we can operate our same two tanks on the basis of making four batches per tank every 36 hours with a settling period as follows: 3 hours for the first batch, 4 hours for the second, 4 hours for the third, and 5 hours for the fourth; 4$^1/_2$ hours settling the first wash and 5 hours settling the second wash. This will give us two and two-thirds batches per tank every 24 hours. It will also mean the loss in washing of 2 per cent of one batch on every four batches, or 0.5 per cent loss as against a 2 per cent loss with poor lime or good bleaching powder. It will also mean that the excess lime is carried along through four batches instead of with each individual batch; consequently, it will reduce the lime consumption very materially. It makes very little difference in the absolute capacity of the tanks, operating with a fair quality of bleach or with liquid chlorine and hydrated lime, whether we are making a solution that contains 20 grams of chlorine per liter or 30 grams of chlorine per liter, and operating on a good schedule about 600 pounds of bleach can be handled for 1000 gallons capacity in 24 hours or the equivalent of 1600 pounds of bleach as liquid chlorine and hydrated lime in the same tankage and in the same period of time. With an inferior lime the capacity of the tankage may be reduced to that of a good bleaching powder.

Characteristics of Suitable Lime

The next question is—what are the characteristics required for suitable lime? The chemical analysis alone will not tell the story. Assuming that we have a lime that contains not over 2 per cent of magnesia, not over 1 per cent of silica, and not over 0.5 per cent alumina, iron, etc., it may be suitable for either bleach or use in the preparation of liquid bleach. If to this we add the fact that, when hydrated to a dry hydrate containing about 25 per cent of water, it does not bulk dry over 200 cc. per 100 grams, we probably have a useful lime. This bulk test can be readily made by adding 60 cc. of water to 100 grams of powdered burned lime, hydrating, and noting the characteristics of the hydrate. A great many hydrates will bulk more than 250 cc. per 100 grams of hydrate.

This will probably point to undesirable features for the manufacture of a good settling bleaching powder but may not mean a poor lime for making liquid bleach. The writer has in mind the characteristics of two limes that act physically very much the same when hydrated, particularly as regards bulk. One of these is extremely pure chemically and when treated with chlorine in the form of liquid bleach gives a low sludge and a large number of runs are possible, in spite of the fact that the hydrate is rather bulky and settles none too well before fully chlorinating. Another lime with very similar hydrating characteristics but containing more magnesia produces an excessive amount of sludge and is not nearly so desirable. A lime that is very dense when hydrated apparently can stand a considerable amount of impurity without giving excessive sludges.

Test for Hydrated Lime

Hydrated lime for mill use in preparing liquid bleach can be tested in the laboratory as follows:

> There should be available a cylinder of liquid chlorine and a hood with a good draft. Mix 40 grams of hydrate with water to 1000 cc. in a 14-inch (36-cm.) liter cylinder. Pass in chlorine from the cylinder through a capillary tube and rubber connection, using the capillary to some extent as a stirring rod in the cylinder. By starting with a temperature of 20° C. chlorine bubbles will not be completely absorbed at the start; however, the rate of the addition of chlorine should be such that there is a temperature rise in the cylinder of about 1 degree every 3 minutes. At the end of a 10-degree temperature rise we will have approximately 30 grams of added chlorine and this can be added in little less than half an hour. After obtaining a 10-degree temperature rise, the solution should be allowed to settle and the amount of sludge noted at the end of 14 minutes. Fourteen minutes' set-

tling in a 14-inch cylinder would correspond to 2 hours' settling in a 10-foot (3-meter) tank the temperature of which would approximate 30° C. We should now be able to pour off more than 800 cc. of clear solution and should, therefore, leave 200 cc. of sludge and solution. If we now add 30 grams of hydrate and again bring up the solution to 1000 cc. and a temperature of 20° C., we can add somewhere between 24 and 27 grams of chlorine without overchlorination.

Assuming that we add 24 grams of chlorine, meaning a temperature rise of 8 degrees, we can again repeat our settling test and again draw off 200 cc. of clear solution, which can be added to the first lot and again make up our solution by the addition of another 30 grams of hydrate. This will give a third batch and into this third batch we can pass chlorine to the point where there is only a slight excess of lime, being careful not to overchlorinate. If we again allow this to settle and note the amount of sludge at the end of 14 minutes, we will have, if the operation has been properly carried out, sufficient data to valuate the hydrate fairly. We will have used 100 grams of hydrate and this should have absorbed a total of about 85 grams of chlorine; hence the added temperature rise should have amounted to about a total of 28 degrees. Anything more than 85 grams of chlorine absorbed would indicate an exceptionally good lime. The most important characteristic, however, would be the amount of sludge at this time. A very good lime would give about 20 per cent of actual sludge where 85 grams of chlorine have been passed into 100 grams of hydrate and the concentration kept between 30 and 40 grams of chlorine per liter. This will clearly point to the fact that four or more batches can be operated before the sludge is washed. On the other hand, if the amount of sludge so obtained is 40 per cent, we can hardly operate more than two batches without washing the sludge and then the loss would be a little above normal. The character of a bleach solution so prepared should be noted by determining the total and available chlorine in the solution; further than that, the solution should be set aside and, particularly the last run, allowed to stand on the sludge for a period of 24 hours to note whether there are any characteristics in the lime which tend to cause undue decomposition of the solution. The development of a pink color in these solutions due to traces of manganese does not of itself offer any objections.

While this method of testing the lime may be a little laborious, it is more enlightening than any other method that the writer has tried. In addition to the qualities adherent in the lime itself, there is a material difference in the density of the hydrate produced according to the way the lime is hydrated. As the method of hydration, however, depends so largely on the mechanical means used in hydrating it, there is only one statement that can be made—aim for the densest possible hydrate with a given quality of lime. The peculiar physical qualities in the limestone itself and in the burned lime which tend to make the ultimate impurities, including magnesia, settle well or poorly do not seem to come out in an ordinary chemical analysis, but are of utmost importance in the washing of sludges, and where a paper mill is pushed to capacity in producing bleach solutions a suitable lime is of utmost importance. It must be remembered that an excess of lime is always used and the more batches that can be run before throwing away this excess, the lower the lime-chlorine ratio will be kept. It should also be borne in mind that the chlorine used costs at least four times as much as the lime and that every sludge loss caused by lime is magnified by the value of the chlorine. A lime of moderate purity which absorbs a considerable amount of chlorine might be used in a plant that had much more than ample settling capacity and a long period of time for washing and give a fairly low lime-chlorine ratio without serious loss. The same lime could not be compared in value with a denser lime that absorbed slightly less chlorine for use in a plant working to capacity.

The Re-Use of Plaster of Paris Molds[1]

By Marie Farnsworth[2]

Nonmetallic Minerals Experiment Station, Bureau of Mines, New Brunswick, N. J.

Plaster of Paris molds deteriorate very rapidly on re-use, the tensile strength becoming much less on each successive recalcination. X-ray photographs of the molds show that the gypsum particles grow larger as the tensile strength becomes less. The addition of about $^1/_4$ per cent aluminum oxide is found to increase the tensile strength markedly and decrease the particle size. This has a possible application in die-casting factories, etc., where molds can only be used once and then thrown away.

Most of the gypsum mined in the United States is calcined and sold as plaster of Paris. The larger part of this calcined material is used in building as wall plaster, wall boards, gypsum blocks, etc., where its use is permanent and there is no need to re-use it. However, certain industries use large quantities of plaster for die-casting metals. When the hot metal is poured into the molds, water is driven off and the molds are pitted so as to be unfit for further use. The anhydrite formed by the action of the heat can be rehydrated to gypsum[3] and calcined again to plaster, but the plaster resulting from a second calcination is found to be unfit for further use, owing to a large decrease in tensile strength. So far no method for utilizing these old molds has been found and in addition to buying new plaster the company must pay to have the old molds hauled away. The desirability of eliminating this industrial waste led to a study of the possibility of utilizing old plaster molds.

While no means has been found for restoring used molds to their original tensile strength, a method has been found for greatly increasing the tensile strength over that of the untreated material.

Effect of Repeated Recalcinations on Plaster

The chemical process underlying the making of plaster molds is

$$\underset{\text{Gypsum}}{CaSO_4.2H_2O} + \text{heat} \longrightarrow \underset{\text{Plaster of Paris}}{CaSO_4.{}^1/_2H_2O} + \text{water} \longrightarrow \underset{\text{Gypsum or plaster of Paris molds}}{CaSO_4.2H_2O}$$

On recalcination the same process repeats itself, so there is no reason from a chemical standpoint why the tensile strength should decrease so markedly. In order to find out just what happens on recalcination, the water of crystallization of both plaster and gypsum, the water-carrying capacity of the plaster (the amount of water necessary to make 100 grams of plaster of the right consistency), the setting time, and the tensile strength were tested for a series of five recalcinations. The plaster employed was a sample from Virginia which was taken from the ordinary commercial run before a retarder

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[1] Received November 17, 1926. Published by permission of the Director, U. S. Bureau of Mines.

[2] Present address, Washington Square College, New York University, New York, N. Y.

[3] Farnsworth, This Journal, 17, 967 (1925).

was added. The methods of testing were all the standard methods of the American Society for Testing Materials.

Methods of Testing

Combined Water—The combined water was tested by first drying the sample in an oven at 45° C. for 2 hours to drive off absorbed moisture. About one gram of the sample was then placed in a platinum crucible and dried at 215–230° C. to constant weight. The loss in weight divided by the weight of the sample gave the water of crystallization.

Consistency—For testing samples of different plasters, it was necessary that all be first brought to the same consistency, by the addition of the proper amount of water. This was done by means of a Southard viscometer. The apparatus consisted of a brass cylinder of 2-inch (5-cm.) bore with a circular disk flange flush with its upper end. The screw actuating the piston was $^5/_8$ inch (16 mm.) in outside diameter, $^1/_4$ (6 mm.) inch pitch, right-hand square threads $^1/_{16}$ (1.6 mm.) inch deep. The top of the brass disk flange was etched with concentric circles which varied in diameter from 6 cm. up to 28 cm. by increments of 2 cm. When in position for use the brass flange was maintained in a true horizontal position.

In using, the piston, cylinder walls, and top of the plate of the viscometer were carefully cleaned. Then by turning the crank the top of the piston was brought exactly flush with the top of the plate. The piston was then depressed by turning the crank ten times in the reverse direction. A mixture of at least 300 grams total of dry calcined gypsum and water was made by shaking the calcined gypsum into the water through a No. 8 mesh sieve and allowing it to soak 2 minutes. It was then stirred to an even fluidity for a time not exceeding 30 seconds. This mixture was immediately poured into the well in the center of the plate of the viscometer, filling the well just flush with the top of the plate. The crank at the bottom of the viscometer was then immediately turned ten turns at the rate of one turn per second. The upward motion of the piston caused the mixture to overflow into a circular pat and the average of the quadrant readings of the concentric lines on the top of the plate could be taken. A neat mortar mixture was of testing consistency, if, with this operation, it gave a circular pat averaging 9.7 cm. in diameter, and is expressed as the number of cubic centimeters of water required to be added to 100 grams of plaster. This is called the water-carrying capacity.

Time of Setting—Two hundred grams of the sample were mixed with enough water to make a paste of testing consistency. A rubber mold such as is used with a Vicat needle was filled with the paste and the time of set was determined by means of a Vicat needle. The needle was allowed to sink into the paste at frequent intervals. After each penetration the needle was wiped clean, and the paste moved slightly so that the needle did not strike the same spot twice. The set was determined complete when the needle no longer penetrated to the bottom of the paste. The minutes elapsed from the time when the sample was first added to the water to the time when the set was complete, was recorded as the time of set of the sample. In this, as in all the other tests, all dishes and utensils were absolutely clean, especially free from all traces of set gypsum which has a marked effect on time of set and other properties of plaster. Also, distilled water was used throughout as small traces of salts markedly affect the properties of plaster.

Tensile Strength—Five hundred grams of plaster were mixed to testing consistency and cast into a five-gang briquet mold of the shape and size used for testing portland cement. The briquet where broken had a cross section of 6.5 sq. cm. (1 sq. in.). Each briquet was not cast successively, but the containing vessel was moved back and forth over the molds while pouring continuously. The briquet was worked slightly with the point of a trowel to remove air bubbles and level off the briquets. When sufficiently hard, they were removed and stored at room temperature for at least 7 days. When the weight had become constant to within 0.1 per cent, the specimens were tested in a standard machine used for the determination of tensile strength. The tensile strength was determined as pounds per square inch.

A tabulation of the results is given in Table I.

Table I—Plaster Tests

Times Calcined	Moisture		Water-Carrying Capacity	Setting Time	Tensile Strength
	Before calcination	After calcination			
	Per cent	*Per cent*	*Cc. H_2O/100 g. plaster*	*Minutes*	*Lbs./sq. in.*
1	...	5.82	72.5	22	249.5
2	18.33	5.50	87.5	12	203.1
3	18.08	5.54	120	8.5	91.98
4	18.15	5.50	150	8	66.2
5	17.88	5.50	175	11	52.1

The material did not change much chemically, as shown by the practical constancy of the water of crystallization. Moreover, it has been definitely proved that the presence of anhydrite ($CaSO_4$ would be shown by a decrease in water of crystallization) does not lower the tensile strength unless in such large amount that it hinders the plaster from sticking together. Since the underlying cause does not seem to be chemical, it is natural to seek a physical explanation of the decrease in plasticity, and therefore an x-ray study of the new plaster and gypsum, and of plaster and gypsum after repeated calcinations, was undertaken.

X-Ray Methods

Since the difference in the original sample and the recalcined sample was probably one of particle size, the pictures taken were the ordinary monochromatic pinhole pictures. These pictures were taken on a multiple diffraction apparatus in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.[4] The tube employed was the usual Coolidge water-cooled molybdenum anode type operated at 15 milliamperes and 30,000 volts, R.M.S. The x-rays were restricted by means of two pinholes 1.5 mm. in diameter 4 inches apart in a brass cylinder with a lead end. Flat cassettes in which a calcium tungstate intensifying screen was mounted back of the film were used to record the patterns. Films $3^1/_4 \times 4$ inches (8.25×10.16 cm.) were used. The cassettes were automatically held perpendicular to the x-ray beam during exposure by means of easels locked in a T-slot guide at a distance of 5 cm. Two pins which fit into slots in the top of the easel permitted quick adjustment or removal of the cassette. Since the plaster was in powder form it was enclosed in gelatin capsules such as can be purchased in any drugstore. Since the gypsum was already in the form of a continuous solid it was employed in pieces about $^1/_{16}$ inch in thickness. These samples were mounted directly over the pinhole.

X-Ray Results

The pattern as thus recorded is circular in form; the diagram depending upon the substance being examined. With amorphous substances the pattern is a general blackening around the darker image of the central beam. With crystals concentric rings appear, diffuse or sharp according to whether the crystals are small or large. If the crystals become still larger, spots appear on the diagram. Pictures taken for

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[4] Clark, Brugman, and Aborn, *J. Optical Soc. Am.*, **12**, 379 (1925).

all the five plaster samples noted in Table I showed no differences. The five gypsum samples made from the plaster samples, however, showed a regular gradation in particle size, the crystals growing continuously larger (though not rapidly) with each successive calcination.

Figure 1 shows gypsum made from the plaster of Paris which had been calcined once and Figure 2 shows gypsum made from plaster of Paris which had been calcined five times. In Figure 1 there are a few large crystals (as shown by the darker spots on the film and lighter spots on the positive; the figures are positives) held together by crystals which are very small (shown by very slight ring formation and the general blackening of the film). Figure 2 shows less real large crystals (fewer spots) but larger crystals in general, as shown by the well-formed rings and less general blackening of the film. Since the $CaSO_4.{}^1/_2H_2O$ pictures showed no appreciable differences, it was assumed that the small amount of uncalcined gypsum invariably left in the plaster acted as centers of crystallization or catalytically to cause the crystals to grow larger and thus cause the molds to be less strong. This is verified by the fact that the presence of old gypsum in even a very small amount greatly impairs the quality of an otherwise excellent plaster.

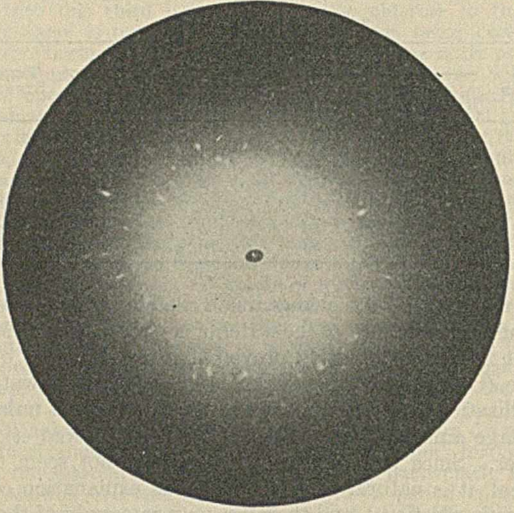

Figure 1—$CaSO_4.2H_2O$ Made from $CaSO_4.{}^1/_2H_2O$ Calcined Once

Prevention of Crystal Growth

From these x-ray results it was decided that if crystal growth could be prevented molds having much greater tensile strength would result. It has been found by Wyckoff and Crittenden[5] that potassium aluminate added to iron catalysts decreases the size of iron crystals and thus better catalysts result. Potassium aluminate made by heating together 3 parts of aluminum oxide and 1 part of potassium oxide at 350° C. for several hours was added to an old sample of plaster in the proportion of 3 grams of salt to 100 grams of plaster. It was found, however, that by the above process of making potassium aluminate some free alkali remained and this made the plaster so quick-setting that any good effect resulting from a prevention of crystal growth was completely masked. Aluminum oxide was next tried and this was found to work very well. Plaster was made by adding 3 per cent aluminum oxide to gypsum made from the plaster calcined five times in Table I and calcining a sixth time. As seen by Table I, the tensile strength of briquets made from plaster calcined five times was only 52.1 pounds per square inch, but that of the briquets after the addition of 3 per cent aluminum oxide and an additional calcination rose to 126 pounds per square inch. A sufficient amount of plaster was not available for additional tests, so tests were started with new samples of plaster.

Effect of Varying Percentages of Al_2O_3

A new sample of plaster of Paris was obtained from the same mine in Virginia and additional tests were carried on with it. Briquets made from this plaster were found to have a tensile strength of 316, setting time 19.5 minutes, and water-carrying capacity 50 cc. water per 100 grams plaster. A sufficiently large amount of this plaster was made up into molds, dried, and reground, and then calcined with the addition of varying proportions of aluminum oxide. Unless the oxide was added before the calcination, it had very little effect. These results are tabulated in Table II.

Table II—Effect of Varying Percentages of Al_2O_3

Property	Per Cent Al_2O_3 Added						
	None	3	2	1	$^1/_2$	$^1/_4$	$^1/_8$
Water-carrying capacity, cc. H_2O per 100 grams plaster	105	95	90	85	80	80	80
Setting time, minutes	8	8	8	11	13	18	16
Tensile strength, lbs. per sq. in.	76	105	143	139	153	183	160

This table shows that the most advantageous percentage of aluminum oxide is $^1/_4$ per cent, and therefore this percentage was used in all other experiments. There was no apparent reason why this sample should decrease in tensile strength so much more on recalcination than the first sample from the same locality. While this sample decreased in tensile strength from 316 to 76 pounds per square inch with one recalcination, with the first sample, the decrease in tensile strength was only from 249.5 to 203.1 pounds per square inch for one calcination, and the tensile strength had only decreased to 52.1 after a series of five recalcinations. Because plaster of Paris is so susceptible to small variables, it is difficult to draw any far-reaching conclusions. However, the addition of aluminum oxide to various samples caused roughly the same percentage increase in tensile strength, so it ought to be possible to re-use an ordinary mold at least once or twice by the simple addition of about $^1/_4$ per cent aluminum oxide before the second calcination.

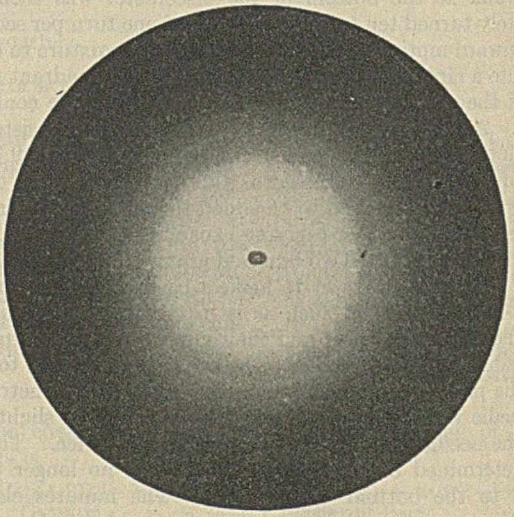

Figure 2—$CaSO_4.2H_2O$ Made from $CaSO_4.{}^1/_2H_2O$ Calcined Five Times

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[5] *J. Am. Chem. Soc.*, **47**, 2866 (1925).

Effect of Al_2O_3 on a Second Recalcination

The next test was to find whether the beneficial action of the aluminum oxide continued or whether it was necessary to add a new supply each time. The molds to which $^1/_4$ per cent aluminum oxide had been added were calcined for the third time, half were calcined without the addition of more oxide and half were calcined after the addition of $^1/_4$ per cent more oxide. These two samples were compared with two additional samples, one calcined for three times without the addition of anything and the second calcined with the addition of $^1/_4$ aluminum oxide on the third calcination. These samples are designated 1, 2, 3, and 4, respectively, and the results are given in Table III.

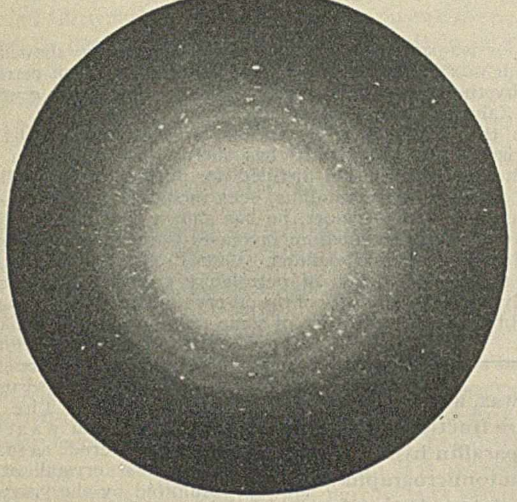

Figure 3—$CaSO_4.2H_2O$ Made from $CaSO_4.{}^1/_2H_2O$ Calcined Once (Second Sample)

Table III—Effect of Al_2O_3 on a Second Recalcination

Sample	Water-Carrying Capacity	Tensile Strength	Setting Time
	Cc. H_2O per 100 g. plaster	*Lbs. per sq. in.*	*Minutes*
1	120	25	6
2	90	70	10
3	128	30	8.5
4	90	75	10

It is seen by this table that the tensile strength of the plaster for this particular sample was very low on the third calcination, but here again the increase in tensile strength on the addition of aluminum oxide is approximately the same as on the second calcination.

This increase in tensile strength was also shown by means of x-ray photographs. Figure 3 is gypsum made from plaster calcined once (tensile strength 316 lbs. per sq. in.); Figure 4 is gypsum made from plaster calcined twice (tensile strength 76 lbs. per sq. in.); Figure 5 is gypsum made from plaster also calcined twice but with the addition of $^1/_4$ per cent aluminum oxide on the second calcination (tensile strength 183 lbs. per sq. in.). These photographs indicate that the particles in Figure 3 are the smallest, largest in Figure 4, and intermediate in Figure 5. This is the same result as was obtained by a direct measurement of the tensile strength.

Discussion of Results

It seems very likely that the deterioration of plaster of Paris on a second calcination results from the traces of uncalcined gypsum remaining. This view is supported by the fact that the addition of small traces of set gypsum to good plaster causes it to deteriorate very markedly. Traces of many foreign substances cause a deterioration of plaster and it is just as likely that traces of many substances would improve it. It has been found that the addition of as small an amount as $^1/_4$ per cent aluminum oxide will cause the tensile strength to increase about threefold, and no doubt other substances would be just as good, or even better, but a search was not made for such substances. X-ray photographs from new plaster and from re-used plaster show that the smaller the tensile strength the larger is the particle size. The addition of aluminum oxide causes a decrease in the particle size and increases the tensile strength. This has a possible application in the re-use of plaster molds where the decrease in tensile strength on recalcination is not too great.

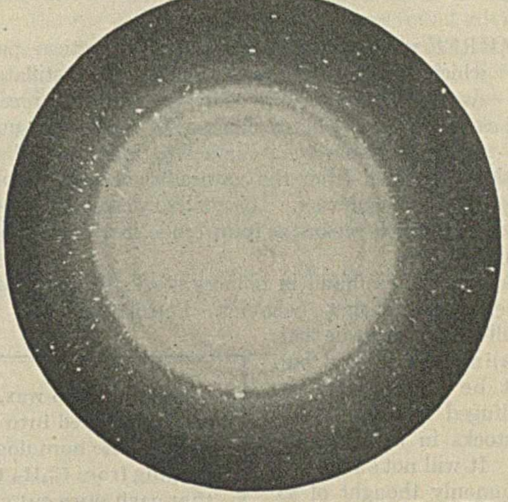

Figure 4—$CaSO_4.2H_2O$ Made from $CaSO_4.{}^1/_2H_2O$ Calcined Twice (Second Sample)

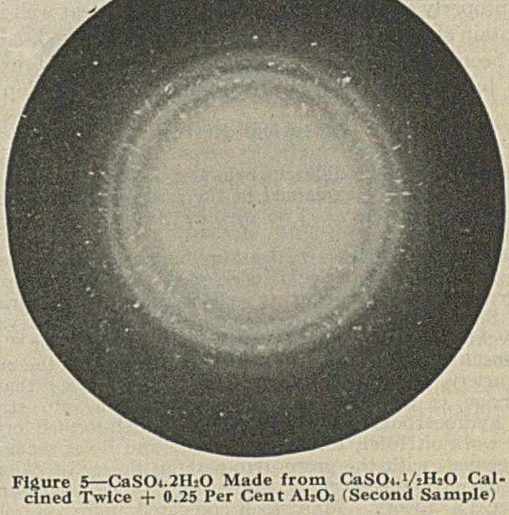

Figure 5—$CaSO_4.2H_2O$ Made from $CaSO_4.{}^1/_2H_2O$ Calcined Twice + 0.25 Per Cent Al_2O_3 (Second Sample)

Acknowledgment

The writer wishes to thank the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology for very kindly extending the complete facilities of the laboratory for carrying out this work and especially Professor G. L. Clark for his many helpful suggestions throughout the course of this work.

The Petroleum Waxes[1]

By C. C. Buchler and G. D. Graves

Standard Oil Company (Indiana), Casper, Wyo.

Paraffin, slop wax, petrolatum wax, and rod wax have been separated into a series of pure fractions belonging to the same homologous series of paraffin hydrocarbons ranging from $C_{18}H_{38}$ to $C_{43}H_{88}$. Photomicrographs show that each pure cut crystallizes in plates whether frozen from the molten state or from solution. In purification two impurities were removed—oil and an unknown mixture called "soft wax." To it is due the formation of needle crystals in impure waxes and the formation of vaselines when high melting waxes are mixed with oil.

THREE waxes are known in refinery practice—paraffin, which is pressed from the lighter wax distillates and sweated free from oil; slop wax, which is present in the heavier wax distillates commonly considered unpressable; and petrolatum wax, characteristic of residual stocks. Ceresin, as refined from the naturally occuring ozokerite, is a fourth petroleum wax. It is probably essentially the same as rod wax which separates from crude in the wells around the sucker rods.

These waxes as found in refinery stocks exhibit markedly different crystallizing behavior. Petrolatum wax forms such ill-defined crystals that it cannot be pressed but must be cold-settled or centrifuged from the cylinder stocks in which it occurs. It will not sweat and is commonly thought of as amorphous or sometimes microcrystalline.

The waxes present in distillate oils form crystals larger than those of petrolatum wax. The lighter wax distillates contain paraffin wax, which forms large crystals well suited for filter-pressing and sweating. The wax found in heavier distillates, on the contrary, does not crystallize so well and has been designated as slop wax. Since a redistillation under cracking conditions greatly improves the pressing qualities of these distillates, it has been assumed that the slop wax "cracks" to paraffin. A distillate which does not press properly or a slack wax which does not sweat well is said to contain slop wax and to be insufficiently cracked. It has even been suggested that paraffin itself does not exist in crude but results entirely from the cracking of slop wax.

Historical Review

The reasons for the different behavior of the petroleum waxes are no more clearly explained in the literature than they are understood by refiners. Two distinct theories have been advanced.

From his extensive investigations on petroleum waxes, including ozokerite, Zaloziecki[2] concluded that there is present in petroleum an amorphous as well as a crystalline variety of wax. Since distillates always contain the crystalline variety, Zaloziecki believes that the amorphous variety, or "proto-paraffins," when subjected to distillation crack into the crystalline variety, "pyro-paraffins." Zaloziecki suggests that this conversion is possibly one of branched-chain into straight-chain hydrocarbons which crystallize in well-formed crystals.

The work of Höfer, Engler and Bohm, and Boleg seems to be in agreement with the proto-pyro-paraffin theory of Zaloziecki. More recently the work of Marcusson[3] further substantiates Zaloziecki's theory. Marcusson prepared pure samples of ceresin wax and paraffin wax of the same melting point and found that the values of molecular weight, specific gravity, and index of refraction were all higher for the ceresin wax, and therefore concluded that ceresin consists of branched-chain hydrocarbons or iso-paraffins. In addition, Marcusson showed that ceresin wax is identical with the amorphous wax of petroleum, and by the slow distillation of ceresin he obtained a crystalline wax, Zaloziecki's pyro-paraffin.

On the other hand, by means of photomicrographs using polarized light, Gurwitsch[4] has shown that petroleum waxes which have been neither distilled nor purified by crystallization from a solvent are crystalline, even including the waxes present in vaseline. Furthermore, he has shown that as the viscosity of the crystallizing medium increases the wax crystals become smaller and less well-defined. Gurwitsch therefore concludes that the crystallization of petroleum waxes is dependent primarily upon the viscosity of the oil-crystallizing medium, and also possibly upon the presence of some unknown colloidal material. He does not agree with Zaloziecki that it is necessary to postulate the existence of proto-paraffin. The view that petroleum waxes are present in crude as such and that good crystallization is inhibited by the viscosity of the oil or the presence of some unknown colloidal substance is supported by the work of Rakusin,[5] Gordon,[6] Sachanen,[7] and Padgett, Hefley, and Henriksen.[8]

A number of investigators have shown that the hydrocarbons present in paraffin wax belong to the C_nH_{2n+2} homologous series of paraffin hydrocarbons. Mabery[9] obtained a series of fractions from commercial paraffin wax melting from 48° to 63° C. (118.4° to 145.5° F.). However, as Gurwitsch points out, the melting points are too low and the specific gravities too high, compared with the series of synthetic straight-chain hydrocarbons prepared by Krafft.[10] Francis, Watkins, and Wallington[11] have isolated seven pure fractions from Scottish shale wax which x-ray analysis[12] has shown to be straight-chain hydrocarbons. Dunstan and Kewley[13] and Carpenter[14] have isolated hydrocarbons from C_{21} to C_{34} from Burma crude.

Considerable work has been done on the crystalline nature of petroleum waxes. Gurwitsch[4] shows photomicrographs of both natural and artificial vaselines taken by polarized light to show their crystalline structure. Padgett, Hefley, and Henriksen[8] show pictures to the same effect. Distilled waxes show larger crystals which may be either of plate or needle form, this latter type being desirable in pressing distillates and sweating waxes.[15] The factors favoring needle formation are, however, unknown. Carpenter[14] noted that needles were obtained on crystallizing at about 39.4° C. (103° F.) from glacial acetic acid while plates were formed at a low temperature from ether without a change in the molecular weight of the wax which separated. He believes that a definite transition temperature exists at which one type changes to the other. Myrick[16] proposes the same idea, presenting photomicrographs of the two types. Padgett, Carpenter, and Myrick all note the formation of needles followed by plates from waxes containing considerable oil.

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[1] Received February 14, 1927. Presented before the Division of Petroleum Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Z. angew. Chem.*, **3**, 126, 261, 318 (1888).

[3] *Chem.-Ztg.*, **38**, 73 (1914); **39**, 578, 613 (1915).

[4] "Wissenschaftliche Grundlagen der Erdölverarbeitung," pp. 16 and 218, Julius Springer, Berlin, 1924.

[5] *J. Russ. Phys.-Chem. Soc.*, **46**, 1544 (1914).

[6] *J. Soc. Chem. Ind.*, **42**, 405T (1923).

[7] *Petroleum Z.*, **22**, 484 (1926).

[8] THIS JOURNAL, **18**, 832 (1926).

[9] *Am. Chem. J.*, **33**, 251 (1905).

[10] *Ber.*, **19**, 2223 (1886); **29**, 1323 (1896); **40**, 4783 (1907).

[11] *J. Chem. Soc. (London)*, **121**, 496, 1529, 2804 (1922).

[12] Piper, Brown, and Dyment, *Ibid.*, **127**, 2194 (1925).

[13] *J. Inst. Petroleum Tech.*, **10**, 503, 511 (1924).

[14] *Ibid.*, **12**, 288 (1926).

[15] Phyala, *7th Intern. Cong. Applied Chem.*, *Pet.* **4**, 1392.

[16] Unpublished report from Whiting Laboratory, Standard Oil Company (Indiana), February, 1918.

Purpose of This Investigation

Obviously, neither the observations of the refiner nor the published information are adequate to explain the differing behavior of the petroleum waxes, important as it is to the processes of pressing, sweating, cold-settling, and centrifuging. These are still the conflicting hypotheses of Zaloziecki and Gurwitsch. For this reason an investigation was directed to determine, first, whether all petroleum waxes belong to the same homologous series of hydrocarbons, and second, the correct explanation of the difference in crystalline form noted by all investigators working with petroleum waxes.

EXPERIMENTAL

Such physical properties as melting or solidifying point, index of refraction, and density of members of a homologous series show a regular increase with increasing molecular weight.

It was therefore determined to isolate a series of pure fractions from paraffin, slop wax, petrolatum wax, and rod wax, and to plot the above-mentioned physical properties. The formation of smooth curves would prove the existence of a homologous series. Since the physical properties as determined give average values for mixtures, it is unnecessary to work with individual compounds, narrow cuts serving as well to prove the point.

Preparation of Materials

The following products furnished the source of raw materials: paraffin wax (slack wax) as removed by pressing wax distillate at −17.8° C. (0° F.); slop wax as present in heavy distillate from the coking process; petrolatum wax centrifuged from residual stocks at −17.8° C. (0° F.); and rod wax as collected from the sucker rods in the field. All represent fractions from Salt Creek, Wyo., crude.

Each wax was recrystallized from ethylene dichloride at 4.4° C. (40° F.) until a wax of constant melting point and index of refraction was obtained, which was used as a criterion of complete removal of accompanying oil. Usually three to four crystallizations were necessary.

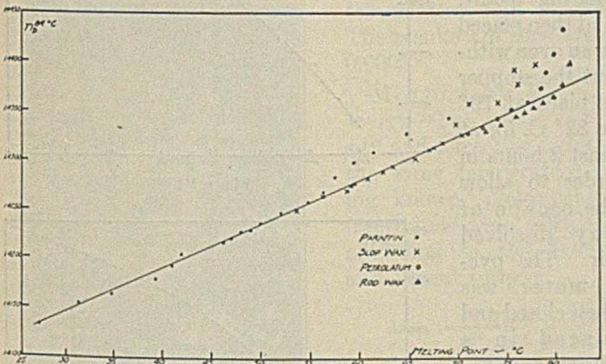

Plate I—Points on All Curves Designated as Shown Above

Among other solvents which are available for the purification of petroleum waxes from oil may be mentioned acetone and methylethyl ketone for the paraffin wax range, while n-butyl alcohol and alcohol-benzene mixtures serve for slop and petrolatum waxes. However, ethylene dichloride is far superior, in that it is miscible in all proportions with oil, which thereby eliminates any possibility of fractionation of the oil during crystallization with resultant contamination of the recrystallized wax. Furthermore, readily filterable crystals are always obtained even from petrolatum wax. The oil-free wax was decolorized either with fuller's earth or decolorizing carbon.

The resulting oil-free wax was then subjected to very careful vacuum fractionation under a pressure of less than 1 mm. of mercury. The flask, which was internally electrically heated, was a modified Claissen provided with a fractionating column of the Skinner type about 25 cm. in length. For the higher boiling waxes it was found advantageous to lag the fractionating column with heavy asbestos rope in order to eliminate excessive refluxing. For the lower boiling waxes a receiver consisting of two bulbs with a stopcock sealed between was found most convenient. The side arm of the distillation flask entered the upper bulb, which received one fraction, while the previous one was drawn off from the bottom bulb. The bottom bulb was then exhausted by a second vacuum pump before being connected to the system. In this way fractions could be obtained without interrupting the distillation. For the higher boiling waxes considerable difficulty was experienced in holding a high vacuum owing to leaking around the stopcocks, which had to be kept above the melting point of the wax. It was therefore necessary to use a receiver which consisted of a number of elongated bulbs with constrictions between them. The condensate flowed to the bottom bulb, and as soon as this bulb was filled a jet of air was at once directed on the constriction and the wax frozen, this operation being repeated as each bulb became full. At the end of the distillation the bulbs were cut apart at the constrictions and the fractions melted out. After each distillation a combination of the various fractions and the residue in the flask in aliquot proportions was made, and a determination of the melting point and index of refraction was always found to be identical with that of the charge to the flask. The fact that the melting point and the index of refraction remained unchanged eliminated any possibility that either decomposition or rearrangement of any of the components had taken place during the distillation.

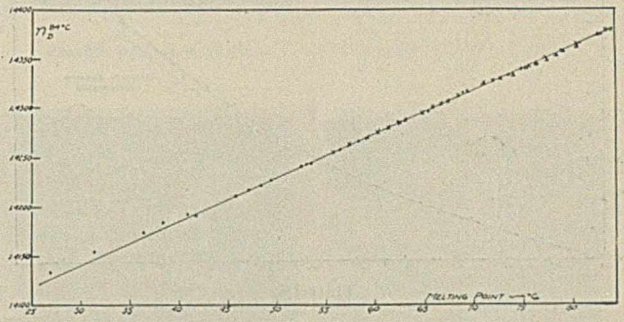

Plate II

By this means each of the four waxes was resolved into a series of oil-free fractions, whose melting points and indices of refraction are given in Table I. When these values were plotted (Plate I) it was immediately evident that, although the lower fractions of each series fell approximately on a straight line, the higher fractions invariably fell sharply above, indicating the presence of some unknown impurity. In attempting to purify further the higher fractions, it developed that a hot crystallization at 35–45° C. from ethylene dichloride removed a very small amount of waxy impurity, called hereafter "soft wax." The curve of index of refraction versus melting point for fractions so purified was a straight line a little below that shown on Plate I (see Plate II). Each fraction was then hot-crystallized from ethylene dichloride until further hot crystallization served merely to move the fraction up the curve owing to the removal of some of the more soluble low-melting com-

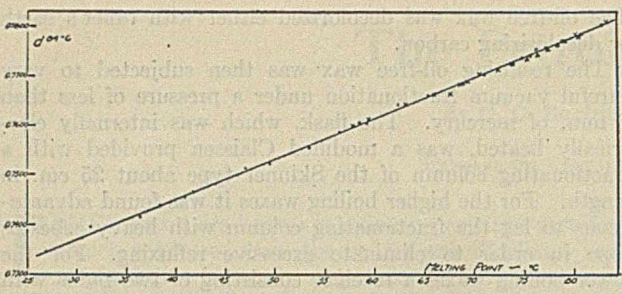

Plate III

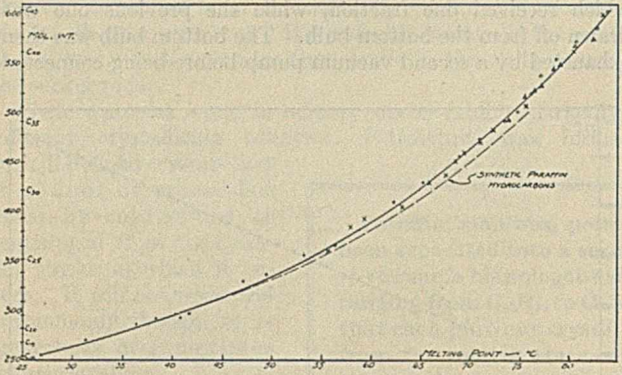

Plate IV

ponents. Even further hot crystallizations at higher temperatures never caused the values of the melting point or index of refraction to move off the curve. In this way a series of fractions was obtained varying in melting point from 41.7° to 83.9° C. (107° to 183° F.). Considerable difficulty was experienced in completely purifying the low-melting fractions ranging from 26.7 to 41.7° C. (80° to 107° F.), owing probably to the converging solubilities of the pure wax and the "soft wax."

Table I—Melting Points and Indices of Refraction of Incompletely Purified Petroleum Waxes

Melting Point ° F.	Melting Point ° C.	n_D^{84}	Melting Point ° F.	Melting Point ° C.	n_D^{84}
	PARAFFIN WAX			SLOP WAX	
80.5	27.0	1.4133	128.5	53.6	1.4250
88.5	31.4	1.4155	133.5	56.4	1.4264
94.7	34.8	1.4165	137.5	58.6	1.4270
101.0	39.3	1.4184	138.5	59.1	1.4275
105.2	41.0	1.4194	139.2	59.5	1.4277
107.7	42.0	1.4201	141.5	60.8	1.4281
109.7	43.2	1.4205	144.2	62.3	1.4289
115.2	46.2	1.4218	146.0	63.3	1.4295
116.7	47.0	1.4222	147.2	64.0	1.4295
120.0	49.0	1.4230	149.5	65.3	1.4302
122.0	50.0	1.4236	152.5	67.0	1.4311
125.0	51.7	1.4243	153.5	67.5	1.4313
125.7	52.0	1.4247	155.2	68.4	1.4318
130.5	54.7	1.4258	157.5	69.7	1.4337
133.5	56.4	1.4268	158.5	70.3	1.4325
135.5	57.5	1.4284	161.7	71.1	1.4358
139.0	59.4	1.4299	165.2	74.0	1.4359
142.5	61.4	1.4307	167.5	75.3	1.4392
148.5	64.7	1.4328	168.7	76.0	1.4377
156.0	69.0	1.4343	172.2	77.9	1.4399
	PETROLATUM WAX			ROD WAX	
159.7	71.0	1.4327	163.0	72.8	1.4330
162.5	72.5	1.4334	165.5	74.2	1.4336
165.2	74.0	1.4342	168.5	75.9	1.4345
167.7	75.4	1.4351	170.0	76.7	1.4349
170.5	77.0	1.4359	171.7	77.6	1.4354
173.0	78.3	1.4372	173.5	78.6	1.4359
174.0	78.9	1.4390	175.7	79.8	1.4365
175.5	79.7	1.4407	177.0	80.6	1.4377
176.5	80.3	1.4434	178.5	81.4	1.4399

Determination of Physical Constants[17]

Solidifying Point (Melting Point)—A test tube about 1.5 cm. in diameter fitted with a cork carrying a thermometer graduated in half degrees Fahrenheit was filled with melted wax to a depth of 3.5 cm. The thermometer was so adjusted that the bulb was completely surrounded by wax. The test tube was then enclosed in a double air jacket so as to insure slow and uniform cooling. The thermometer was read every 30 seconds and the first three constant consecutive readings were taken as the melting point of the sample. The determination is accurate to 0.5° F. (0.2° C.).

Refractive Index—The indices of refraction were determined on the usual Abbé type refractometer with water-jacketed prisms and provided with a special thermometer reading to 100° C. All determinations were made at 84° C. (183.2° F.).

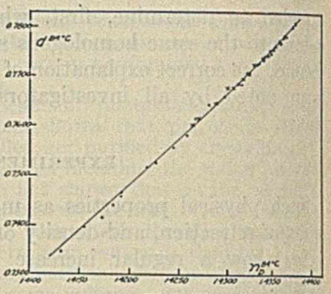

Plate V

Molecular Weight—The molecular weight was determined by the cryoscopic method using the usual standard Beckman apparatus. The solvent used was *p*-dichlorobenzene, which had been previously purified by distillation. No correction was applied either for the amount of solvent which sublimed to the cold part of the freezing point tube or for the amount of undercooling, since the constant *K* of the solvent was determined under exactly the same conditions as prevailed in the molecular weight determinations. Triphenylmethane, which had been very carefully purified, was used as the solute in the determination of the constant. The results are accurate within 3 per cent.

Density—The densities were determined in a 5-cc. Gay-Lussac specific gravity bottle previously standardized with water at 25° C. (77° F.), from which the volume at 84° C. (183.2° F.) was calculated. The pycnometer was filled with the melted wax just above its melting point, and then placed in an oven without the stopper in place at 79° to 82° C. for at least 2 hours in order to allow the escape of any dissolved air. The pycnometer was then closed and placed in a thermostatically controlled water bath, which was maintained at 84° ± 0.3° C. After the pycnometer had remained in the constant temperature bath for at least 1 hour, excess wax was removed, and the bottle immediately immersed in ice water in order to cause the wax to shrink away from the sides of the pycnometer and thus minimize breaking due to the wax adhering to the walls. The pycnometer was allowed sufficient time to come to room

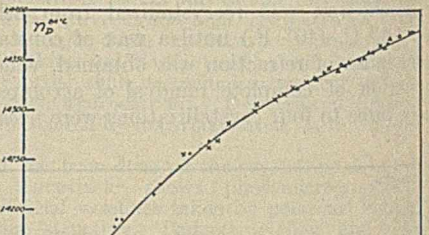

Plate VI

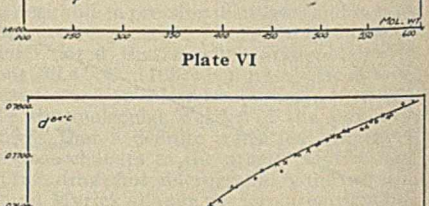

Plate VII

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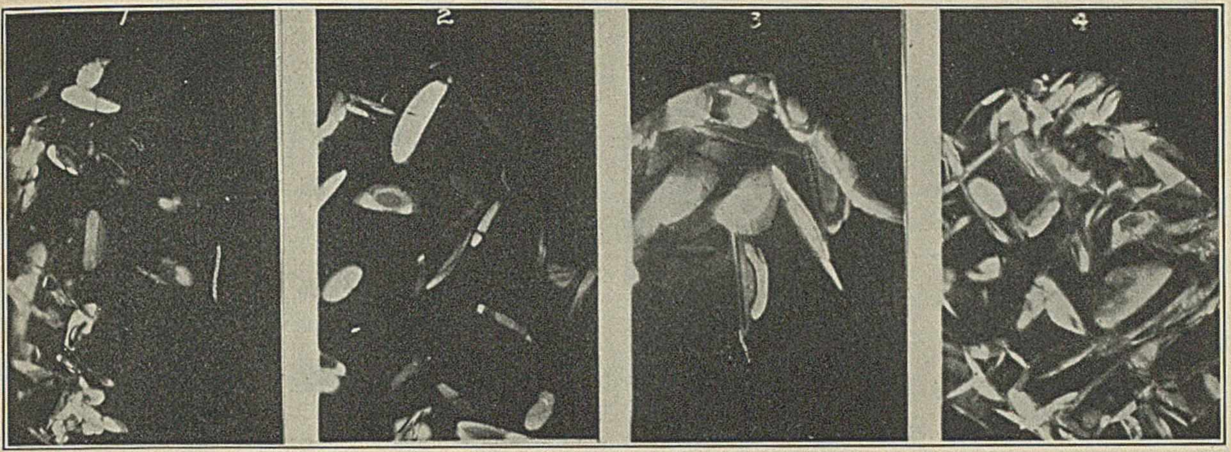
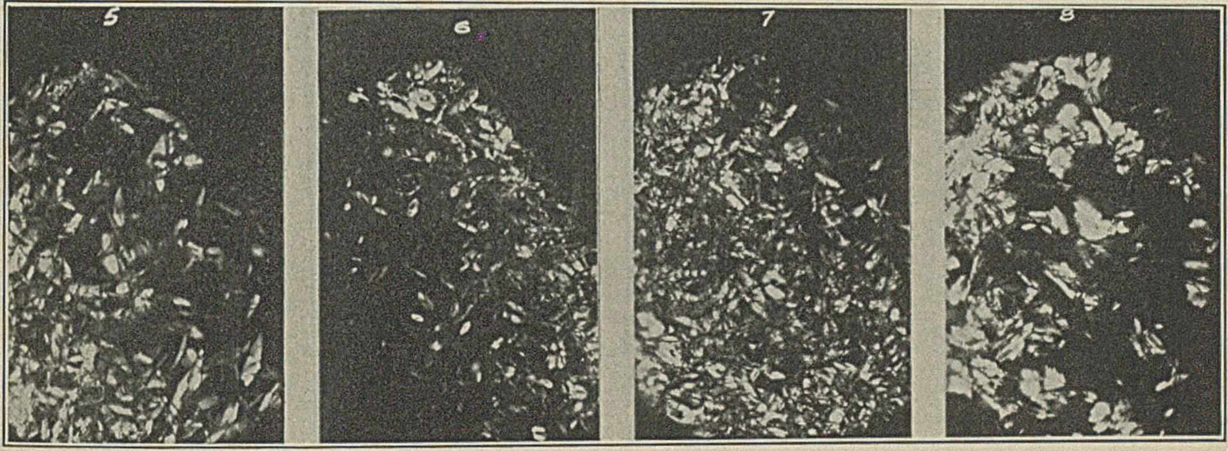
[17] The authors are indebted to A. H. Boenau and R. W. Boyd for the determinations of certain of the physical constants, also to G. M. Whitney for several combustion analyses.



Paraffin wax, m. p. 27.0° C. Paraffin wax, m. p. 38.3° C. Paraffin wax, m. p. 41.7° C. Paraffin wax, m. p. 49.4° C.



Paraffin wax, m. p. 68.9° C. Slop wax, m. p. 59.4° C. Slop wax, m. p. 83.3° C. Rod wax, m. p. 82.5° C.

Fractions from Purified Waxes

Petrolatum wax, m. p. 83.8° C.

temperature and weighed. The results are accurate to 0.0005.

MOLECULAR REFRACTIVITY—The values of density and refractive index at the same temperature being known, molecular refractivities were calculated according to the Lorentz and Lorenz formula,

$$Mr_L = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Theoretical values were calculated taking values for carbon of 2.501 and for hydrogen of 1.051.

Photomicrographs

In order to characterize further the various crude and purified waxes a series of photomicrographs was obtained. They were taken using a Bausch & Lomb microscope fitted with a Leitz "Macca" camera. The waxes were crystallized in a hanging drop, the slide being held in a warm stage at such a temperature that the crystals formed very slowly. Magnifications are × 80. Both ordinary and polarized light were used, the figures described herein being taken with polarized light.

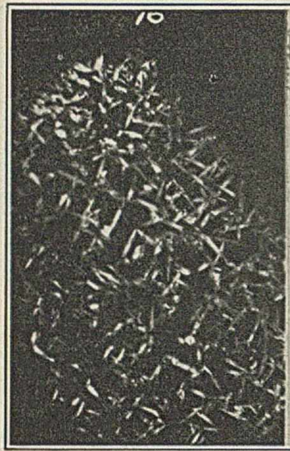
DISCUSSION OF RESULTS

The Existence of a Homologous Series

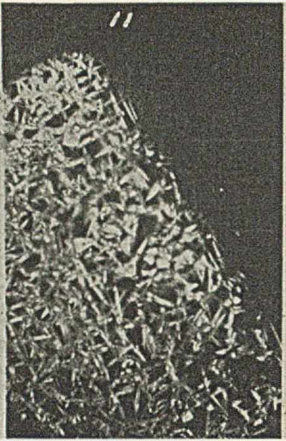
The physical constants given in Table II and shown graphically on Plates II to VII make it evident at once that, regardless of the source of raw material, whether paraffin, slop, petrolatum, or rod wax, the physical constants of the purified fractions fall on the same smooth curves. The photographs (Figures 1 to 9) show that all have the same crystalline form. Thus the fact is established that all belong to the same homologous series. Otherwise it would be inconceivable that all would fall upon the same smooth curves, overlapping from one series to the next.

Numerous previous investigators have shown that paraffin wax belongs to the C_nH_{2n+2} homologous series; it therefore follows from the above results that slop, petrolatum, and rod waxes (the latter corresponding to ceresin wax) must likewise belong to this same homologous series. Combustion analyses given in Table II further support this view. The close agreement between the theoretical and calculated values of molecular refractivity also class all the hydrocarbons as paraffins.

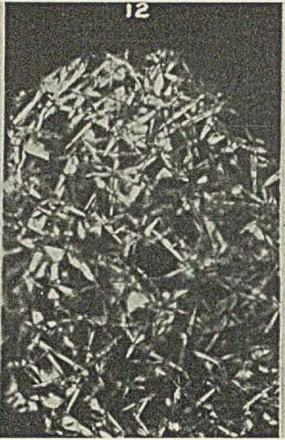
It should be further noted that, notwithstanding the fact



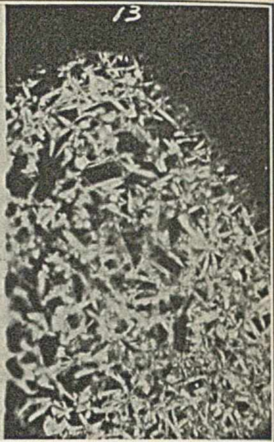
Paraffin wax containing oil. Needles



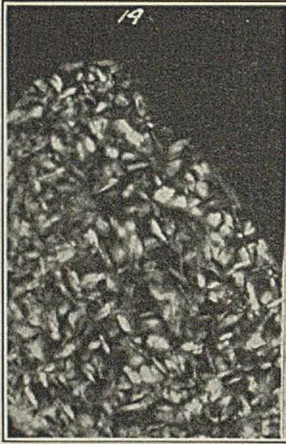
Slop wax containing oil. Needles



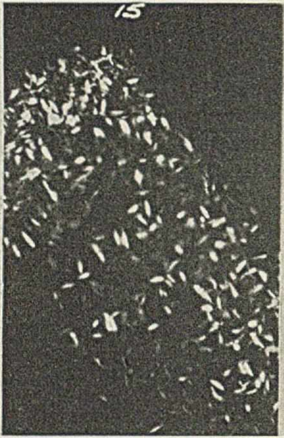
Paraffin wax free from oil. Needles



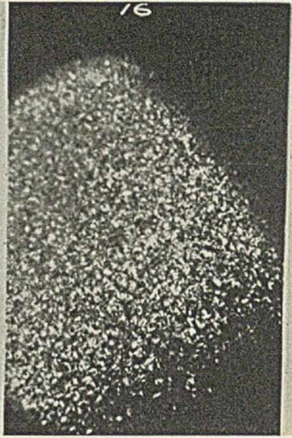
Slop wax free from oil. Needles



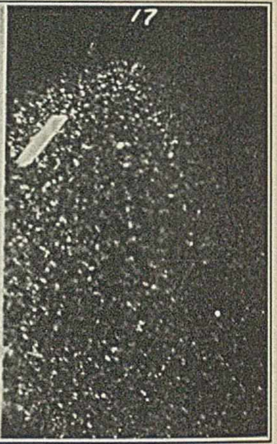
Mixture of 27.0° and 68.9° C. Fractions. Plates



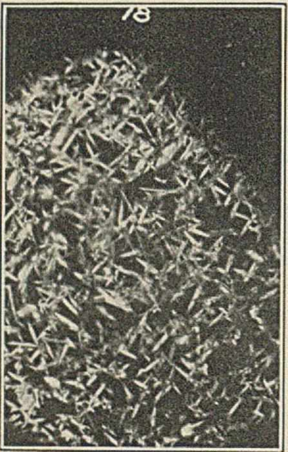
Mixture of 59.4° and 83.3° C. Slop fractions. Plates



Petrolatum wax containing oil



Petrolatum wax free from oil



Concentrate of "soft wax" as removed by hot crystallization of paraffin wax. Needles

that the purified fractions are not individual homologs but mixtures, they are in very close agreement in melting point for a corresponding molecular weight with the synthetic normal paraffin hydrocarbons prepared by Krafft. This is illustrated on Plate IV, where the broken line indicates Krafft's synthetic hydrocarbons.

It would therefore seem that not only is the conclusion that all petroleum waxes belong to the C_nH_{2n+2} homologous series justifiable but, furthermore, that the petroleum waxes are straight-chain hydrocarbons. This latter conclusion is further substantiated by the close agreement in melting point and molecular weight between the purified fractions as prepared in this paper and the pure fractions isolated from Scottish shale wax, which x-ray analysis has shown to be straight-chain hydrocarbons.

Crystalline Form of Petroleum Waxes

Figures 1 to 9 represent a number of the pure cuts of Table II, being perfectly characteristic of the entire number. The same type of plate crystal is formed by all, the size decreasing with increasing molecular weight.

This plate crystal is in distinct contrast to the needle type of crystal hitherto considered characteristic of paraffin waxes. Such needle crystals are shown in Figures 10 to 13, the first two being paraffin and slop waxes containing oil, and the second two, oil-free waxes prepared from them. The needle structure cannot therefore be attributed to the oil. Nor is this effect due to the wide spread of molecular weights contained in the sweated waxes, since Figures 14 and 15 show that mixtures of the high and low pure cuts of the paraffin and slop series still show plate formation.

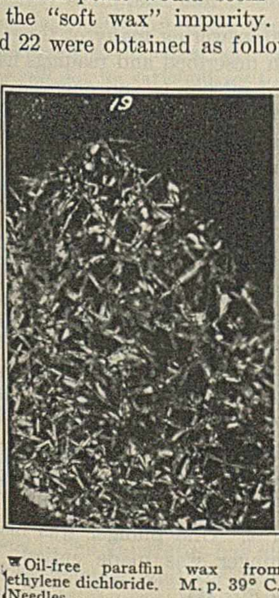
Petrolatum wax itself forms very small crystals. Figures 16 and 17 show a partially purified wax melting at 72.2° C. (162° F.) and an oil-free sample melting at 74.4° C. (166° F.).

Since the pure fractions of Table II differ from the above needle-forming waxes only in their freedom from the "soft wax" impurity, it seems clear that the needle structure is in some way dependent upon the presence of this material. Figure 18 bears out this idea, showing the needle structure of the material in which "soft wax" is concentrated as removed in hot crystallization from ethylene chloride. Figures 23 and 24 show needles and plates, respectively, which have formed very slowly. The crystal form is clearly shown.

Table II—Data on Purified Petroleum Waxes

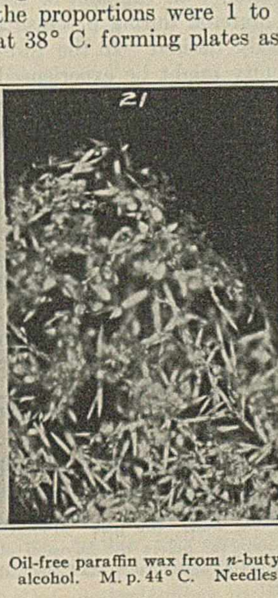
Melting Point °F.	Melting Point °C.	n_D^{84}	d^{84}	Observed Mol. wt.	Observed Mr_L	Observed % C	Observed % H	Formula	Calculated Mol. wt.	Calculated % C	Calculated % H	Calculated Mr_L
						PARAFFIN WAX						
80.5	27.0	1.4133	0.7347	255	86.5	84.55	15.04	$C_{18}H_{38}$	254	85.04	14.96	86.9
88.5	31.4	1.4155	0.7397	271	92.0			$C_{19}H_{40}$	268			89.6
97.5	36.4	1.4173	0.7417	287	97.6			$C_{20}H_{42}$	282			94.1
101.0	38.3	1.4183	0.7440	292	99.1			$C_{21}H_{44}$	296			98.8
105.5	40.8	1.4191	0.7458	294	99.6	84.86	14.98	$C_{21}H_{44}$	296	85.10	14.90	98.8
107.0	41.7	1.4191	0.7466	298	100.8			$C_{21}H_{44}$	296			98.8
114.2	45.7	1.4210										
116.7	47.1	1.4217	0.7513	330	111.2	84.75	14.91	$C_{23}H_{48}$	324	85.18	14.82	107.9
118.7	48.2	1.4221										
121.0	49.4	1.4226	0.7526	337	113.5			$C_{24}H_{50}$	338			112.6
126.5	52.5	1.4240										
127.5	53.0	1.4242										
128.0	53.3	1.4244	0.7558	357	121.2	85.31	14.75	$C_{25}H_{52}$	352	85.21	14.79	117.2
131.5	55.3	1.4252										
133.5	56.4	1.4257	0.7580	367	123.9			$C_{26}H_{54}$	366			121.8
137.2	58.4	1.4266	0.7607									
138.5	59.1	1.4269	0.7609	385	129.9			$C_{27}H_{56}$	380			126.3
144.2	62.3	1.4285	0.7642	410	137.7			$C_{29}H_{60}$	408			135.5
149.5	65.3	1.4297	0.7660	430	144.7	85.22	14.74	$C_{31}H_{61}$	436	85.32	14.68	144.7
156.0	68.9	1.4315	0.7687	456	153.7			$C_{32}H_{66}$	450			149.3
						PETROLATUM WAX						
159.7	71.0	1.4323	0.7706	474	159.6			$C_{34}H_{70}$	478			159.6
164.5	73.6	1.4333	0.7727	492	164.4	85.45	14.78	$C_{35}H_{72}$	492	85.36	14.64	163.2
166.7	74.8	1.4339	0.7739	502	168.9			$C_{36}H_{74}$	506			169.9
169.2	76.2	1.4347	0.7753	520	174.9			$C_{37}H_{76}$	520			172.4
170.7	77.1	1.4351	0.7759	539	181.3			$C_{38}H_{78}$	534			177.0
173.7	78.8	1.4359	0.7771	555	186.7	85.13	14.62	$C_{39}H_{80}$	548	85.40	14.60	181.6
177.2	80.7	1.4366	0.7784	572	192.3			$C_{41}H_{84}$	576			190.8
181.2	82.9	1.4375	0.7803	586	194.9			$C_{42}H_{86}$	590			195.4
182.7	83.8	1.4378		603		85.54	14.47	$C_{43}H_{88}$	604	85.43	14.57	200.0
						SLOP WAX						
132.2	55.7	1.4255		360		84.87	14.83	$C_{26}H_{54}$	366	85.23	14.77	
136.2	57.9	1.4263	0.7600	385	129.7			$C_{27}H_{56}$	380			126.3
138.5	59.2	1.4270										
139.0	59.4	1.4270	0.7614	394	133.0			$C_{28}H_{58}$	394			130.9
140.5	60.3	1.4275										
142.5	61.4	1.4280										
144.5	62.5	1.4284										
145.5	63.1	1.4287	0.7644	405	136.5	85.18	14.81	$C_{29}H_{60}$	408	85.29	14.71	135.5
148.5	64.7	1.4294										
150.5	65.9	1.4300	0.7677	431	145.1	85.19	14.74	$C_{31}H_{64}$	436	85.32	14.68	144.7
152.0	66.7	1.4303										
153.5	67.5	1.4306	0.7677	437	147.5			$C_{31}H_{6}$	436			144.7
156.0	68.5	1.4312	0.7684	451	152.1			$C_{32}H_{66}$	450			149.3
157.0	69.4	1.4316	0.7695	460	155.0			$C_{33}H_{68}$	464			153.9
160.0	71.1	1.4323	0.7706	470	158.1			$C_{33}H_{68}$	464			153.9
161.5	72.0	1.4327										
162.2	72.3	1.4329	0.7715	483	162.7	85.22	14.65	$C_{34}H_{70}$	478	85.35	14.65	163.1
168.0	75.6	1.4342	0.7741	508	171.6			$C_{36}H_{74}$	506			167.7
176.5	80.3	1.4365	0.7785	563	189.2			$C_{40}H_{82}$	562			186.1
182.0	83.3	1.4379	0.7810	600	201.8	85.21	14.65	$C_{43}H_{88}$	604	85.43	14.57	199.9
						ROD WAX						
165.0	73.9	1.4334	0.7728	493	165.9			$C_{35}H_{72}$	492			163.2
167.5	75.3	1.4340	0.7739	516	173.6	85.40	14.55	$C_{37}H_{76}$	520	85.38	14.62	172.4
169.5	76.4	1.4345	0.7743	524	176.4			$C_{37}H_{76}$	520			172.4
171.0	77.2	1.4349	0.7757	527	177.2			$C_{38}H_{78}$	534			177.0
172.7	78.2	1.4353	0.7761	545	183.3	85.38	14.68	$C_{39}H_{80}$	548	85.40	14.60	181.6
174.2	79.0	1.4358	0.7771	550	185.0			$C_{39}H_{89}$	548			181.6
176.7	80.5	1.4363	0.7780	569	191.3			$C_{40}H_{82}$	562			186.2
180.5	82.5	1.4372		575		85.39	14.60	$C_{41}H_{84}$	576	85.41	14.59	190.8

As has been noted above, Myrick and Carpenter report an apparent transition temperature at which plate crystals change to needles. Since pure waxes form plates only, this transition point would seem to depend upon the presence of the "soft wax" impurity. Figures 19 and 20 with 21 and 22 were obtained as follows: The oil-free paraffin wax (Figure 12), which contains enough impurity to form needles, was dissolved in ethylene chloride in the proportions 3 to 2. This solution solidified at 39° C., forming the needles of Figure 19. More ethylene chloride was then added until the proportions were 1 to 1. The solution then solidified at 38° C. forming plates as shown in Figure 20. This pro-



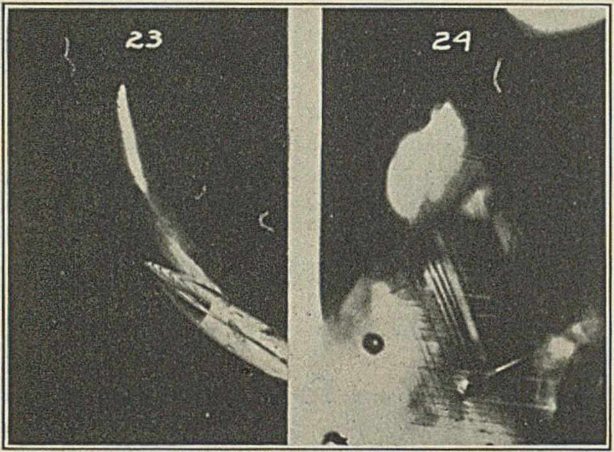
Oil-free paraffin wax from ethylene dichloride. M. p. 39° C. Needles

Wax of Figure 19 with more solvent. M. p. 38° C. Plates



Oil-free paraffin wax from *n*-butyl alcohol. M. p. 44° C. Needles

Wax of Figure 21 with more solvent. M. p. 42° C. Plates cedure was repeated using *n*-butyl alcohol, obtaining a solution solidifying at 44° C. forming needles (Figure 21) and one solidifying at 42° C. showing plates (Figure 22).



Well-grown needle crystal Well-grown plate crystal

The "transition temperature" here is *not* independent of the solvent and is tentatively explained as follows: For a solution to crystallize in needles a certain quantity of the "soft wax" must separate at the crystallizing temperature. This happens in concentrated solutions. In more dilute solutions, however, the "soft wax" is not present in sufficient quantity to separate at the crystallizing temperature and plates are formed. This gives an apparent transition temperature. Butyl alcohol is a poorer solvent for soft wax than ethylene chloride, so that this effect is noted at a higher temperature when it is used as the solvent. A further study of this phenomenon will be undertaken when the "soft wax" impurity has been better characterized.

Conclusions

The characteristic crystallization behavior of petrolatum, slop, and paraffin waxes can now be attributed, not to inherent differences in crystallizing medium as postulated by Gurwitsch (although this is significant in its effect on crystal size as shown by Padgett, *et al.*), nor to the proto-pyroparaffin hypothesis of Zaloziecki, but rather to the "soft wax" impurity which governs needle formation. A certain quantity is necessary to needle formation, while excessive amounts lead to an amorphous or microcrystalline appearance. Apparently this material is present in large amount in petrolatum, causing the formation of vaselines, a phenomenon hitherto unexplained. Slop wax contains a considerable amount, so that pressing and sweating are seriously hindered when it is present in wax distillates. Paraffin contains an amount too small to interfere with proper crystallization but sufficient to promote good needle formation so that pressing and sweating proceed smoothly.

The factors, then, which govern the type of crystallization shown by various refinery stocks are, first, the viscosity of the oil and the solubility and molecular weight of the wax; and second, of greater importance, the content of "soft wax" impurity.

Further work is now in progress towards isolation and identification of this material and a more quantitative study of its effect.

Some Further Applications of a Mobilometer[1]

By **H. A. Gardner** and **A. W. Van Heuckeroth**

Institute of Paint and Varnish Research, Washington, D. C.

MANUFACTURERS, having determined upon a satisfactory consistency for a certain product, naturally desire to reproduce this consistency on each batch. Early attempts in this direction rested with the skill of the foreman, who stirred a batch of material during processing until it assumed the apparent body desired. If the foreman left the factory, some difficulty might be experienced by other working men in attempting to reproduce such a body. As a result of this condition, a demand arose for a type of instrument to control consistency.

The first types of consistometers which came upon the market were of such a nature that the pressure could not be varied and only one point on a pressure-flow curve could be obtained. For work with plastic substances, there later came a demand for instruments in which the pressure could be varied so that a curve could be plotted for the product. Unfortunately, however, instruments of this type which covered the entire field of consistency, from products of low viscosity to those of great plasticity, were large, cumbersome, and expensive. An instrument adapted to factory control use should be of low cost, easily reproducible, simple in operation, easy to clean, constructed of durable material, and adaptable to variations in pressure over wide limits. It should also be capable of being used with opaque as well as transparent materials.

Description of Mobilometer

A simple type of apparatus answering many of these requirements has previously been described and readings have been given upon many types of oil paints and enamels and various types of pigmented nitrocellulose lacquers.[2]

This apparatus (Figure 1) consists of a brass cylinder 3.89 cm. in diameter and 22.85 cm. in length. This cylinder has a removable bottom, for cleaning purposes, which screws into the baseboard, making the cylinder absolutely firm and rigid over its entire length. A mark is placed inside the cylinder 2 cm. from the top. When filling the cylinder the paint is always brought up to this mark. When the cylinder is filled, the time of fall of a piston is determined in seconds with a stop-watch. The plungers are 0.635 cm. in diameter and 50.8 cm. long. On the top end there is a small platform on which the weights are placed. On the lower end is placed a disk 0.08 cm. thick and 3.81 cm. in diameter. This allows a clearance of 0.04 cm. all around the plunger when it is inserted in the cylinder. One of these plungers was made completely of brass, having a bottom end with 51 holes 0.153 cm. in diameter drilled in it. One plunger was made without holes. The other plunger was made entirely of

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[1] Received March 11, 1927. Presented under the title "Mobility Tests on Paint, Varnish, and Lacquer Products" before the Division of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Am. Paint Varnish Manuf. Assoc. Circ.* **265.**

aluminum, the bottom end having 51 holes in it. The weight of the brass plunger, consisting of a brass rod, a perforated brass disk at the bottom, and a brass weight pan at the top was 75 grams ± 1 gram, and the weight of the aluminum plunger was 33 grams. Each plunger is prevented from striking the bottom of the cylinder by a tip 0.85 cm. long. The plunger therefore falls through 20 cm. of material. A bracket holds the upper end of the plunger rod so that it travels in a true line to the bottom, practically without friction.

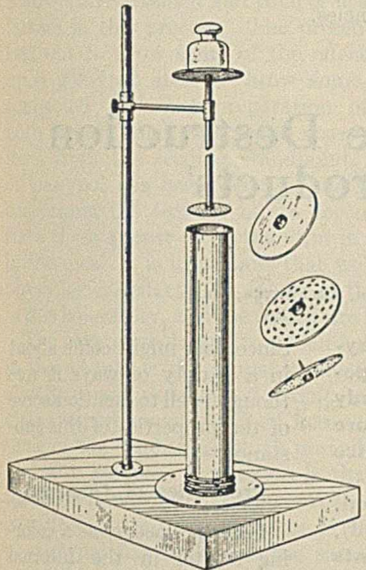

Figure 1—Gardner-Parks Mobilometer

Method of Use

Temperature must be taken into consideration just as with instruments for the measurement of viscosity. Provided the room temperature is approximately 20° C. (68° F.), the paint or other products used will not change in temperature in the short time required to make the tests. It is therefore suggested that measurements be made at this temperature. The cylinder is filled with material to the mark. The plunger to be used is inserted and forced to the bottom. It is then raised to the point where the bottom end is flush with the upper surface of the paint. A weight is applied and the time in seconds for the plunger to fall to the bottom is determined with a stop-watch. When the tip at the bottom of the plunger disk touches the bottom of the cylinder, an audible click may be heard. This procedure is repeated with a number of different weights and the points plotted on a curve.

Applications in Paint and Varnish Industry

This apparatus has been found useful in controlling the consistency of dipping paints and japans, where evaporation of volatile constituents may cause the products to increase in consistency so that they become difficult to use. A hydrometer would not be satisfactory for such work as the thinning material might be of the same specific gravity as the coating product, and the addition of any quantity of such thinners would not change the density. The apparatus has also proved useful in gaging the consistency of spraying paints, such as those used on railroads, to determine if proper amounts of thinner have been added by the painters. It has also been found of interest in the linoleum industry to gage the consistency of printing paints, which are generally thinned with substantial quantities of volatile petroleum products. These paints, which are used on a printing machine, must be kept at a definite body if satisfactory results are to be obtained. The apparatus has also been useful in gaging the apparent consistency of pigmented lacquers. Heretofore the method used for gaging the consistency of clear lacquers was to determine the number of seconds required for a steel ball to fall through a column of the product. Obviously such a method could not be applied to colored opaque lacquers. The apparatus has also been used in determining the consistency of and the possible relation of consistency to the flowing power of brushing enamels, which have been produced with different grades of the same pigment ground in the same oil or with the same pigment ground in different grades of oils and varnishes.

Tests of Reproducibility

Some doubt has been expressed as to the ability of a mechanic to reproduce the perforated disk plunger used in the mobilometer. It was thought that the openings in the apparatus would be very difficult to reproduce. In this connection, however, some coöperative committee work is now being carried on by members of a subcommittee of Committee D-1 of the American Society for Testing Materials to determine the value of the mobilometer in various plants upon the same type of products. The mobilometers used in these coöperative tests were made by two different mechanics.

Table I—Readings with Gardner—Parks Mobilometer

Viscous Products	Seconds	Plastic Products	Seconds
A Lubricating oil	1.4	Flat white paint	5.7
J Lubricating oil	5.4	Flat white paint	9.4
M Lubricating oil	6.6	Exterior gloss	21
Heavy cylinder oil	22	Exterior gloss	22

In Table I are given a few readings obtained with the Gardner-Parks mobilometer when run with a brass plunger, a perforated brass disk attached and a weight pan, these having a combined weight of 74 grams. No additional load was applied to the weight pan. Constant temperature was maintained throughout.

Table II—Mobilometer Tests on Materials Other than Paints and Varnishes

Tomato Catsup

Load Grams	100% Catsup Seconds	95% Catsup 5% Water Seconds	90% Catsup 10% Water Seconds	85% Catsup 15% Water Seconds
100	35.0	14.8	9.0	6.3
150	17.2	7.8	5.3	3.8
200	11.0	6.0	4.2	3.0
300	6.0	4.2	2.5	..

Mayonnaise Dressing

Load Grams	100% Mayonnaise Seconds	95% Mayonnaise 5% Olive Oil Seconds
500	42.0	29.0
600	27.0	18.0
700	18.4	13.4
800	12.8	9.4
1000	7.6	6.8

Coal Tar

Load Grams	100% Coal Tar Seconds	85% Coal Tar 15% Benzene Seconds
500	86.0	([a])
0	([a])	8.6

Vaseline

Load Grams	60% Vaseline 40% Mineral Oil Seconds	55% Vaseline 45% Mineral Oil Seconds	50% Vaseline 50% Mineral Oil Seconds
100	...	21.0	5.7
200	16.6	7.9	2.9
500	3.00	2.5	1.4

[a] In the case of 100 per cent coal tar a load of 500 grams would take 86.0 seconds, while with a load of zero the movement of the plunger would hardly be perceptible. In the next case where the coal tar is diluted with 15 per cent benzene a load of 500 grams would make the plunger drop at such a speed that one would not be able to record the time accurately. It can be seen that a zero load takes less time than the 500-gram load on 100 per cent coal tar. Wherever zero load is referred to, it is the weight of the plunger, all other loads are additional grams added to the weight pan.

Applications in Other Industries

The writers have conducted a few experiments with the mobilometer to determine its possible usefulness in other industries. Tests have been made with tomato catsup, mayonnaise dressings, mustard, and similar food products, vaseline, mineral oils, coal tar, and glue and soap solutions. The latter two substances, however, were tested at temperatures or concentrations at which they would not gel. In the results obtained with some of the materials which are presented in Table II, it will be noted that wherever a small amount of diluent is added to the original product the mobilometer usually showed an appreciable difference in the time of flow, thus indicating the sensitivity of this apparatus to small differences in the consistency of the product experimented with. If pressure-flow curves are desired for a product, a number of different readings are made with different loads, taking care that the product remains at a fairly constant temperature. Should it be desired to reproduce a certain consistency, a standard pressure or load which is best suited for the product should be used and the time in seconds of the rate of flow of the product be noted.

All these above products were run at 20° C. (68° F.) ± 1° C. To each load should be added the weight of the brass plunger, a perforated disk attached and a weight pan, which was 74 grams. The load, or pressure, denotes the amount of weight added to the brass plunger. These tables should give interesting information upon what weights should be used for various products—that is, what weight will show the greatest difference in time of flow and be applicable to a wide range of consistencies.

Heat and Moisture as Factors in the Destruction of Gossypol in Cottonseed Products[1]

By Willis D. Gallup

Department of Agricultural Chemical Research, Oklahoma Experiment Station, Stillwater, Okla.

Cotton seeds contain a toxic substance called gossypol, the destruction of which appears justifiable especially if the seeds are to be used as a cattle food. A study was therefore made of the effects of heat and moisture in bringing about the destruction of this substance within the seeds.

Cotton seeds were heated dry in an electric oven, heated in the presence of excess moisture (autoclaved), and germinated. The time of the first two treatments was varied between wide limits and the decrease in gossypol determined by chemical and biological methods.

Heating the seeds in a dry condition effected a change in the form of the gossypol but only slowly reduced their toxicity. Heating the moist seeds in the autoclave rapidly destroyed the gossypol and produced a non-toxic product. Germination was not effective in reducing the toxicity of the seeds.

FOR some time the manufacturers of cottonseed oil have known that during the expression of the oil from the cotton seeds there is removed, along with the oil and other impurities, certain substances which impart to the oil a dark reddish color. One of these substances has recently aroused considerable interest in view of its toxic properties, which have been demonstrated by Withers and Carruth[2] in an effort to explain the toxicity of cottonseed meal. Marchlewski[3] had previously isolated the same compound from the "foots" of cottonseed oil and gave it the name "gossypol." Following the work of Carruth there was much discussion in the literature as to the real cause of the deleterious effects produced in animals by feeding large quantities of cottonseed meal, and Schwartze and Alsberg[4] quite definitely established a relationship between the toxicity of cotton seeds and their gossypol content.

Since the meal consists of cottonseed kernels which have gone through a heating and pressing process to remove the larger portion of the oil, these investigators offer indirect evidence as to the cause of the toxicity of the cottonseed meal. However, there is still considerable question as to the toxicity of the cottonseed meal as determined by its gossypol content, since we know that the process of manufacture has a very definite effect upon the gossypol which was contained in the original seeds, and Sherwood[5] has shown that not only is the amount lowered but it is possibly changed in form. The present problem involves the elimination of gossypol so that it no longer remains in the press cake to impair its feeding value after the oil has been removed. Since this might come about in a variety of ways it was thought well to mention some of the properties of this substance.

Properties of Gossypol

Gossypol occurs as a coloring matter in the internal glands of the cottonseed kernels, and probably throughout the cotton plant. It is quite insoluble in petrolic ether, but soluble in diethyl ether, chloroform, carbon tetrachloride, ethylene dichloride, acetone, and carbon disulfide. The amount found in "hull-free" kernels by extraction with diethyl ether varies from 0.4 to 1.2 per cent. According to Carruth[6] its molecular weight is about 532, it is very unstable in alkaline solution, and decomposes at about 176° C. to a dark mass. It combines with aniline and some other compounds with the $-NH_2$ grouping to form a less soluble compound, and Carruth used this property as a means of its quantitative determination.

Gossypol is readily oxidized in alkaline solution by hydrogen peroxide and other oxidizing agents and its solution in organic solvents turns greenish black on the addition of iron salts. It may be isolated easily from cotton seeds by first removing the oil with petrolic ether followed by extraction with diethyl ether, which removes the gossypol and considerable coloring matter. After evaporating the ether completely at a low temperature, the gossypol is liberated by adding petrolic ether. The purification of this product is best effected by dissolving it in a mixture of ether and 80 per cent acetic acid and allowing it to stand for several days. The gossypol crystallizes out in combination with acetic acid, from which it is liberated by dissolving in ether and washing several times with water. The water removes the acetic acid and the free gossypol is recovered on evaporation of the ether. Schwartze and Alsberg[7] found gossypol purified in a similar manner, when fed to experimental animals, to produce "nearly all the manifestations reported as char-

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[1] Received February 4, 1927. Published with the permission of the Director of the Oklahoma Experiment Station, C. T. Dowell, who initiated the study of factors influencing the gossypol content of cottonseed meal in this laboratory.

[2] *J. Agr. Research*, **5**, 261 (1915).

[3] *J. prakt. Chem.*, **60**, 84 (1899).

[4] *J. Agr. Research*, **28**, 173 (1924).

[5] *Ibid.*, **32**, 793 (1926).

[6] *J. Am. Chem. Soc.*, **40**, 647 (1918).

[7] *J. Agr. Research*, **28**, 191 (1924).

acteristic of the cottonseed intoxication of the farm animal." They further studied its pharmacological action.

Purpose of Investigation

During some investigations on the feeding value of cottonseed meal and methods of treating it such that it might be used more extensively and with less precaution as a stock feed, the writer and his collaborators became convinced that autoclaving the meal was of considerable benefit.[8,9] The temperature attained and time of heating are both important factors in this process. The present investigation was carried out to show some of the effects of heat and moisture upon gossypol and to throw some light on the problems connected with the preparation of the cottonseed meal, both factors being considered necessary to produce the best meal from the feeding standpoint. Although the toxicity of gossypol has been definitely established, little is known concerning the toxicity of its decomposition products, and since these appear to be the form in which gossypol is found in the meal, it is important that we know more about their physiological effects. A study of this type has been begun in this laboratory, and the results are forthcoming.

The severe treatment to which cotton seeds are subjected in the oil mill is the probable cause of the change gossypol undergoes and the reduced toxicity of the meal. The results of the experiments described herein show the importance of some of the conditions which prevail during this process. A generally accepted hypothesis is that during the cooking of the seeds previous to pressing out the oil some of the gossypol is entirely destroyed and some is changed to another form of gossypol having about the same molecular weight and properties except that it is no longer soluble in the ordinary fat solvents and therefore cannot be removed by the usual methods. This form of gossypol, which is quite insoluble in ether but soluble in hot aniline, will be called *d*-gossypol throughout this paper.

Sherwood[5] determined by chemical methods the gossypol and *d*-gossypol content of a large number of cottonseed meals which had been prepared by different processes, and found the gossypol content to vary from 0.007 to 0.150 per cent and the *d*-gossypol content to vary from 0.335 to 1.076 per cent. He further states that "seventy-five per cent or more of the gossypol present in the cottonseed kernels is converted, in the manufacture of cottonseed meal, into the less toxic *d*-gossypol." The main factors in the preparation of cottonseed meal which seem to bear directly upon its gossypol content are the temperature at which the seeds are heated, the time of such heating, the amount of moisture present, and the amount of oil expressed. Occasionally a meal has been found entirely free of gossypol as determined by Carruth's method modified by Schwartze and Alsberg[10] for cotton seeds, but in all cases there has been present a substance with properties similar to those of gossypol which is believed to be one of its decomposition products, probably the *d*-gossypol. Previous work in this laboratory had indicated that heat alone was not sufficient to destroy the gossypol, although no determinations for this substance had been made. Osborne and Mendel[11] found cotton seeds to be toxic to rats even after heating the whole kernels at 110° C. for 22 hours, although these investigators did not make chemical determinations of the gossypol content of the products fed. The writer desired to know if heating under more favorable conditions would destroy the gossypol and to what extent water would aid in this process.

The plan of this experiment was to subject cotton seeds to the action of heat and moisture both separately and combined, if possible, within limits which would not be detrimental to the final product and yet be sufficient to destroy the gossypol and produce a feed of good quality. Chemical determinations were to be made of the gossypol content of the seeds before and after such treatment and the products fed to experimental animals to note the effects upon growth as an index of toxicity.

Chemical Determinations of Gossypol Content before and after Treatment

The cotton seeds, which were of one variety, were delinted with sulfuric acid, washed, air-dried, and divided into four portions. One portion was kept moist at about 40° C. until the seeds had sprouted. A second portion was soaked in water for 4 hours and then autoclaved for different periods of time under 20 pounds (1.4 kg.) steam pressure. A third portion was finely ground, spread in thin layers, and placed in an electric oven at 110° C. for the same and longer periods of time. In this manner cottonseed products were obtained which had been subjected to the action of moisture alone, heat and moisture, and heat alone. These were sampled after being brought to room temperature and determinations made for gossypol and *d*-gossypol.

Table I—Gossypol and *d*-Gossypol Content of Cotton Seeds Treated in Various Ways

TIME OF HEATING	FINAL MOISTURE CONTENT	ANILINE-GOSSYPOL COMPOUND	ANILINE-*d*-GOSSYPOL COMPOUND	GOSSYPOL	*d*-GOSSYPOL
	Per cent	*Grams*	*Grams*	*Per cent*	*Per cent*
GROUND COTTON SEEDS HEATED DRY AT 110° C.					
10 min.	2.40	0.0931	0.0914	0.137	0.135
15 min.	1.97	0.0147	0.2089	0.021	0.309
20 min.	1.65	0.0145	0.1503	0.021	0.222
30 min.	1.15	Trace	0.1643	...	0.243
1 hour	0.42	None	0.1602	...	0.237
2 hours	0.11	None	0.1468	...	0.217
4 hours	None	None	0.1256	...	0.185
8 hours	None	None	0.1180	...	0.174
16 hours	None	None	0.0760	...	0.112
WHOLE COTTON SEEDS SOAKED 4 HOURS AND AUTOCLAVED AT 20 LBS. PRESSURE					
10 min.	43.70	0.0560	0.0618	0.082	0.091
30 min.	44.24	0.0393	0.0510	0.058	0.075
1 hour	46.85	None	0.0326	...	0.048
2 hours	48.01	None	None	...	...
ORIGINAL COTTON SEEDS					
Unheated	7.51	0.1860	None	0.275	...
Unheated, germinated		No determinations			

Soaking the seeds in the second portion was for the purpose of softening the hulls and allowing the seeds to take up considerable water, so that when they were autoclaved the steam was able to penetrate the kernel. During the procedure there is no packing and very little loss of oil as is the case if the seeds are first ground. The seeds were ground in the third portion to expose the gossypol and increase the opportunities for oxidation or other chemical reactions to take place. The initial moisture content of the seeds, which was 7.51 per cent, was decreased during the dry-heating process to the amounts shown in Table I. This small amount is believed from other studies to be of little consequence in bringing about the destruction of gossypol. The autoclaved seeds, however, contained 45.25 per cent moisture, which was varied as shown during the periods of autoclaving and in such amounts was instrumental in bringing about the rapid destruction of gossypol.

The results of the gossypol and *d*-gossypol determinations on these products using 50-gram samples are given in Table I. The gossypol determinations were made by Carruth's method as modified by Schwartze and Alsberg,[10] and the *d*-gossypol was determined by the method used by Sherwood.[5] The gossypol content of the aniline-gossypol precipitates

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[8] Dowell and Menaul, *J. Agr. Research*, **26**, 9 (1923).

[9] Gallup, *J. Dairy Sci.*, **9**, 359 (1926).

[10] *J. Agr. Research*, **25**, 285 (1923).

[11] *J. Biol. Chem.*, **29**, 289 (1917).

was determined by using the factor 74 in assuming the composition of this precipitate to be $C_{30}H_{28}O_9.2C_6H_5NH_2$. The *d*-gossypol was calculated in the same way, as it has been shown[5] that the composition of the two precipitates is practically the same. No determinations were made upon the germinated seeds, as the feeding experiments showed no decrease in toxicity between the germinated and the original seeds.

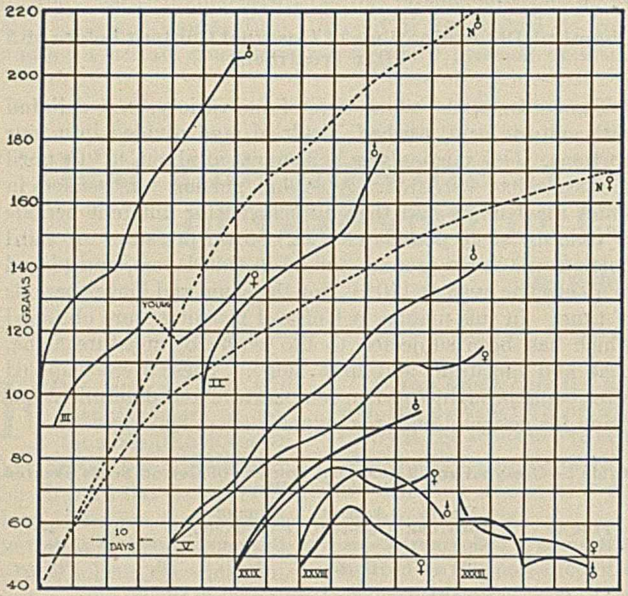

Figure 1—Growth Curves of Rats on Cottonseed Product Diets

From the results in Table I it appears that through the agency of heat gossypol is readily changed to *d*-gossypol, even though the time of heating is short. Longer heating tends to destroy the *d*-gossypol. This change is most apparent after 15 minutes' heating, and in only one instance when a large quantity of ground seeds was used was there an appreciable amount of gossypol left in the seeds that had been heated in the electric oven for one hour. The amount of *d*-gossypol was decreased very slowly and could be detected after 16 hours of such heating. Whether or not gossypol is destroyed by heat after first being converted to *d*-gossypol is still a question. Heating the seeds in the presence of excess moisture, as in autoclaving, destroyed both the gossypol and the *d*-gossypol in relatively short periods of time. The optimum time of such heating under these conditions was one hour. These results are based upon chemical determinations for the two compounds and represent the average of no less than two determinations for each compound.

Test on Rats

Some of the products described above were incorporated in diets of young rats to observe the effect upon growth as a further check upon the destruction of the toxic principle. The cottonseed products were used in a ration made up as follows: Cottonseed product 35, wheat 60, $CaCO_3$ 1, NaCl 1, and cod-liver oil 3 parts. Such a ration had been previously employed for rats over short periods and good growth and reproduction[12] were obtained when using both cotton seeds and cottonseed meal which had been autoclaved for one hour. When the germinated seeds were fed, they made up 50 per cent of the ration, thereby decreasing the wheat to 45 per cent. This change, however, did not affect the general results. The results of this feeding are shown in Table II.

Table II—Rats on Cottonseed Product Diets

Number of Rats	Ration No.	Duration of Expt. Days	Cottonseed Treatment	Growth	Lived	Died
4	XXXIV	30	Ground, heated dry 1 hour, 110° C.	None	...	4
4	XXVIII	50	Ground, heated dry 8 hours, 110° C.	None	1	3
4	XXIX	60	Ground, heated dry 16 hours, 110° C.	Poor	4	...
4	V	100	Soaked 4 hours; autoclaved wet 30 min., 20 lbs. pressure	Fair	4	...
4	II	60	Soaked 4 hours; autoclaved wet 1 hr., 20 lbs. pressure	Good	4	...
4	III	60	Soaked 4 hours; autoclaved wet 2 hours, 20 lbs. pressure	Very good	4	...
4	XXXIII	40	Untreated	None	...	4
4	XXXV	40	Germinated	None	...	4

The average growth curves of the animals are shown in Figure 1. Those animals receiving in their diet cotton seeds which had been autoclaved for 2 hours in the presence of excess moisture made the best growth and were in the best condition throughout the experiment. The animals receiving the germinated seeds and seeds heated dry at 110° C. for one hour showed no improvement over those animals receiving the untreated seeds. None of these animals made any gain in weight, but all slowly declined and died, following along the general growth curve for the rats on the untreated seeds. Heating the seeds at 110° C. for 16 hours decreased their toxicity, and the rats fed on this product are still alive after 90 days although their growth is below normal.

Conclusion

The destruction of gossypol, the toxic principle in cotton seeds as indicated by feeding tests and chemical determinations of both gossypol and *d*-gossypol, is brought about slowly by heat if the seeds are first ground and spread out in thin layers. The time of such heating necessary to produce a non-toxic product is much longer than that employed at the oil mill. The toxic principle is rapidly destroyed by steaming the seeds as in autoclaving in the presence of excess moisture. Under the conditions employed, one hour of such treatment was sufficient to reduce the toxic principle such that it could not be determined by the usual chemical methods. Germination does not decrease the toxicity of the seeds.

Acknowledgment

The author desires to express his appreciation of the interest taken in this work by V. G. Heller, who sprouted the cotton seeds and did that portion of the feeding work which had to do with the germinated seeds. Thanks are also due to N. B. Guerrant for his helpful suggestions and advice.

Pulp Mill Waste Utilized in Tanning—The possibility of converting a waste product of the paper industry into a necessary material for the leather industry has been revealed as a result of research conducted by the Bureau of Standards.

It has found that leather filled with materials derived from waste liquors is equally as durable as leather filled with such tanning materials as chestnut wood and quebracho wood extracts. The bureau then investigated the suitability of sulfite cellulose extracts (treated and concentrated waste liquors) for use in the actual tanning operations. Chemical examinations of various extracts showed them to contain usable amounts of materials which would firmly combine with hide to form leather. The color imparted to leathers by the use of these materials was satisfactory. Actual tanning tests produced leather of good strength, wearing quality, and appearance.

The investigation shows that sulfite cellulose extracts can be satisfactorily used for tanning when blended with other materials such as quebracho wood and chestnut wood extracts. Both the tanner and the paper manufacturer would benefit by this utilization.

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[12] Unpublished work.

Sulfur in Coal and Coke[1,2]

Check Determinations by the Eschka, Bomb-Washing, and Sodium Peroxide Fusion Methods

By W. A. Selvig and A. C. Fieldner

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

Sixteen samples of coal and coke, ranging in sulfur content from about 0.5 to 17 per cent, have been analyzed for sulfur by five laboratories by the Eschka, bomb-washing, and sodium peroxide fusion methods. Detailed methods of procedure are given for the three methods.

The bomb-washing method requires care in the slow and uniform release of the gases after the combustion, and thorough washing of the inside of the bomb, including the valve opening in types not equipped with needle valves. Most of the laboratories were able to obtain good checks in making duplicate determinations by any of the three methods. The best average checks between duplicate determinations were obtained with the sodium peroxide fusion method.

In general, the laboratories were able to obtain results with the bomb-washing and sodium peroxide fusion methods which checked those of the Eschka method sufficiently close to show that these methods may be used alternately with the Eschka method, which has for long been the recognized standard for sulfur determination in coal and coke.

THE Eschka method for the determination of sulfur in coal has long been recognized as a standard method for use as a basis for specifications for the purchase of coal. It was recommended by the joint committee on coal analysis of the American Society for Testing Materials and the AMERICAN CHEMICAL SOCIETY, and has been adopted as a standard method by these societies.[3] Laboratories making calorimetric determinations find it convenient to determine sulfur in the washings from the bomb calorimeter. Another rapid method is the sodium peroxide fusion method. Both of these methods were investigated to some extent by the joint committee and were found to give results in close agreement with the Eschka method.

In order to obtain additional information regarding the bomb-washing and sodium peroxide fusion methods, Committee D-5, on Coal and Coke, of the American Society for Testing Materials appointed a subcommittee to make check determinations of sulfur. Sixteen samples of coal and coke, ranging in sulfur content from about 0.5 to 17 per cent, were submitted to various laboratories and the sulfur was determined by the Eschka, bomb-washing, and sodium peroxide fusion methods. The results of these check determinations are given in this paper.

Table I—Source of Coal and Coke

SAMPLE	SOURCE	APPROXIMATE ANALYSIS, MOISTURE-FREE BASIS Volatile matter	
		Volatile matter	Ash
		Per cent	*Per cent*
A	Pennsylvania	24	11.0
B	Washington	45	7.8
C	Illinois	32	14.8
D	Appalachian field	37	12.6
E	West Virginia	25	11.2
F	Kansas	35	8.8
G	Appalachian field	22	5.9
H	Appalachian field	26	14.5
I	Unknown	45	13.2
J	Interior Province	39	8.4
K	Illinois	43	12.1
L	Mississippi lignite	27	44.0
M	Illinois	39	10.6
N	Interior Province	37	16.0
O	Anthracite	..	16.9
P	Metallurgical coke	..	16.3

Source and Preparation of Samples

The samples were prepared by air-drying and then crushing to pass a 60-mesh sieve. After thorough mixing, portions were placed in rubber-stoppered glass bottles. Sulfur was determined by the Bureau of Mines on each bottle sample and these determinations showed that the individual samples were representative. The source of the various samples of coal and coke is shown in Table I.

Methods Used for Determination of Sulfur

A set of the samples was sent to each laboratory participating in the work, with detailed instructions as to the procedure to be used in determining sulfur. Each laboratory was directed to follow the methods exactly as outlined, also to determine the moisture of each sample, at 105° C., and report the sulfur in the moisture-free sample. Following are the methods as submitted to the laboratories:

ESCHKA METHOD—The Eschka method is the standard method for sulfur in coal of the American Society for Testing Materials[4] and is as follows:

> *Preparation of Sample and Mixture.* Thoroughly mix on glazed paper 1 gram of coal and 3 grams of Eschka mixture. Transfer to a porcelain capsule, $^7/_8$ inch (18 mm.) deep and $1^3/_4$ inches (37 mm.) in diameter, or a porcelain crucible of 30 cc. capacity, high or low form, or platinum crucible of similar size, and cover with about 1 gram of Eschka mixture.
>
> *Ignition.* On account of the amount of sulfur contained in artificial gas, heat the crucible over an alcohol, gasoline, or natural gas flame as in procedure (*a*) below, or in a gas or electrically heated muffle, as in procedure (*b*) below. The use of artificial gas for heating the coal and Eschka mixture is permissible only when the crucibles are heated in a muffle.
>
> (*a*) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.
>
> (*b*) Place the crucible in a cold muffle and gradually raise the temperature to 870–925° C. (cherry-red heat) in about 1 hour. Maintain the maximum temperature for about $1^1/_2$ hours and then allow the crucible to cool in the muffle.
>
> *Subsequent Treatment.* Remove and empty the contents into a 200-cc. beaker and digest with 100 cc. of hot water for $^1/_2$ to $^3/_4$ hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc., with 10 to 20 cc. of saturated bromine water, make slightly acid with HCl and boil to expel the liberated bromine. Make just neutral to methyl orange with NaOH or Na_2CO_3 solution, then add 1 cc. of normal

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[1] Received March 3, 1927. Presented before the Division of Gas and Fuel Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] THIS JOURNAL, **9**, 100 (1917).

[4] Am. Soc. Testing Materials, Standards, p. 990 (1924).

HCl. Boil again and add slowly from a pipet, with constant stirring, 10 cc. of a 10 per cent solution of $BaCl_2 . 2H_2O$. Continue boiling for 15 minutes and allow to stand for at least 2 hours or preferably overnight, at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until an $AgNO_3$ solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of $BaSO_4$ in a weighed platinum, porcelain, silica, or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925° C. and heat to constant weight.

The residue of MgO, etc., after leaching, should be dissolved in HCl and tested with great care for sulfur. When an appreciable amount is found this should be determined quantitatively. The amount of sulfur retained is by no means negligible.[5]

Blanks and Corrections. In all cases a correction must be applied either (1) by running a blank exactly as described above, using the same amount of all reagents that were employed in the regular determination or, more surely, (2) by determining a known amount of sulfate added to a solution of the reagents after these have been put through the prescribed series of operations. If this latter procedure is adopted and carried out, say, once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulfur content likely to be met with in coals, it is only necessary to add to or subtract from the weight of $BaSO_4$ obtained from a coal whatever deficiency or excess may have been found in the appropriate "check" in order to obtain a result that is more certain to be correct than if a "blank" correction as determined by the first procedure is applied. This is due to the fact that the solubility error for $BaSO_4$, for the amounts of sulfur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. Barium sulfate is soluble in acids and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent.[6] Hence, in the event of using reagents of very superior quality or of exercising more than ordinary precautions, there may be no apparent "blank" because the solubility limit of the solution for $BaSO_4$ has not been reached, or at any rate not exceeded.

BOMB-WASHING METHOD—As sulfur is determined in the bomb washings from the calorimetric determination, it was specified that the type of bomb, amount of water in the bomb, and oxygen pressure conform to the A. S. T. M. Standards.[7] The type of bomb specified is one having an inner surface of platinum, gold, porcelain enamel, or other material not attacked by nitric and sulfuric acids, or other products of combustion. The bomb is filled with oxygen to a pressure of 20 atmospheres for the larger bombs and about 30 atmospheres for the smaller bombs, so there will be at least 5 grams of oxygen per gram of coal. The initial charge of air in the bomb is not removed by rinsing out with oxygen, as it is necessary to have nitrogen oxides formed during the combustion to act as a catalyst in converting the sulfur completely to sulfuric acid and prevent the formation of sulfur dioxide.[8]

The nitrogen oxides are formed from the nitrogen of the air entrapped in the bomb and from the nitrogen of the coal sample. About 0.5 cc. of water is placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. About 1 gram of coal or coke is burned.

The laboratories were instructed to take special precautions in releasing the gases slowly and uniformly after the combustion, and to wash all parts of the interior of the bombs carefully, including the valve openings in types of bombs not equipped with needle valves. If this is not done the results may be too low through loss of some of the sulfuric acid.

Following is the procedure which the laboratories were instructed to follow:

Sulfur may be determined in the washings from the oxygen bomb calorimeter following the calorimetric determination. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination.[7]

The bomb shall stand in the calorimeter water for not less than 5 minutes after firing. Then remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate in order that the pressure is reduced to atmospheric in not less than 1 minute. Bombs equipped with valves other than needle valves, such as compression valves, should be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Then open the bomb and examine the inside for traces of unburned material or sooty deposit. If they are found, discard the determination. If the combustion appears complete, carefully wash all parts of the interior of the bomb, including the tray, with a fine jet of distilled water containing 1 cc. per liter of a saturated solution of methyl orange, until no acid reaction is observed. It is also essential to wash through the valve opening in the case of bombs equipped with compression valves or other types of valves with large openings, as considerable spray may collect in such valve openings during the release of the gases.

Collect the washings in a 250-cc. beaker and titrate with standard alkali solution to obtain the "acid correction" for the heating value as specified under the calorimetric determination. Add 1 cc. of NH_4OH (sp. gr. 0.90), heat the solution to boiling, and filter through qualitative filter paper. Wash the residue and filter paper thoroughly five or six times with hot distilled water. To the filtrate and washings, amounting to about 250 cc., add 1 cc. of saturated bromine water and sufficient HCl to make it slightly acid. Boil the solution to expel the excess bromine. Adjust the acidity of the solution and precipitate the sulfur with barium chloride solution and determine, both as described for the Eschka method.

The types of bombs, capacity, and oxygen pressure used by the laboratories that determined sulfur by the bomb-washing method are shown in Table II.

Table II—Details of Bombs Employed

LABORATORY	TYPE OF BOMB	CAPACITY	OXYGEN PRESSURE
		Cc.	*Atmos.*
1	Parr illium	350	30
	Special illium	400	27
2	Parr illium	390	27 and 35
3	Parr illium	375	30
4	Parr illium	400	30
5	Emerson gold-lined	545	20

Laboratory 2 used 35 atmospheres oxygen pressure except for coals *A*, *B*, *C*, *H*, *I*, *J*, *K*, *L*, and *M*. (See Tables III to VII.) These coals were reported to give trouble due to coking and incomplete combustion with 35 atmospheres oxygen pressure, so 27 atmospheres were used. Laboratory 3 used 0.5-gram samples of coal *L* in the bomb-washing method; otherwise 1-gram samples were used. Laboratory 3 did not report bomb-washing results on sample *L*, as only 6 to 8 per cent was obtained on three determinations and a strong odor of sulfur dioxide was noted when the bomb was opened; also sulfur was found in the residue left in the bomb. Laboratory 2 also reported that the residue in the bomb from coal *L* contained sulfur. Coal *L* is unusual in that it contained over 17 per cent sulfur and about 44 per cent ash.

SODIUM PEROXIDE FUSION METHOD—The Parr coal sulfur bomb was used by all the laboratories which determined sulfur by this method. The bomb is made of alkali-resistant metal and ignition of the charge may be effected either electrically or by the application of a pointed flame to the bottom of the bomb, according to the type of bomb used. The special sodium peroxide and potassium chlorate regularly supplied with the equipment were used, as these chemicals should be sulfur-free. If the sodium peroxide contains considerable sulfur, difficulty may be experienced in obtaining the proper blank correction due to non-uniform distribution of sulfur. The following procedure is used:

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[5] *J. Am. Chem. Soc.*, **21**, 1125 (1899).

[6] *Ibid.*, **32**, 588 (1910); **33**, 829 (1911).

[7] Am. Soc. Testing Materials, Standards, p. 1007 (1924).

[8] Register, THIS JOURNAL, **6**, 812 (1914); Bradley, Corbin, and Floyd, *Ibid.*, **18**, 583 (1926).

Table III—Determinations of Sulfur by the Eschka Method

(Percentage of dry coal or coke)

Sample	Laboratory 1		Laboratory 2		Laboratory 3		Laboratory 4		Laboratory 5	
	Individual	Av.	Individual	Av.	Individual	Av.	Individual	Av.	Individual	Av.
A	2.66, 2.61, 2.59	2.62	2.46, 2.57, 2.59	2.54	2.62, 2.70, 2.75	2.69	2.58	2.58	2.71, 2.71	2.71
B	0.49, 0.49, 0.47, 0.47, 0.52, 0.52	0.49	0.46, 0.42, 0.32	0.40	0.62, 0.63, 0.64	0.63	0.49	0.49	0.60, 0.59	0.60
C	1.07, 1.07, 1.03, 1.03, 1.06	1.05	1.04, 1.06, 1.02	1.04	1.04, 1.10, 1.10	1.08	1.01	1.01	1.17, 1.22	1.20
D	3.57, 3.61, 3.64	3.61	3.61, 3.49, 3.53	3.54	3.62, 3.57, 3.66	3.62	3.65	3.65	3.82, 3.76	3.79
E	1.40, 1.41, 1.36, 1.37, 1.38	1.38	1.24, 1.31, 1.36	1.30	1.30, 1.36, 1.34	1.33	1.31	1.31	1.41, 1.42	1.42
F	4.30, 4.34, 4.32	4.32	4.18, 4.22, 3.94	4.11	4.41, 4.37, 4.39	4.39	4.27	4.27	4.41, 4.38	4.40
G	1.94, 1.94, 1.90	1.93	1.76, 1.68, 1.86	1.77	1.94, 1.99, 1.98	1.97	1.87	1.87	1.99, 2.05	2.02
H	4.31, 4.34, 4.33	4.33	4.19, 4.31, 3.71	4.07	4.44, 4.50, 4.50	4.48	4.36	4.36	4.42, 4.44	4.43
I	6.19, 6.16, 6.18	6.18	6.55, 6.64, 6.58	6.59	6.35, 6.25, 6.35	6.32	6.20	6.20	6.75, 6.78	6.77
J	3.19, 3.20, 3.16	3.18	3.11, 3.11, 2.87	3.03	3.25, 3.29, 3.26	3.27	3.19	3.19	3.27, 3.30	3.29
K	8.05, 8.07, 8.06, 8.14, 8.04	8.07	7.87, 7.83, 8.00	7.90	8.34, 8.32, 8.20	8.29	7.98	7.98	8.47, 8.54	8.51
L	17.38, 17.20	17.29	15.50, 15.46, 16.10	15.69	16.30, 16.42, 16.48	16.40	16.18	16.18	14.06, 13.93	14.00
M	5.08, 5.14, 5.05, 5.25	5.13	4.80, 5.38, 4.99	5.06	5.18, 5.24, 5.13	5.18	5.18	5.18	5.39, 5.41	5.40
N	11.29, 11.30, 11.30, 11.12	11.25	10.45, 10.78, 10.43	10.55	10.54, 10.65, 10.64	10.61	11.17	11.17	10.74, 10.90	10.82
O	0.91, 0.94	0.93	0.81, 0.77, 0.83	0.80	1.03, 1.00, 0.99	1.01	Not determined		1.11, 1.14	1.13
P	0.63, 0.64, 0.58, 0.60	0.61	0.49, 0.47, 0.47	0.48	0.60, 0.59, 0.60	0.60	Not determined		0.70, 0.79	0.75

Table IV—Determinations of Sulfur by the Bomb-Washing Method

(Percentage of dry coal or coke)

Sample	Laboratory 1		Laboratory 2		Laboratory 3		Laboratory 4		Laboratory 5	
	Individual	Av.	Individual	Av.	Individual	Av.	Individual	Av.	Individual	Av.
A	2.71, 2.61, 2.74, 2.61	2.67	2.50, 2.55	2.53	2.62, 2.55, 2.60	2.59	2.60, 2.60	2.60	2.64, 2.54	2.59
B	0.65, 0.62. 0.58, 0.70, 0.73, 0.52, 0.50	0.61	0.55, 0.51	0.53	0.54, 0.58, 0.59	0.57	0.53, 0.54	0.54	0.50, 0.51	0.51
C	1.04, 1.05, 1.05, 1.07, 1.14, 1.14	1.08	1.09, 1.09	1.09	1.04, 1.07, 1.04	1.05	1.08, 1.10	1.09	1.05, 1.11	1.08
D	3.59, 3.67, 3.55, 3.63, 3.61, 3.62	3.61	3.48. 3.48	3.48	3.56, 3.58, 3.50	3.55	3.65, 3.70	3.68	3.68, 3.66	3.67
E	1.35, 1.28, 1.29, 1.32, 1.24	1.30	1.34, 1.42	1.38	1.30, 1.38, 1.40	1.36	1.46, 1.40	1.43	1.36, 1.32	1.34
F	4.33, 4.20, 4.26, 4.32, 4.23	4.27	4.07, 4.10	4.09	4.37, 4.25, 4.23	4.28	4.32, 4.38	4.35	4.18, 4.34	4.26
G	1.85, 1.90, 1.88, 1.95, 1.82, 1.76, 2.05	1.89	1.75, 1.80	1.78	1.92, 1.90, 1.85	1.89	1.92, 1.93	1.93	1.98, 1.99	1.99
H	4.22, 4.40, 4.30, 4.28	4.30	4.17, 4.21	4.19	4.40, 4.37, 4.44	4.40	4.38, 4.42	4.40	4.53, 4.40	4.47
I	6.21, 6.31, 6.31	6.28	6.78, 6.81	6.80	6.32, 6.28, 6.36	6.32	6.24, 6.30	6.27	6.72, 6.69	6.71
J	3.18, 3.38, 3.30, 3.20, 3.22, 3.33,	3.27	3.35, 3.34	3.35	3.06, 3.16, 3.12	3.11	3.20, 3.24	3.22	3.18, 3.29	3.24
K	7.99, 8.08, 8.09	8.05	8.00, 7.80	7.90	8.06, 8 13 7.98	8.06	8.06, 8.10	8.08	8.18, 8.18	8.18
L	16.28, 16.05	16.17	15.65	15.65	16.35, 16.37, 16.26	16.33	([a])	...	15.66. 15.03	15.35
M	5.29, 5.34, 5.02, 4.98, 4.94	5.11	5.47, 5.39	5.43	5.15, 5.09, 5.11	5.12	5.24, 5.20	5.22	5.37, 5.24	5.31
N	11.00, 10.94, 11.41, 11.37, 11.06, 10.91	11.12	10.25, 10.31	10.28	10.55, 10.44, 10.54	10.51	11.16, 11.24	11.20	10.85, 10.56	10.71
O	0.98, 0.85	0.92	1.17, 1.13	1.15	1.09, 1.05, 1.07	1.07	Not determined		0.96, 0.92	0.94
P	0.49, 0.53	0.51	0.62, 0.59	0.61	0.60, 0.57, 0.58	0.58	Not determined		0.70, 0.76	0.73

[a] See text.

Place 1 gram of powdered potassium chlorate in a dry Parr sulfur bomb and break up any lumps that occur. Then add one measure (about 15 grams) of sodium peroxide, close the bomb with the temporary top, and shake thoroughly until the chemicals are evenly mixed, after which add 0.5 gram of coal and thoroughly mix the charge again by shaking. In the case of coke and anthracite add 0.3 gram powdered C. P. benzoic acid directly after the sodium peroxide, mix the chemicals thoroughly, after which add 0.5 gram of coke or anthracite and mix the charge thoroughly by shaking. It should be noted that a mixture of potassium chlorate and organic matter alone produces a mixture of extremely explosive properties. One of

Table V—Determinations of Sulfur by the Sodium Peroxide Fusion Method

(Percentage of dry coal or coke)

SAMPLE	LABORATORY 1 Individual	Av.	LABORATORY 2 Individual	Av.	LABORATORY 3 Individual	Av.	LABORATORY 6 Individual	Av.
A	2.83, 2.65	2.74	2.92, 2.92	2.92	2.51, 2.57	2.54	2.80, 2.82	2.81
B	0.52, 0.51	0.52	0.60, 0.62	0.61	0.53, 0.55	0.54	0.55, 0.51	0.53
C	1.10, 1.06	1.08	1.23, 1.22	1.23	1.12, 1.16	1.14	1.12, 1.12	1.12
D	3.68, 3.61	3.65	3.88, 3.90	3.89	3.72, 3.78	3.75	3.75, 3.79	3.77
E	1.42, 1.37	1.40	1.47, 1.51	1.49	1.45, 1.48	1.47	1.46, 1.42	1.44
F	4.41, 4.35	4.38	4.45, 4.47	4.46	4.26, 4.26	4.26	4.44, 4.49	4.47
G	1.88, 1.95	1.92	2.00, 2.00	2.00	1.88, 1.93	1.91	1.83, 1.89	1.86
H	4.42, 4.47	4.45	4.58, 4.51	4.55	4.40, 4.46	4.43	4.60, 4.50	4.55
I	6.77, 6.80	6.79	6.94, 6.97	6.96	6.36, 6.33	6.35	6.87, 6.91, 6.95	6.91
J	3.22. 3.24	3.23	3.25, 3.26	3.26	3.10, 3.11	3.11	3.32, 3.31	3.32
K	8.44, 8.20	8.32	8.60, 8.50	8.55	8.27, 8.35	8.31	8.44, 8.55	8.50
L	17.22, 17.27	17.25	17.72, 17.64	17.68	16.44, 16.51	16.48	17.59, 17.69	17.64
M	5.45, 5.46	5.46	5.69, 5.61	5.65	5.29, 5.20	5.25	5.48, 5.47	5.48
N	11.24, 11.27	11.26	11.13, 11.14	11.14	10.71, 10.60	10.66	11.50, 11.39	11.45
O	0.91, 0.92	0.92	0.97, 0.94	0.96	1.01, 1.00	1.01	0.91, 0.94	0.93
P	0.55, 0.53	0.54	0.59, 0.57	0.58	0.59, 0.62	0.61	0.54, 0.55, 0.56	0.55

Table VI—Maximum Differences between Individual Determinations

SAMPLE	ESCHKA METHOD				BOMB-WASHING METHOD					SODIUM PEROXIDE FUSION METHOD			
	Lab. 1	Lab. 2	Lab. 3	Lab. 5	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 1	Lab. 2	Lab. 3	Lab. 6
A	0.07	0.13	0.13	0.00	0.13	0.05	0.07	0.00	0.10	0.18	0.00	0.06	0.02
B	0.05	0.14	0.02	0.01	0.23	0.04	0.05	0.01	0.01	0.01	0.02	0.02	0.04
C	0.04	0.04	0.06	0.05	0.10	0.00	0.03	0.02	0.06	0.04	0.01	0.04	0.00
D	0.07	0.12	0.09	0.06	0.12	0.00	0.08	0.05	0.02	0.07	0.02	0.06	0.04
E	0.05	0.12	0.06	0.01	0.11	0.08	0.10	0.06	0.04	0.05	0.04	0.03	0.04
F	0.04	0.28	0.04	0.03	0.13	0.03	0.14	0.06	0.16	0.06	0.02	0.00	0.05
G	0.04	0.18	0.05	0.06	0.29	0.05	0.07	0.01	0.01	0.07	0.00	0.05	0.06
H	0.03	0.60	0.06	0.02	0.18	0.04	0.07	0.04	0.13	0.05	0.07	0.06	0.10
I	0.03	0.09	0.10	0.03	0.10	0.03	0.08	0.06	0.03	0.03	0.03	0.03	0.08
J	0.04	0.24	0.04	0.03	0.20	0.01	0.10	0.04	0.11	0.02	0.01	0.01	0.01
K	0.10	0.17	0.14	0.07	0.10	0.20	0.15	0.04	0.00	0.24	0.10	0.08	0.11
L	0.18	0.64	0.18	0.13	0.23	...	0.11	...	0.63	0.05	0.08	0.07	0.10
M	0.20	0.58	0.11	0.02	0.40	0.08	0.06	0.04	0.13	0.01	0.08	0.09	0.01
N	0.18	0.35	0.11	0.16	0.50	0.06	0.11	0.08	0.29	0.03	0.01	0.11	0.11
O	0.03	0.06	0.04	0.03	0.13	0.04	0.04	...	0.04	0.01	0.03	0.01	0.03
P	0.06	0.02	0.01	0.09	0.04	0.03	0.03	...	0.06	0.02	0.02	0.03	0.02
Av. diff. per sample	0.08	0.24	0.08	0.05	0.19	0.05	0.08	0.04	0.11	0.06	0.03	0.05	0.05

Table VII—Variations of Average Bomb-Washing and Sodium Peroxide Results from Eschka Results, as Reported by the Laboratories

SAMPLE	BOMB-WASHING METHOD					SODIUM PEROXIDE METHOD			
	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5	Lab. 1	Lab. 2	Lab. 3	Lab. 6[a]
A	+0.05	−0.01	−0.10	+0.02	−0.12	+0.12	+0.38	−0.15	+0.08
B	+0.12	+0.13	−0.06	+0.05	−0.09	+0.03	+0.21	−0.09	−0.07
C	+0.03	+0.05	−0.03	+0.08	−0.12	+0.03	+0.19	+0.06	−0.03
D	0.00	−0.06	−0.07	+0.03	−0.12	+0.04	+0.35	+0.13	+0.02
E	−0.08	+0.08	+0.03	+0.12	−0.08	+0.02	+0.19	+0.14	+0.04
F	−0.05	−0.02	−0.11	+0.08	−0.14	+0.06	+0.35	−0.13	+0.10
G	−0.04	+0.01	−0.08	+0.06	−0.03	−0.01	+0.23	−0.06	−0.14
H	−0.03	+0.12	−0.08	+0.04	+0.04	+0.12	+0.48	−0.05	+0.09
I	+0.10	+0.21	0.00	+0.07	−0.06	+0.61	+0.37	+0.03	+0.15
J	+0.09	+0.32	−0.16	+0.03	−0.05	+0.05	+0.23	−0.16	+0.02
K	−0.02	0.00	−0.23	+0.10	−0.33	+0.25	+0.65	+0.02	+0.16
L	−1.12	−0.04	−0.07	...	+1.35	−0.04	+1.99	+0.08	+0.43
M	−0.02	+0.37	−0.06	+0.04	−0.09	+0.33	+0.59	+0.07	−0.17
N	−0.13	−0.27	−0.10	+0.03	−0.11	+0.01	+0.59	+0.05	+0.12
O	−0.01	+0.35	+0.06	...	−0.19	−0.01	+0.16	0.00	−0.04
P	−0.10	+0.13	−0.02	...	−0.02	−0.07	+0.10	+0.01	+0.03

[a] Laboratory 6 did not determine sulfur by the Eschka method. The figures given are the variations from the Eschka results (one determination) by Laboratory 1 on the set of samples submitted to Laboratory 6.

the important functions of the sodium peroxide is to provide a diluent, thus slowing down the reaction, so care should be taken that it is not omitted in the charge.

After the cover has been securely fastened to the bomb, ignite the charge by applying a sharply pointed flame to the bottom of the bomb, or by electric ignition according to the type of bomb used. Allow one minute for complete combustion to take place after igniting the charge and then cool under the tap, or in a vessel of water.

Remove the cover from the bomb, place the bomb on its side in a 400-cc. beaker, wash off the top, and cautiously add hot water, placing a watch glass over the top of the beaker before so doing. After solution is complete, remove the bomb and rinse it carefully with water. Slowly add about 30 cc. of HCl (sp. gr. 1.18) to complete neutralization, then add 1 to 2 cc. of the acid in excess. At this point the solution should be filtered and diluted to approximately 400 cc. and the sulfur precipitated with barium chloride solution and determined, both as described for the Eschka method.

A blank determination is to be made on the chemicals, using the same amounts of all reagents that were employed in the regular determination.

Results Obtained by Laboratories

Tables III, IV, and V give the results reported by the various laboratories in determining sulfur by the three methods. The results of individual determinations, as well as average values, are given to show how closely each laboratory could check itself. Table VI gives the maximum differences between individual determinations by each laboratory. Laboratories 1, 2, and 3 determined sulfur by all three methods, and the figures in Table VI show that the best average checks between duplicate determinations were obtained with the sodium peroxide fusion method. Laboratory 2 reported considerably greater differences by the Eschka method than by the bomb-washing or sodium peroxide methods. Laboratory 1, on the other hand, had more trouble in obtaining check results with the bomb-washing method than by the other two methods. Taken as a whole, the check results as given in Table VI can be considered satisfactory, except the Eschka differences of Laboratory 2 and the bomb-washing differences of Laboratory 1.

Variations in Results of Methods

If the bomb-washing and sodium peroxide fusion methods were made alternate methods with the present standard Eschka method, it would be essential that a laboratory be able to obtain results by these two methods in close agreement with the Eschka method. Table VII gives the variations of the average bomb-washing and sodium peroxide results from the average Eschka results, as determined by each of the laboratories. These results indicate that the bomb-washing and sodium peroxide fusion methods check those of the standard Eschka method sufficiently close to permit them to be used as alternate standard methods. Laboratory 2 for some reason or other obtained considerable differences between the Eschka and sodium peroxide methods, but the other laboratories had no difficulty in obtaining good checks between these two methods.

From the tables it will be noted that some of the laboratories had considerable trouble with coals *L* and *N*, especially with coal *L*. As a whole, the sodium peroxide results on these two coals are more consistent than the Eschka or bomb-washing results. These two coals were unusual in that *L* contained about 17 per cent of sulfur and *N* about 11 per cent. Such high-sulfur coals are rare and apparently require special treatment. The laboratories that determined sulfur in these two coals by the sodium peroxide method were instructed to add 0.3 gram of benzoic acid in making up the charge, as is done for anthracite and coke. Laboratory 1 found that coal *L* would not ignite without the addition of benzoic acid. This is explained by the large ash content of the coal—about 44 per cent. Laboratory 1 found that coal *N* gave the same results with or without the addition of benzoic acid.

Acknowledgments

The sulfur determinations were made by or under the direction of Max Hecht, chief chemist, Duquesne Light Company; J. F. Kohout, director of laboratories, Commercial Testing and Engineering Company; C. A. Lunn, chief chemist, Consolidated Gas Company of New York; S. W. Parr and J. M. Lindgren, University of Illinois; N. F. Prince, acting laboratory director, Rochester Gas and Electric Corporation; and H. M. Cooper, associate chemist, and W. L. Parker, junior chemist, U. S. Bureau of Mines.

Action of Sulfur Monochloride on Petroleum Hydrocarbons[1]

By Eugene Lorand

DIVISION OF INDUSTRIAL RESEARCH, PENNSYLVANIA STATE COLLEGE, STATE COLLEGE, PA.

The action of sulfur monochloride on petroleum hydrocarbons has been investigated on both single hydrocarbons and petroleum fractions, and found to be a general reaction of unsaturated hydrocarbons. It consists probably of chlorination and subsequent condensation or polymerization.

Two methods are suggested for testing the degree of unsaturation of hydrocarbons and petroleum products on the basis of this reaction.

IN SEARCHING for a solvent for petroleum fractions which could be removed without distillation, a surprisingly energetic reaction was observed between sulfur monochloride and the different fractions. Heat development, change of color of the solution, effervescence, and the escape of hydrogen chloride mark the reaction. The higher boiling the fraction, the more violently it reacts when mixed with sulfur monochloride.

It is peculiar that the literature of organic chemistry, especially that of the aliphatic hydrocarbons, contains very little about this reaction. The action of sulfur monochloride on ethylene as used in the manufacture of mustard gas, and a similar reaction with amylene described by Guthrie[2] are apparently the only exceptions.

Meigs[3] described the action of sulfur monochloride on certain substances which he designated as "asphalt B," "tar binder B," and "gas engine oils." He attributed the reaction to the presence of bituminous substances, and tried to develop a testing method for them, based on the use of sulfur monochloride. In careful experiments he excluded the presence of moisture and determined the rate of hydrochloric acid evolution during the reaction. However, the present experiments showed that the higher fractions (above 300° C.) and crude oils react more violently than water alone. Thus the reaction, especially the evolution of hydrogen chloride, is not due to the presence of moisture.

In the present work the reaction was found much more general than Meigs supposed. Different kinds of lubricating oils reacted violently; higher kerosene fractions were attacked a little less vigorously; various motor gasolines changed color when mixed with sulfur monochloride and after standing a dark sediment settled out. Moderate heating started a more energetic reaction.

The reaction can be carried further by heating after the first energetic action is over, as the following experiment will show:

> Thirty-five grams of sulfur monochloride were allowed to flow gradually from a separatory funnel into an Erlenmeyer flask containing 100 grams of a petroleum fraction boiling between 225° and 250° C. When the reaction became less vigorous, the mass was heated for several hours on a water bath with refluxing. The oil became tarry, and after cooling monoclinic sulfur crystallized. The liquid was freed from the unchanged sulfur monochloride by distillation. On account of foaming, the further fractionation of the reaction product was made at an absolute pressure of about 50 mm. of mercury. The first drop came over at about 120° C., and the temperature rose to as high as 175° C. toward the end of the distillation. About 75 per cent of oil was recovered. A considerable amount of carbonized product remained in the flask. Seventy-five cubic centimeters of the distillate were fractionated under normal pressure. The first drop came over at 210° C. and 7 cc. distilled below 225° C. The volume of the 225–250° C. fraction was 49 cc. The end point was 278° C.

The results indicate that the distillate contains not only the hydrocarbons unaffected by sulfur monochloride but also polymerized and condensed or chlorinated compounds or their cracked products.

Tests on Single Hydrocarbons

A detailed study of this reaction was made on single hydrocarbons. The first step was to determine what types of hydrocarbons do react with sulfur monochloride. Nor-

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[1] Received January 24, 1927.

[2] *J. Chem. Soc.* (*London*), **12**, 112 (1860).

[3] THIS JOURNAL, **9**, 655 (1917).

mal pentane, normal hexane, decane (diisoamyl), and commercial amylene were available. In all cases the procedure was the same:

Thirty to fifty grams of the hydrocarbon were mixed cold with about half as much sulfur monochloride and then refluxed on a water bath for 5 to 8 hours. The saturated hydrocarbons apparently did not react when cold, nor did heating start a reaction except in the case of diisoamyl, the color of which was changed. However, more thorough examination showed that there was some reaction in all cases. The unchanged sulfur monochloride was hydrolyzed by dilute sodium hydroxide, and the oil was washed until neutral. The sulfur was filtered off and the reaction products were tested for chlorine and sulfur. Both reactions were positive. As sulfur crystallized on longer standing, the liquid was distilled and tested again. The chlorine reactions remained positive, but the sulfur test was negative.

Since these saturated hydrocarbons were not chemically pure, the same experiments were repeated after treating them with fuming sulfuric acid in order to eliminate the unsaturated hydrocarbons. No difference was found in the behavior of the treated hydrocarbons with sulfur monochloride.

The behavior of commercial amylene was entirely different. There was no reaction at ordinary temperature, but after heating slightly violent evolution of heat and change of color took place. The reaction product became brownish black and tarry. Chlorination could be proved easily, but no test for sulfur could be carried out on account of its solubility in the reaction product. Further, it was not possible to separate the two by solvents because of their similar solubility. Chemical agents such as hot sodium hydroxide would also react with any combined sulfur present. Distillation, even under vacuum, caused cracking and carbonization.

Tests on Petroleum Fractions

These facts indicate an outstanding difference between saturated and unsaturated hydrocarbons as regards their behavior with sulfur monochloride. It seemed advisable to check the above results on petroleum fractions which were freed from their unsaturated constituents by a treatment with fuming sulfuric acid. The following results were obtained:

COMMERCIAL GASOLINE—The same procedure was carried out with various samples as in the case of the single hydrocarbons. The sulfur monochloride did not seem to react either cold or hot. However, before distillation, both chlorine and sulfur reactions were positive. The distillation was smooth and gave about the same fractions as the untreated gasoline; but at the end the undistilled portion turned brown and the temperature rose suddenly. The distillate was colorless and contained no sulfur, but gave a distinct chlorine reaction. Sublimed sulfur could be seen in the flask.

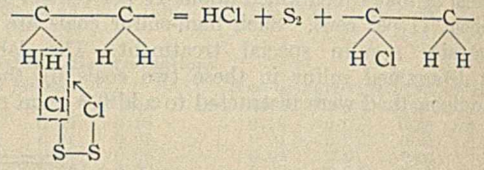
LIGHT KEROSENE FRACTION (distilling between 200° and 225° C.)—The sulfur chloride treatment was carried out between 100° and 150° C. Apparently no change occurred. However, the distillation of the product freed from sulfur chloride gave fractions that were somewhat different from those of the original sample. About 13 per cent went over below 200° C. and about 12 per cent above 225° C. The distillate was colorless until the temperature reached 230° C. From this point the temperature rise was rapid and the distillate became yellow. The fraction below 230° C. was found to contain chlorine but no sulfur. The yellow distillate contained both, but the sulfur may have been carried over mechanically with the distillate.

HIGHER BOILING FRACTIONS—The higher boiling fractions gave similar results.

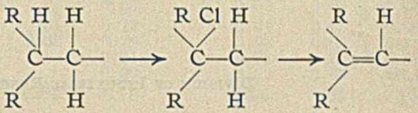
Diisoamyl was found to occupy a position between the saturated and the unsaturated hydrocarbons. At ordinary temperatures there was no sign of reaction, but a continued heating at 100° C. and higher with an equal volume of sulfur chloride resulted in a marked reaction. Hydrogen chloride escaped slowly, and after 6 hours of heating the color of the mixture became dark brown. After cooling, monoclinic sulfur crystallized. The same amount of sulfur chloride as before was added and the mixture heated for 6 hours more. Hydrogen chloride developed and the liquid turned black. A tarry substance separated similar to that in the case of amylene. The sulfur crystallized in rhombic form.

Nature of Reaction

This incomplete analysis of the action of sulfur monochloride shows an outstanding difference between the behavior of saturated and unsaturated hydrocarbons. The sulfur monochloride is a general reagent for the unsaturated chain. It reacts even with such low-boiling members as amylene. The slow and moderate action on saturated straight chains is essentially different. It is probably a mere chlorination of the following type:

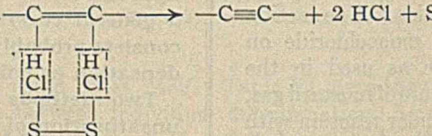


The paraffin hydrocarbons with side chains give the same type of reaction when moderately heated, but the reaction rate is higher. By continued heating to a higher temperature, probably two neighboring carbon atoms lose a molecule of HCl and form a double bond:



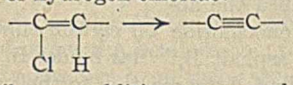
Furthermore, the resulting compound, like other unsaturated hydrocarbons, undergoes polymerization and condensation.

The nature of these latter reactions could not be established, but Meigs' ideas about sulfur compounds and their condensation and polymerization do not seem very probable. The fact that a considerable amount of sulfur crystallizes from the reaction product shows that here also the action of sulfur monochloride probably consists in chlorination and the subsequent formation of a double or triple bond. The condensation probably occurs between two molecules, with elimination of hydrogen chloride. Meigs himself points out the possibility of triple-bond formation, and this reaction seems very probable:



$$\text{—C}{=\!=}\text{C—} \longrightarrow \text{—C}{\equiv}\text{C—} + 2\,\text{HCl} + \text{S}_2$$

This reaction might immediately produce the triple bond, or at lower temperature chlorination might occur, with subsequent removal of hydrogen chloride:



$$\underset{\text{Cl}}{\text{—C}}{=}\underset{\text{H}}{\text{C—}} \longrightarrow \text{—C}{\equiv}\text{C—}$$

Guthrie[2] describes an addition compound of sulfur monochloride and "amylene" analogous to mustard gas. It would be conceivable that whenever sulfur monochloride acts on unsaturated hydrocarbons a similar product is primarily formed which decomposes by heating. However, the unsaturated hydrocarbons, with the increase of the carbon atoms, react more and more violently, and thus the formation of such a primary addition product is improbable.

Tests for Degree of Unsaturation

Meigs developed a method for determining the hydrogen chloride as one product of the reaction and proposed to use it as a comparative test for bituminous substances. Since the reaction has been shown to be more general, it could serve as a basis of a test for unsaturated hydrocarbons.

This test might be worked out along two different lines, one being a modification of Meigs' method.

METHOD I—Meigs stated that the action of sulfur monochloride is a "time reaction," since the evolution of hydrogen chloride continued for many hours without stopping. The above observations show that in a mixture of saturated and unsaturated hydrocarbons the latter react vigorously and cause the major part of the reaction. The saturated compounds or, better, the saturated chains react slowly and are responsible for the "time reaction." Therefore the test should be carried out in such a way that after the main reaction and a subsequent heating for a definite short period the absorption of the hydrogen chloride is stopped. A solvent is necessary for higher fractions or crude oils, since they react too violently if mixed direct with sulfur monochloride. Meigs used carbon disulfide for this purpose, but carbon tetrachloride, or another chlorine derivative with a higher boiling point, seems to be preferable, irrespective of the fact that carbon disulfide reacts with sulfur monochloride. This is unquestionably true for the liquid which has the function of absorbing the sulfur chloride vapors which would hydrolyze in water and increase the amount of absorbed hydrogen sulfide. Meigs was obliged to use water as absorbent for the hydrogen chloride since the carbon disulfide vapors would react with the alkali. By the substitution of a chlorine derivative for the carbon disulfide, sodium hydroxide could be used without fear.

This is one method which was tried in a few cases. It turned out to be practicable and gave comparative results. A more thorough study is necessary to decide its value in comparison with other methods.

METHOD II—A few experiments were carried out in another direction for the purpose of developing a testing method. The petroleum fractions were dissolved in carbon tetrachloride and mixed with about half as much sulfur chloride. The mixture was refluxed on a water bath for 2 hours. About an equal amount of water was added to the reaction mixture to hydrolyze it and this mixture was then slowly neutralized by sodium hydroxide. The whole mass was washed with carbon tetrachloride in a separatory funnel. After removing the alkali layer the content of the funnel was washed with water until neutral. The carbon tetrachloride was driven off and the residue distilled at an absolute pressure of 30 mm. of mercury. The lowering of the boiling point was taken into account in determining the end point of the distillation. This corresponded to the higher limit of the original range of the fraction. Both distillate and residue were weighed. Either the amount of the residue or that of the distillate subtracted from the original quantity of the petroleum sample could be used as a comparative basis for the degree of unsaturation.

This is a second method which seems to be especially useful for testing lower fractions, since there is a considerable difference between the boiling range of the unchanged part of the fraction and that of the polymerized or condensed products.

Further Investigations Planned

The writer plans to continue the preceding investigations in various directions:

(1) More thorough study of the condensation or polymerization products obtained by the action of sulfur monochloride on unsaturated hydrocarbons with regard to their possible sulfur content.

(2) Study of the behavior of higher saturated, pure hydrocarbons with sulfur monochloride, with special reference to tertiary carbon atoms.

(3) Experiments with unsaturated hydrocarbons from other series than olefins.

(4) Testing the two suggested methods for the determination of the degree of unsaturation on various petroleum products and checking the results with other methods.

Effectiveness of Laboratory Rectifying Columns[1]

By M. J. Marshall and B. P. Sutherland

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, B. C.

Values have been obtained for the effectiveness of a lagged Hempel column with reflux, with a view to determining the relation between this quantity and reflux ratio. At the same time, similar data have been obtained for the same column unlagged and without reflux. These two sets of data have been compared on a common basis to obtain values for the relative effectiveness of the two arrangements.

THE ordinary unfilled laboratory column separates almost entirely by partial condensation, while a filled column of the Hempel type separates by partial condensation at the top and in addition rectification for a short distance from the bottom. Now it is generally considered that partial condensation is neither so effective nor so efficient as rectification. Experimental evidence of the superior efficiency of rectification over partial condensation has been obtained by Leslie.[2]

It is evident, therefore, that the effectiveness of the ordinary laboratory column can be vastly improved by lagging the sides and providing reflux, as in commercial columns. Laboratory columns of this type have been devised by Leslie[3] and Peters.[4]

Although a number of investigators have obtained values for the effectiveness of small packed columns, largely for the purpose of verifying distillation equations, no numerical values are available for the relative effectiveness of the ordinary laboratory column and the lagged column provided with reflux.

Theory

Lewis[5] has derived an equation giving the change in composition of a volatile mixture from plate to plate in a rectifying column as follows:

$$x_{n+1} = y_n - \frac{P}{O}(x_e - y_n) \qquad (1)$$

where x_{n+1} = mol fraction of the more volatile component in the liquid on the $n + 1$th plate
y_n = mol fraction of more volatile component in the vapor over the nth plate
x_e = mol fraction of the more volatile component in the distillate
P = mols of distillate per unit time
O = overflow in mols per unit time from one plate to the other
V = mols of vapor per unit time passing up the column

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[1] Received September 27, 1926.

[2] "Motor Fuels," p. 120, Chemical Catalog Co., 1923.

[3] *Ibid.*, p. 555.

[4] THIS JOURNAL, **18**, 69 (1926).

[5] THIS JOURNAL, **14**, 492 (1922).

Peters[6] used this relation in the form

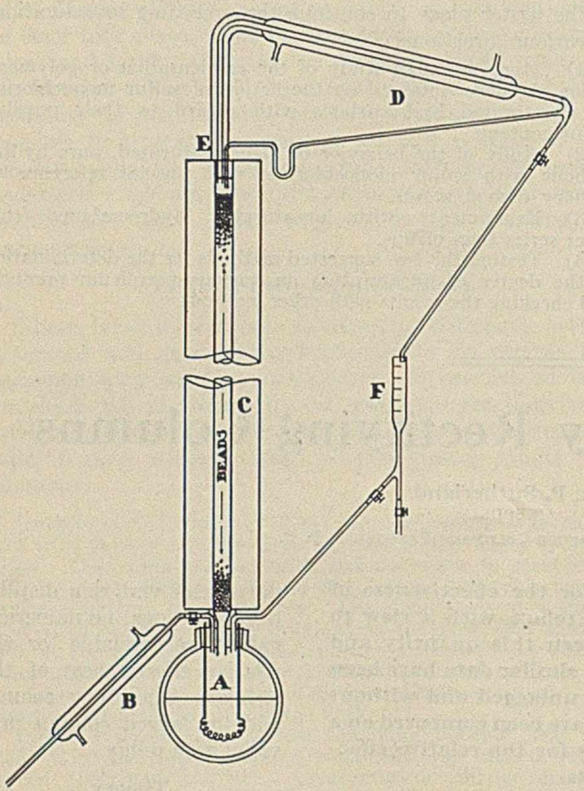
$$x_{n+1} = \frac{y_n - (1 - \rho)x_c}{\rho} \qquad (2)$$

where $\rho = \frac{O}{V}$. The reflux ratio of Lewis and others is defined as $\frac{O}{P}$, and is equal to $\frac{\rho}{1 - \rho}$.

By means of this equation the number of theoretical plates necessary to separate a mixture between any given compositions can be determined. If the column is of the packed type, then the total length divided by the theoretical number of plates gives the height equivalent to a theoretical plate. This quantity, called the H. E. T. P. by Peters, was calculated by him for ring packings of various sizes. These results will be referred to later.

Experimental Details

An alcohol-water mixture was chosen as the most suitable medium because so much study has been devoted to the distillation of this mixture, and also because analysis can readily be made by density measurements. The vapor-liquid composition data used were those calculated by Lewis[7] from the data of Wrewsky.[8] This curve agrees fairly well with the data of Bergström[9] and Blacher,[10] which were considered by Hausbrand[11] to be the most accurate values available at the time of publication. The density tables in the Smithsonian Physical Tables (6th edition) were used to determine the composition.



The liter Pyrex flask, *A*, was covered with asbestos 0.25 inch (6 mm.) thick. The column *C* was a glass tube 0.827 inch (2.1 cm.) in diameter. The beads were of the ordinary Hempel variety with an average diameter of 0.213 inch (0.541 cm.) and filled the column to a depth of 39 inches (99.06 cm.).

Reflux was regulated by the pinchcock. The apparatus was run at constant reflux until equilibrium was established. The rate of distillation was then measured at *F* and samples collected from *B* and *F*.

Heat was supplied by passing 110-volt a. c. current through a bare nichrome wire at *A*. The input was measured by means of a wattmeter. The loss of heat through the walls of the flask was determined for various mixtures by noting the watts just necessary to distil over a very small amount of liquid without the use of a column. This amounted to 14.7 calories per second. Correcting for this value, the heat ascending the column per unit time could be calculated.

One series of runs was made with the column covered with ordinary steam pipe lagging about 1.5 inches (3.8 cm.) thick, and the tube leading to the condenser covered with several thicknesses of asbestos paper. Another series was made with all this insulation removed and no reflux except that supplied by condensation on the walls of the column.

Calculation of Results

The following is a typical calculation (Run 7):

Time for 5 cc. distillate, 73 seconds
Specific gravity of distillate, 0.8114 = 92.4 per cent alcohol
Grams of distillate per second, 0.0556 gram
Latent heat of distillate (92.4 per cent alcohol), 230 calories per gram
Watts supplied to heating coil, 278 = 66.2 calories per second
Radiation loss from flask, 14.7 calories per second
Heat in vapor passing up column, 51.5 calories per second

$$\rho = \frac{O}{V} = \frac{51.5 - 230 \times 0.0556}{51.5} = 0.752$$

Mol fractions of alcohol in vapor and distillate are 0.344 and 0.8263, respectively, then from equation (2)

$$x_1 = \frac{0.334 - (1 - 0.752) \times 0.8263}{0.752} = 0.169$$

The mol fraction of alcohol in the vapor in equilibrium with this is 0.539 from the liquid-vapor composition curve. Applying equation (2) once more we get a value for x_2 and in the regular stepwise fashion arrive at 10.6 plates for the total separation obtained. Then H. E. T. P. is $\frac{39}{10.6}$ = 3.68 inches (9.35 cm.).

Results for Lagged Column

The H. E. T. P. values (Table I) vary slightly, although no trend is apparent with increase in vapor velocity, and only a very slight trend with increase in ρ. Unfortunately, conditions were such that high values of ρ coincided with high content of alcohol in the product. It is hard, therefore, to determine whether the trend is due to variation of the reflux ratio or the composition of the product. The authors have obtained rather low H. E. T. P. values for runs in which the composition of the product was over 93 per cent. These values are not reported in the present paper because of lack of agreement between duplicate runs. Peters also noticed variation of H. E. T. P. with the composition of the product, although he obtained H. E. T. P. above the average for this range. It seems more probable, therefore, that any variation of H. E. T. P. will be found to be due to variation of the composition of the product rather than variation of the reflux ratio. It is evident that more determinations of H. E. T. P. are necessary over this range. Because of the nature of the vapor-liquid composition curve at this point, a curve of proved accuracy must be used, and the experimental work must be done with considerable precision in order to obtain even reasonably accurate H. E. T. P. values.

Peters[6] obtained constant values of H. E. T. P. for acetic acid and water mixtures, using values of ρ between 0.8 and 1.0, while the present writers' H. E. T. P. are practically

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[6] THIS JOURNAL, **14**, 476 (1922).

[7] *Ibid.*, **12**, 496 (1920).

[8] *Z. physik. Chem.*, **81**, 1 (1912).

[9] *Jern-Kontorets Annaler, Bihang.*

[10] Private communication of Blacher to Hausbrand.

[11] "Industrial Distillation," p. 95, John Wiley & Sons, Inc., 1926.

constant for ρ values between 0.551 and 0.771. With alcohol and water mixtures, using $^1/_4$-inch rings, he obtained an H. E. T. P. of 3.65 inches (9.27 cm.) below 88 per cent alcohol and 4.2 inches (10.67 cm.) above this percentage. He found $^1/_4$-inch rings to be 73 per cent as efficient as the spheres. This would give an H. E. T. P. for the spheres 2.66 inches (7.42 cm.) below 88 per cent alcohol and 3.07 inches (7.80 cm.) above this figure. The average of the writers' values is 3.92 inches (9.96 cm.), and this can be considered as comparable with Peters' values above 88 per cent alcohol. While their beads are not strictly equivalent to either rings or spheres, it is evident that their average value approximates more closely to Peters' value for the rings than for the spheres.

In a recent paper Leslie and Geniesse[12] obtained constant H. E. T. P. for variable reflux ratio and variable vapor velocity, using chloroform and toluene mixtures. Calingaert and Huggins[13] did obtain variation in effectiveness for variable vapor velocity and reflux ratio with ammonia and water solutions, although they worked at extremely low concentrations. So, while there is a preponderance of evidence in favor of a constant effectiveness, nevertheless, more work must be done with various mixtures, covering a wide range of vapor velocities and reflux ratios.

Table I—Effectiveness of Lagged Column at Varying Reflux Ratio

RUN	$\rho = \frac{O}{V}$	PRODUCT	VAPOR VELOCITY	COMPOSITION: Product	COMPOSITION: Vapor in still	COMPOSITION: Liquid in still	NUMBER OF PLATES	H. E. T. P.	H. E. T. P.
		Gram/sec.	*Cal./sec.*	*Per cent alcohol by weight*				*Cm.*	*Inches*
1	0.551	0.0917	48.5	90.3	74.5	35.1	10.2	9.70	3.82
2	0.569	0.0268	14.7	90.5	75.7	39.2	9.2	10.76	4.24
3	0.585	0.0517	45.8	90.4	67.8	22.0	9.0	11.00	4.33
4	0.653	0.0628	41.1	91.6	73.3	31.7	10.3	9.60	3.78
5	0.734	0.0414	35.6	92.5	78.8	55.5	10.3	9.60	3.78
6	0.748	0.0402	37.1	91.7	46.8	6.0	9.2	10.76	4.24
7	0.752	0.0556	51.6	92.4	57.2	9.4	10.6	9.35	3.68
8	0.771	0.0284	28.5	92.5	43.6	5.6	11.1	8.91	3.51

The percentage of alcohol in both the liquid in the still and the vapor above it were determined for each run. These values are included in the tables. The vapor-liquid composition relations are just about what we would expect from the equilibrium curve. The still itself can therefore be regarded as a perfect plate, and allowance must be made for this rectification in the still when making practical calculations of necessary column lengths.

Study of Unlagged Column

The change in composition of a vapor passing through the unlagged column is undoubtedly due to a combination of rectification and partial condensation. It is evident that this could not be handled by any simple mathematical treatment. For our present purpose, however, this is not necessary. We can regard our unlagged column simply as a device in which vapor undergoes a change Δy in composition on passing through it. No assumptions need be made with respect to what goes on inside.

We know from experience that for any fixed composition, y_1, of entering vapor, that Δy will vary almost entirely with the rate of distillation. On the other hand, for the lagged column with reflux, Δy will vary with the reflux ratio and the rate of distillation. Either of these variables will be independent until priming occurs in the column. At this point one variable disappears and Δy varies as the rate of distillation only. That is, to each rate of distillation there corresponds a finite maximum reflux ratio. This point also represents the maximum separation attained by the lagged column for any fixed rate of distillation. It appears then that Δy for the two columns should be compared at equal rates of distillation with maximum possible reflux in the lagged column. It is evident that a direct comparison of the two values for Δy would have only qualitative significance. A quantitative comparison can be made in the following manner:

Suppose that we are operating the lagged column at its maximum reflux ratio with a certain rate of distillation. Suppose that the unlagged column gives us a certain separation Δy_1 for the same rate of distillation. We can calculate the number of theoretical plates n_1 of the lagged column which would be required, at the maximum reflux ratio, to give the same separation as that attained by the unlagged column. The ratio of this number of plates to the total number of theoretical plates in the column would be a measure of the relative effectiveness of the two columns under comparable conditions. We have shown that the lagged column corresponds to 9.95 perfect plates, and this value can be considered to be independent of the reflux ratio and vapor velocity. Then the relative effectiveness of the two columns would be $\frac{n_1}{9.95} \times 100$ per cent. For some purposes this relation can be more effectively expressed as $\frac{9.95}{n_1}$ which is the improvement effected in the unlagged column. We will call this quantity the "improvement factor."

It should be noted that n is a measure, not of the separation attained, but rather of the relation between the actual and possible separations under similar conditions. In cases where separations only are being compared, as, for instance, in comparing different types of partial condensation columns, relative separations can be determined by calculating the number of plates at total reflux corresponding to the measured separation. Such a value is identical with the number of perfect redistillations without column necessary to give the measured separation. This can be determined by stepping off points on the vapor-liquid composition curve between initial and final concentrations and taking the arithmetic mean for fractions of a plate. For small separations involving less than one plate, standard integration curves would be more accurate. Values obtained by the former method are included in Table III.

It should be noted in this connection that Young[14] measured the relative effectiveness of various partial condensation columns by noting the number of redistillations, using an empty tube as a column, necessary to give the same separation as that attained in the column under examination. As his standard still and column would be roughly equivalent to a finite number of plates, his relative values, after correction for rectification in the distillation flask, should be comparable with any obtained by the method outlined above. The authors have found no other data on partial condensation columns in the literature which can be interpreted in similar terms.

The maximum ρ values corresponding to various rates of

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[12] This Journal, **18**, 590 (1926).

[13] *Ibid.*, **16**, 584 (1924).

[14] "Fractional Distillation," p. 146 (1922).

distillation have been determined experimentally and are given in Table II. Values of ρ for intermediate rates were obtained by interpolation.

Table II—Variation of Maximum Reflux with Rate of Distillation

$\rho = \frac{O}{V}$	Product *Gram per second*
0.85	0.025
0.80	0.040
0.75	0.065
0.70	0.075
0.65	0.085
0.60	0.100
0.55	0.115
0.45	0.150

Table III—Relative Effectiveness of Unlagged and Lagged Columns

Run	$\rho = \frac{O}{V}$		Product	Composition			Equiv. Plates at Max. Reflux (n_1)	Relative Effectiveness	Improvement Factor	Number of Plates at Total Reflux
	Actual measured	Max. used in calcn.		Product	Vapor in still	Liquid in still				
			Gram/sec.	*Per cent alcohol by weight*				*Per cent*		
9	0.644	0.81	0.0354	68.0	32.2	3.9	1.0	10.1	10.0	0.8
10	0.565	0.78	0.0482	90.5	77.3	47.9	4.2	42.2	2.4	3.1
11	0.485	0.77	0.0566	26.9	14.0	1.9	0.2	2.4	41.5	0.2
12	0.406	0.72	0.0708	89.6	74.1	34.0	4.2	42.2	2.4	2.8
13	0.439	0.70	0.0744	89.7	80.3	62.5	3.7	37.2	2.7	2.4
14	0.415	0.67	0.0808	89.3	82.6	69.6	2.9	29.2	3.4	1.9
15	0.344	0.64	0.0894	82.2	69.6	23.0	1.9	19.1	5.2	1.0
16	0.365	0.55	0.1120	58.0	46.6	6.2	0.3	3.3	29.3	0.3
17	0.368	0.44	0.1530	86.8	82.0	67.4	2.2	22.1	4.5	1.0
18	0.204	0.44	0.1544	84.0	74.7	35.1	2.2	22.1	4.5	1.0
19	0.182	0.40	0.1845	77.5	69.0	22.5	0.9	9.1	11.1	0.6

Taking Run 13 as an example, we have 0.0744 gram of product per second. This corresponds to a maximum ρ value of 0.70. The vapor entering the column was 80.3 per cent alcohol, and that leaving it 89.7 per cent. Substituting these values in equation (2) we find that this separation corresponds to 3.7 plates of a perfect column. Then the relative effectiveness is $\frac{3.7}{9.95} \times 100 = 37.2$ per cent, while the improvement factor is $\frac{9.95}{3.7} = 2.7$. Values obtained for the unlagged column are tabulated in Table III.

The improvement factor reaches a very considerable value in some cases, being highest for low concentrations of alcohol. Other conditions remaining constant, the improvement factor would also vary with the length of the column. However, the authors have not considered it advisable to investigate columns of various lengths, as the object of the investigation is simply to develop a method for obtaining an approximate estimate of the improvement effected in a laboratory column of average length. The values in the last column give a measure of the separation attained in terms of a common unit. The separation is low for high rates of distillation, as would be expected, although it is rather surprising to note that the range over which distillation takes place has an even more marked effect on this quantity.

It is evident that the separation attained in the short unlagged Hempel columns used in most laboratories would be even less than the figures given, so that in many cases the larger part of the observed separation would be due to simple rectification in the distilling flask alone.

For sharp cuts such columns as those developed by Leslie[3] or Peters[4] are recommended. For the purification of quantities of material, however, the experimental column, described herein, suitably modified, would be equally effective. Comparatively large quantities of material might be easily handled by introducing the feed at an intermediate point on the column and operating as a continuous still.

Summary

1—The height equivalent to a theoretical plate for alcohol-water mixtures, with a filling of beads 0.213 inch (0.541 cm.) average diameter, was found to be 3.92 inches (9.96 cm.).

2—This height was found to be practically constant for variable reflux between $\rho = 0.53$ and $\rho = 0.77$, and for distillates up to 92.5 per cent alcohol. It was also found to be independent of the vapor velocity in the few cases where this quantity was varied greatly.

3—The effectiveness of a properly lagged Hempel column 99 cm. long provided with the maximum reflux is 2.4 to 41.5 times as great as that of the same column unlagged and operating at the same rate of distillation. This improvement factor increases for low alcohol concentrations and high rates of distillation.

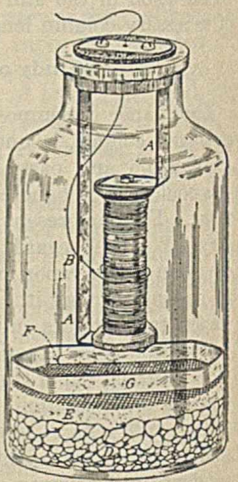
Protection of Iron Wire Used for Standardization[1]

By Marion Hollingsworth

The Ohio State University, Columbus, Ohio

THE annoyance caused by the rusting and entangling of C. P. iron wire used for standardization purposes has led to the development of the apparatus shown in the accompanying sketch.

For the ordinary $^1/_4$-pound spool of wire a wide-mouth bottle of 1.5 to 2 liters capacity is a convenient size. The metal strip, *A*, supporting the spool is about an inch wide, and contains holes as shown in the drawing, B being located opposite or, better, a little above the center of the spool. The strip is made so that it can be readily inserted with the spool through the neck of the bottle.



A layer of lime, *D*, covers the bottom of the bottle. On top of this is a layer of cotton, *E*. The cotton and lime are held in position by a wire gauze, *F*, which in turn is secured by the spring, *G*. To make the disk of wire gauze easy to insert, imagine two parallel cords that will divide a diameter perpendicular to them into three almost equal parts. Cut the gauze on either end of these cords, leaving about an inch for support. The gauze can then be folded on these cords, passed through the neck of the bottle, and again straightened.

A test spool of wire kept for three years in such a container shows no sign of rusting.

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[1] Received March 4, 1927.

The Oil from Port Orford Cedar Wood[1]

By F. H. Thurber and L. J. Roll

Oregon State College, Corvallis, Ore.

An ANALYSIS and some observations on the properties of Port Orford cedar wood oil (*Chamaecyparis lawsoniana* (*Murr.*) *Parlatore*) were made by Schorger.[2] The sample that he analyzed was four years old and was obtained from selected resinous pieces of wood. It perhaps was not a representative sample, and this may account for the wide variation between the present writers' results and those of Schorger. However, contrary to the statement in Schorger's paper, it should be noted that, although the oil has some physiological effect as a diuretic, its action is not noticeable enough to prevent continuous operation on this kind of timber in the lumber mills.

The oil from Port Orford cedar wood was distilled with steam, then dried, and carefully fractionated. Each of the following fractions, obtained from the distillate, is named from the chief component which it contained: *d*-α-pinene, 45.7 per cent; *d*-limonene, 3.2 per cent; *d*-borneol, 26 per cent; *d*-cadinene, 21 per cent; *l*-cadinol, 3.9 per cent.

The following compounds were isolated and purified: (1) *d*-α-pinene (probably isomeric with *d*-α-pinene isolated from American turpentine oil); (2) *d*-borneol; (3) *d*-cadinene.

This oil is now being manufactured on a commercial scale at the Western White Cedar Lumber Company's Mill at Marshfield, Ore. Port Orford cedar is native only to northwestern California and southwestern Oregon. The lumber from the mill is used in the manufacture of storage battery separators and in construction work of various types in which the timber may be subjected to the action of bacteria or to the ravages of termites. The dust from the saws is conveyed to large vats arranged for steam distillation The vats are 5 feet in diameter and are constructed of wooden staves 2 inches thick and 16 feet high. Steam under a boiler pressure of 110 pounds is passed through the sawdust for 60 minutes. By this procedure a yield of approximately 1.6 per cent of oil is obtained from the wood. The temperature remains constant (100° C.) throughout the distillation, and the pressure in the vats, noted by means of a steam gage rarely exceeds one pound.

The experiments here described were undertaken with two objects in view: (1) to obtain a more accurate analysis of the oil than is now available in the literature; (2) to isolate and purify some of the more common compounds that are commercially important. Both of these objects were attained.

The crude oil has the following physical constants: color, light brown; the odor differs from that of cedar oil produced in the eastern part of the United States, being somewhat similar to the odor of a mixture of pinene and borneol; d_{20}, 0.8913; n_D^{20}, 1.4760; $[\alpha]_D^{20}$, +46.68; acid value, 0.19; ester value, 19.3; ester value after acetylation, 88.3. The ester values before and after acetylation are equivalent to 5.1 per cent of bornyl acetate and 20.4 per cent of free borneol. These values are taken up in detail under the discussion of borneol in the latter part of the paper.

Fractionation of Port Orford Cedar Oil

Steam Distillation—Nineteen hundred and seventy cubic centimeters of crude oil were distilled with steam over 10 per cent sodium carbonate solution; after the completion of this process approximately 15 grams of a gummy mass remained in the distillation flask and a total of 1905 cc. of oil were recovered. Some of the distillate was lost because of (1) the volatility of the warm oil as it came from the condenser, (2) its slight solubility in the large amount of water obtained from the condensed steam, and (3) the small amounts of the oil adhering to the apparatus used in separating the oil from the water.

After the distillation the oil had a slight cloudiness due to its water content, but a water-white product resulted after the cloudy oil had stood over anhydrous sodium sulfate for a day. The last traces of water were removed from the oil by heating it to 150° C. for a few minutes in a flask connected with a condenser. The dry oil had a volume of 1871 cc. It was carefully fractionated in the apparatus which is mentioned below.

First Fractionation—There is some decomposition of the ester, bornyl acetate, which is present in the oil when it is heated to a temperature higher than 180° C. For this reason the distillation was carried out at atmospheric pressure until the temperature of the vapor reached 178° C. At that point the source of heat was removed, the pressure reduced to 14 mm., and the fractionation completed at reduced pressure. A column stillhead patterned after the one described by Loveless[3] was used in the fractionation.

From the results of preliminary distillations it was expected that the oil could be separated into four rather sharply defined fractions—namely, pinene, b. p., 155–159° C.; *d*-limonene, b. p., 170–178° C.; borneol and bornyl acetate, b. p., 100–122° C. at 14 mm.; and cadinene, b. p., 132–138° C. at 14 mm. On the whole, the expected results were obtained; however, the *d*-limonene fraction was not definitely defined and a fraction with a boiling point higher than that of cadinene was found to be present. After a number of distillations fourteen fractions were obtained, the boiling points and other physical constants of which are given in Table I.

Table I—First Fractionation of Port Orford Cedar Oil

Fraction	Boiling Point[a] ° C.	Volume Cc.	Per Cent of Total Volume	n_D^{20}	$[\alpha]_D^{20}$	d_{20}
	Crude oil	1871	100	1.4760	+46.68	0.8912
1	155–159	742	39.65	1.4644	+52.98	0.8582
2	159–161	52	2.78	1.4662	+56.18	0.8576
3	161–167	63	3.36	1.4664	+58.45	0.8604
4	167–178	44	2.35	1.4704	+60.81	0.8618
5	78–100	63	3.36	1.4748	+51.87	0.8928
6	100–110	123	6.66	1.4764	+47.99	0.9376
7	110–118	267	14.24	1.4742	+53.55	0.9307
8	118–122	29	1.55	1.4733	+25.15	0.9150
9	122–132	58	3.10	1.4848	+21.77	0.9122
10	132–136	266	14.20	1.5025	+40.97	0.9178
11	136–145	24	1.28	1.5058	+34.62	0.9367
12	145–155	13	0.69	1.5058	+15.57	0.9436
13	155–170	17	0.91	1.5108	−10.54	0.9727
14	170–180	38	2.03	1.5075	...	0.9581
15	Losses	72	3.84	...	...	...

[a] The first four fractions were fractionated at 760 mm. and the rest at 14 mm. pressure.

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[1] Received February 14, 1927.

[2] This Journal, **6**, 631 (1914).

[3] This Journal, **18**, 826 (1926).

Curve 1 in Figure I is made up from the boiling point–percentage composition data given in Table I. Curve 2, Figure I, was made up from data obtained by noting the boiling point range for each 10 cc. of distillate collected when a previously dried 250-cc. sample of the crude oil was distilled at atmospheric pressure. The same breaks are distinguishable in both curves, but in curve 1 the breaks are much more abrupt because of the careful fractionation carried out.

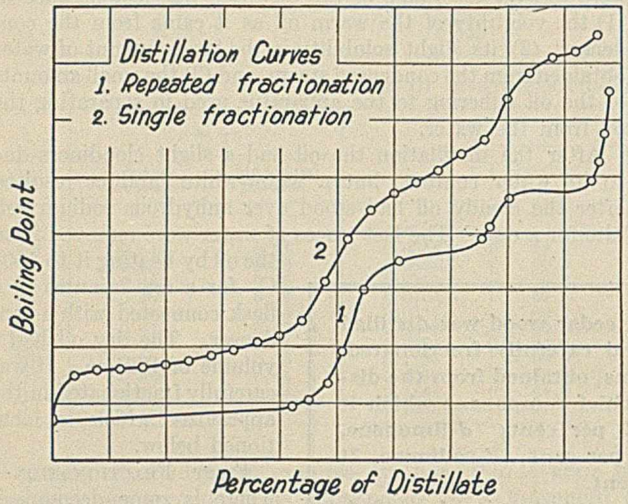

Figure I

Fractionation over Sodium—The four fractions mentioned above are all clearly defined on the curve, with the exception of *d*-limonene. Since the break in the curve was not definite in the section in which this compound should occur, it was thought that the distillate obtained in fractions 2 to 5 might be composed of a mixture, possibly of pinene, *d*-limonene, and borneol. For this reason a second distillation was made by combining fractions 2 to 5 and distilling the mixture over sodium to remove the borneol. The remaining components of the mixture were then readily separated by fractional distillation, as is shown in Table II.

Table II—Fractionation over Sodium
(Total volume, 222 cc.; fractions 2 to 5, Table I)

Fraction	Boiling Point °C.	Volume Cc.	Fraction	Boiling Point °C.	Volume Cc.
1	155–159	80	6	122–132 (14 mm.)	3
2	159–167	9	7	132–145 (14 mm.)	27
3	167–178	34	8	145–170 (14 mm.)	3
4	78–100 (14 mm.)	15	9	Combined with sodium (detd. by diff.)	46
5	100–122 (14 mm.)	5			

An attempt was also made to separate fraction 9 (Table I) into its components by distillation over sodium. Some of the distillate came over above 132° C. at 14 mm., indicating the probable presence of cadinene, but the decomposition was so great that accurate results cannot be reported. After the redistribution of the distillate produced by the second fractionation, the curve shown in Figure II was constructed. In making the curve, fraction 9, Table II, was added to the borneol portion, b. p. 100–122° C. at 14 mm., since the sodium undoubtedly combined with the alcohol content of the oil.

The breaks in this second curve are more definite than those shown in the curve in Figure I. They show the presence of five fairly well defined fractions. From the values given in Tables I and II, these fractions may be seen to have the boiling points and percentage composition given in Table III.

Analysis of Port Orford Cedar Oil

Analysis of each of these final fractions (Table III) was now made. The chief components of each fraction were identified and also isolated and determined quantitatively whenever it was possible. The methods used and the results obtained are given below.

d-α-Pinene (Fraction 1; b. p., 155–159° C.; volume 822 cc.)—The crude pinene fraction was purified by distillation over sodium; 64 per cent of the original 822 cc. came over at an almost constant boiling point (156–156.5° C.). This constant boiling fraction was considered to be a pure sample. It had the following physical constants; b. p., 156–156.5° C.; d_{20}, 0.8584; n^{20}_{D}, 1.4608; $[\alpha]^{20}_{D}$, +53.01. The constants reported by Schorger[2] were b. p., 156–156.1° C.; d_{15}, 0.8631; n^{15}_{D}, 1.4684; $[\alpha]^{20}_{D}$, +51.52. (Short-scale thermometers were used in checking all melting points and boiling points reported.) The specific rotation of pinene obtained from this oil is of interest because it is higher than the specific rotation of any sample of pinene previously reported. This pinene does not form a trace of the inactive crystalline nitroso chloride compound. Since the formation of this derivative is a characteristic property of nearly all samples of *d*-α-pinene, it is probable that this product is a pure *d*-α-pinene isomeric with the ordinary form of α-pinene, which is isolated from American turpentine oil. That the compound was a *d*-α-pinene was determined by the preparation of pinene hydrochloride (m. p. 126–127° C.), by saturating the oil at a temperature of 5–15° C. with dry hydrochloric acid gas, and by the preparation of α-pinonic acid (m. p. 68° C.). The melting point reported in the literature for α-pinonic acid (prepared from *d*-α-pinene) is 67–69° C.

Method of Preparation. An emulsion of 50 grams of pinene in 300 cc. of water was gradually added to 120 grams of potassium permanganate contained in a liter of water. The mixture was cooled in an ice bath and stirred continuously during the addition. After completion of the oxidation the manganese sludge was removed by filtration; the filtrate was saturated with carbon dioxide gas and distilled with steam to remove unoxidized products. The liquid was evaporated in a current of carbon dioxide to a volume of 400 cc. and was then extracted with two 50-cc. portions of ether. The pinonic acid was set free from the potassium salt by the addition of dilute sulfuric acid. After extraction with ether and recrystallization from petroleum ether, the acid melted at 68° C.

No trace of pinonic acid was noted, which indicates that β-pinene is not a component of the oil. From these tests, and from the results obtained by fractional distillation, (Table III), approximately 46 per cent of *d*-α-pinene is shown to be present in the oil.

Table III—Final Fractionation of Port Orford Cedar Oil
(Total volume, 1799 cc.; fractions 1 to 14, Table I)

Fraction	Boiling Point °C.	Fractions from: Table I	Fractions from: Table II	Volume Cc.	Per Cent of Total Volume
1	155–159	1	1	822	45.7
2	159–100 (14 mm.)	...	2–4	58	3.2
3	100–122 (14 mm.)	6–8	5 and 9	470	26.1
4	122–145 (14 mm.)	9–11	6–7	378	21.0
5	145–180 (14 mm.)	12–14	8	71	3.9

d-Limonene (Fraction 2; b. p., 159–178° C. and 78–100° C. (14 mm.); volume 58 cc.)—This fraction does not contain a high percentage of *d*-limonene, for a large amount of gummy residue remained in the flask after the distillation of the sample over sodium. In this fractionation a small portion (b. p., 170–176° C.) was obtained which had a characteristic lemon-oil odor and formed a tetrabromide (m. p., 124° C.) when dissolved in glacial acetic acid and treated with bromine. In this fraction, which makes up approximately 3 per cent of the original oil, *d*-limonene is shown to be present.

d-**Borneol** (Fraction 3; b. p., 100–122° C. (14 mm.); volume 470 cc.)—Since borneol is a compound which crystallizes readily, it might be expected that a solid would separate from this fraction on refrigeration. However, a sample when cooled to −15° C. did not yield a trace of solid material. Two other refrigeration experiments were tried.

(1) A nearly constant boiling point fraction (104–107° C., 13 mm.) was refrigerated for a 2-hour period.

(2) A sample of the oil (b. p., 104–107° C., 13 mm.) which had been previously saponified with alcoholic potash was also refrigerated.

In both cases negative results were obtained.

To isolate borneol it evidently is necessary to separate it from the liquid constituents of the oil. The isolation was finally accomplished by means of the preparation of the acid phthalate. The methods used in the preparation of the acid phthalate and in the separation of borneol are described briefly below, since borneol had never been isolated from Port Orford cedar oil up to the time of the carrying out of these experiments.

Three hundred grams of crude oil were hydrolyzed by refluxing for 1 hour with 25 grams of sodium hydroxide and 30 cc. of 80 per cent alcohol. The hydrolyzed product was washed with water, then dried, and the borneol present changed to the acid phthalate by heating the oil to 160° C. for 16 hours, with 100 grams of phthalic anhydride. After the heating period, the reaction product was poured into 150 cc. of water and an excess of sodium carbonate added to produce the soluble sodium salt of bornyl acid phthalate. The oil which had not reacted with phthalic anhydride formed a layer on top of the water. It was separated from the water by decantation, the last traces of oil being removed by extraction of the water solution with petroleum ether. The insoluble phthalic acid ester was then obtained by acidifying the solution with 50 per cent sulfuric acid; bornyl acid phthalate separated as an oily layer, which crystallized on cooling. A small portion of this product, after recrystallization from 50 per cent alcohol, melted at 164° C.; melting point for bornyl acid phthalate reported in the literature, 164.5° C. An excess of 20 per cent sodium hydroxide was added to the remainder of the ester and the borneol, which soon separated in the form of an oil, was removed by steam distillation.

After two recrystallizations from petroleum ether, 18 grams of borneol with the following physical constants were obtained: m. p., 201° C., m. p. after sublimation, 201° C.; $[\alpha]^{20}_{\mathrm{D}}$, +32.6, in 10 per cent alcohol solution, in a l-dc. tube, +3.26. Constants reported for *d*-borneol in the literature m. p., 203–204° C.; $[\alpha]^{20}_{\mathrm{D}}$, +37.6–39.5.[4] After the petroleum ether was removed by evaporation, 15 grams of a liquid which would not crystallize, b. p., 98–129° C. (13 mm.), were obtained. The major portion of this product distilled between 104–107° C. (13 mm.) That this is a pure alcohol with a molecular weight equal to that of borneol is shown from the acetylation values given in Table IV.

A part of the borneol present in the oil was destroyed during the fractionation. For this reason a second portion of the crude oil was dried and distilled to obtain a new sample for use in the quantitative estimation of borneol. The method outlined below, which is essentially the one described by Martin,[5] was used in the determination of borneol and borneol acetate:

Five cubic centimeters of the oil were heated with an excess (15 cc.) of acetic anhydride to 145–150° C. for 3 hours. The acetylated oil was then washed with water and 10 per cent sodium carbonate solution to free it from acid. After careful drying, a weighed portion was saponified by refluxing it for one-half hour with alcoholic potassium hydroxide solution. Saponification values before and after acetylation are given in Table IV.

Table IV—Saponification Values

Substance	Sample	0.4140 *N* KOH	0.2540 *N* HCl	Alcohol Calcd. as Borneol	Bornyl Acetate	Cadinol
	Gram	*Cc.*	*Cc.*	*Per cent*	*Per cent*	*Per cent*
Acetylated crude oil	1.3900	10	7.65	26.0	...	...
Unacetylated crude oil	1.0140	10	14.95	...	5.2	...
Liquid alcohol from phthalic acid ester	1.3000	20	6.55	99.75	...	...
Acetylated cadinol fraction	1.1400	10	10.8	19.9	...	28.3

It should be noted that the saponification values obtained on the crude oil include borneol, the secondary alcohol similar to borneol, and cadinol calculated as borneol. The values given in Table IV under cadinol are equivalent to 0.7 per cent of this compound when calculated as borneol content of the crude oil. The percentage of secondary alcohol present should then be decreased by this amount, which would leave 25.3 per cent of secondary alcohol, of which 5.2 per cent is present as the acetate and 20.1 per cent as free alcohol.

The total percentage of borneol and of liquid secondary alcohol present in the oil may be calculated by assuming that the percentage of solid *d*-borneol in the alcohol, which was not isolated as the phthalate, is identical to that separated rom the alcohol, which was isolated. If this assumption is correct, then there is a total of 13.8 per cent solid *d*-borneol and 11.5 per cent of a liquid secondary alcohol similar to borneol present in the oil.

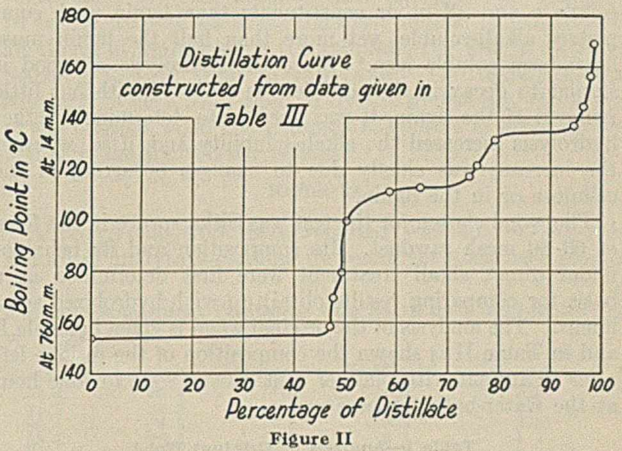

Figure II

d-**Cadinene** (Fraction 4; b. p. 122–145° C. (14 mm.); volume 378 cc.)—To prove the presence of cadinene in this fraction, the pure product was prepared in the following manner:

Two hundred grams of the oil, which had been dissolved in 400 cc. of dry ether and cooled in an ice bath, were saturated with dry hydrochloric acid gas. The product which separated after recrystallization from alcohol yielded 30 grams of cadinene dihydrochloride, m. p. 118° C. The cadinene was set free from the hydrochloride by heating the product on a steam bath for 4 hours with 100 grams of glacial acetic acid and 30 grams of anhydrous sodium acetate. The reaction mixture was poured into water and the oil which separated was washed with sodium carbonate solution, dried over anhydrous sodium carbonate, and fractionated.

Fifteen grams of cadinene having the following physical constants were obtained: b. p., 272–274° C. (760 mm.); d_{20}, 0.9255; n^{20}_{D}, 1.5065; $[\alpha]^{20}_{\mathrm{D}}$, +103.7. The constants for cadinene reported in the literature[6] are as follows: b. p. 272–275° C. (760 mm.); d_{20}, 0.9215; n^{20}_{D}, 1.5065; $[\alpha]^{20}_{\mathrm{D}}$ 105.5.

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[4] Parry, "The Chemistry of Essential Oils and Artificial Perfumes," 3rd ed., Vol. II, p. 134.

[5] *J. pharm. chim.*, [7] **23**, 168 (1921).

[6] Parry, *op. cit.* p. 73

Cadinene is shown to be present in this fraction of the oil which makes up 21 per cent of the original sample.

l-CADINOL (Fraction 5; b. p. 145–180° C. (14 mm.); volume 71 cc.)—Cadinol has been characterized by Semmler and Jonas.[7] It is a sesquiterpene alcohol with a boiling point about 15° C. higher than that of cadinene.

Practically all the alcohol in the cadinene fraction is cadinol, for this fraction did not react appreciably with phthalic anhydride when heated with it to a temperature of 160° C. If borneol or other secondary alcohols were present, an appreciable reaction would have been obtained. The cadinol fraction possesses a negative specific rotation, $[\alpha]^{20}_{D}$, 10.54, and makes up approximately 3.9 per cent of the total volume of the oil. As is shown in the table of saponification values, this fraction contains 28.3 per cent of alcohol calculated as cadinol.

Note—Further work on Port Orford cedar oil is now in progress in this laboratory.

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[7] *Ber.*, **47**, 2068 (1914).

Effect of Partial Hydrolysis on the Alkali-Solubility of Wood[1]

By L. F. Hawley and W. G. Campbell[2]

U. S. FOREST PRODUCTS LABORATORY, MADISON, WIS.

IT HAS been pointed out by Bray[3] that during the decay of wood by several different fungi the alkali-solubility of the residue rapidly increases. When the decay has resulted in a loss in weight of about 30 per cent, the alkali-solubility of the residue may amount to as much as 57 per cent. Bray did not determine how much of this alkali-solubility was due to lignin or how much to cellulose, but in certain cases, even if the assumption were made that the cellulose and all other constituents than lignin were completely alkali-soluble, yet more than half the lignin must have been soluble also.[4] Since the hydrolysis of wood is similar to decay in that cellulose is removed with but little removal of the lignin, it was decided to determine whether hydrolysis increased the alkali-solubility and, if so, whether the increase was chiefly due to changes occurring in the cellulose or in the lignin.

The wood chosen for the test was Sitka spruce in the form of 60–80 mesh sawdust. Its composition and its behavior under direct alkali treatment were first determined as a basis for comparing results obtained with hydrolyzed specimens. The analysis of the original wood is given in Table I, and in Table II is shown the composition of the residue left after treatment with one per cent caustic soda for one hour at the water-bath temperature.

Table I—Analysis of Original Wood

(Results on basis of weight of original dry wood)

	Per cent
Water-soluble	4.1
Ether-soluble	0.7
Alkali-soluble	12.0
Cellulose	62.5
Lignin	29.3
Methoxyl	4.8
Total pentosans	9.9
Pentosans not in cellulose	6.2

Table II—Analysis of Wood Residue after Treatment with 1 per cent NaOH for 1 Hour at 100° C.

(Results on basis of weight of original dry wood)

	Per cent
Loss on alkali treatment	13.7
Cellulose	59.2
Lignin	27.7
Methoxyl	4.3
Total pentosans	7.4
Pentosans not in cellulose	3.9

In each of the tables there is given a figure unusual in records of wood analysis—viz., "pentosans not in cellulose." Pentosans are determined on the total sample and then in the crude cellulose and are commonly recorded as "total pentosans" and "pentosans in cellulose." In the interpretation of the analytical data here presented, however, it was found that the value for the pentosans *not* in the cellulose was used frequently but the pentosans in cellulose not at all. The values for the former were therefore computed and used in the tables.

Experimental

In studying the alkali-solubility of the hydrolyzed wood, the general plan was to subject samples to different degrees of hydrolysis, analyze them, treat them with caustic soda, and analyze the residue. It has frequently been found, however, that on account of the difficulty of obtaining the same conditions throughout the mass, a chemical reaction which takes place with small quantities of wood, such as the sample for analysis, cannot be reproduced exactly when larger quantities are used. For this reason it was not attempted to hydrolyze enough wood so that the residue would be sufficient for an analysis, alkali treatment, and the further analysis of the residue. Instead, two samples were hydrolyzed under as nearly as possible the same conditions, one of which was used for intermediate analysis and the other for alkali treatment and final analysis. The analyses are shown in Tables III and IV. The loss in weight on hydrolysis as given in the second columns of these tables shows the relatively slight variation in the results obtained by the duplicate hydrolyses.

Table III—Analysis of Wood Residue after Treatment for 6 Hours with HCl at 100° C.

(All results expressed as percentages of weight of original wood)

Acid Concn.	Loss on Hydrolysis		Cellulose	Lignin	Methoxyl	Total Pentosans	Pentosans not in Cellulose
	Detd.	Calcd.					
0.05	6.0	12.5	55.6	28.9	4.6	7.5	5.1
0.25	10.0	13.9	55.3	28.7	4.7	6.4	4.2
1.5	17.6	23.9	49.0	26.7	4.7	4.4	3.5
8.0	22.9	27.4	46.2	26.4	4.2	3.4	2.1
15.0	36.2	42.5	32.7	26.3	4.3	0.9	0.6

Comparison of Results

In Table III the values headed "calculated loss in weight" are obtained by adding together the losses in cellulose, lignin, and "pentosans not in cellulose" as determined from the analyses of the original wood (Table I) and of the residue after hydrolysis, to which is also added the water-soluble in the original wood, on the assumption that this is all removed by hydrolysis. It is immediately noticeable that the calculated loss is always considerably higher than that

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[1] Received February 14, 1927.

[2] Commonwealth Fund Fellow.

[3] *Paper Trade J.*, **78**, No. 1, 58 (1924).

[4] Hawley and Wise, "The Chemistry of Wood," p. 299, The Chemical Catalog Company, Inc., New York, 1926.

actually determined. This difference can be explained only on the basis of some constituent being present in the partly hydrolyzed wood which was not isolated or determined as cellulose, lignin, or pentosans. Looking at the figures a little more closely, it is seen that while the sum of the four main constituents of the original sample of wood is 102.1 per cent, the sums of the three main constituents of the partly hydrolyzed samples all lie between 93 and 98 per cent of the weight of the residue. It is not intended to imply that the sum of the main constituents, such as cellulose, lignin, "pentosans not in cellulose," and water-soluble, should add up to exactly 100 per cent, but when the original wood totals more than 100 per cent and all the partly hydrolyzed samples to considerably less than 100 per cent, there is good reason to assume the presence of some material in the latter which was not present in the original and which does not show in any of the determinations. Whatever the substance, there is evidence that it is largely removed by the alkali treatment, in that the sums of the three main constituents determined on the alkali-treated wood (Table IV) all come very close to 100 per cent of the actual weight of residue, the extreme variations being between 99.2 and 100.5 per cent.

The figures in Table III, aside from the differences between determined and calculated losses, give little information that has not been available previously. The slight effect of hydrolysis on the amount of lignin and methoxyl and the continuous but not complete removal of the pentosans have been shown in previous work. This set of analyses is furnished mainly for comparison with Table IV in order to show the quantitative effect of the alkali treatment. Table IV gives the loss in weight of the duplicate samples on hydrolysis, their loss in weight on alkali treatment, and then the analysis of the residues after the alkali treatment. The alkali treatment was identical with that used in the analytical determination of the alkali-soluble content of the original wood—viz., treatment with 1 per cent sodium hydroxide at boiling water temperature for 1 hour.

Despite the small differences in the loss on hydrolysis between the second column of Table IV and the second column of Table III, some conclusions may safely be drawn from a comparison of the analytical determinations as they stand. It will be noticed that in every case the loss in weight due to the alkali treatment is made up of losses in each of the constituents determined, and this is also the case in the alkali treatment of the original wood (compare Table II and Table I). Moreover, in every case the amount of each constituent is less in Table IV than in the corresponding part of Table III. There is always a decrease in the constituents shown in Table IV as the severity of the hydrolysis increases, with the exception that the lignin during the first three hydrolyses remains practically constant.

Table IV—Analysis of Wood Residue after Treatment with HCl for 6 Hours and Subsequent Treatment with NaOH for 1 Hour at 100° C.

(All results expressed as percentages of weight of original dry wood)

Acid Concn.	Loss on Hydrolysis	Loss on Alkali Treatment	Total Loss Detd.	Total Loss Calcd.	Cellulose	Lignin	Methoxyl	Total Pentosans	Pentosans not in Cellulose
0.05	6.1	12.9	19.0	21.5	52.4	26.4	4.6	4.9	2.5
0.25	11.4	18.2	29.6	32.4	42.5	26.3	4.1	3.6	1.4
1.5	17.2	16.1	33.3	36.4	38.1	26.3	3.9	3.3	2.0
8.0	26.9	12.8	39.7	43.0	33.4	25.2	3.7	2.1	1.4
15.0	34.3	17.1	51.4	54.2	25.1	23.2	2.7	0.8	0.4

The largest variations between the two tables, however, are in the cellulose. Comparing the sixth column of Table IV with the fourth of Table III, it is seen that the alkali-solubility of the cellulose becomes very high after the last four hydrolyses, although there is no orderly increase in the alkali-solubility with increasing severity of hydrolysis. The lignin, on the other hand, is rendered only slightly soluble by the hydrolysis, and even after the most drastic treatment, with 15 per cent hydrochloric acid, only 3 per cent out of the 26 per cent present after hydrolysis is removed by the subsequent alkali treatment.

The methoxyl is removed by the alkali treatment in increasing amounts as the hydrolysis progresses. Although after the first three hydrolyses the amount of methoxyl decreases while the lignin determination remains stationary, this fact should not be considered an indication that the methoxyl was not a part of the original lignin, since the chemical method by which the lignin was isolated has been shown to result in the loss of a considerable portion of the methoxyl,[5] and it is in this relatively unstable portion that the principal methoxyl loss on alkali treatment may be supposed to occur.

The first mild hydrolysis, while without great influence on the alkali-solubility of the cellulose, lignin, and methoxyl, nevertheless has a considerable effect on the alkali-solubility of the pentosans. The 7.5 per cent pentosans in the hydrolyzed wood were decreased to 4.9 per cent by the alkali treatment, although in the original wood pentosans to the amount of 7.4 per cent were insoluble in alkali (Table II). This high alkali-solubility of the pentosans in the partly hydrolyzed wood was progressive as hydrolysis became more severe.

Unlike the action of decay, a partial hydrolysis of wood does not greatly increase the alkali-solubility of the residue. It is noticeable, however, that after hydrolysis the alkali-solubility is due to different constituents. In the original wood the alkali-solubility (Table II) is due more to the water-soluble constituents (4.1 per cent) than to any other one constituent, with the cellulose next (3.3 per cent soluble). In partly hydrolyzed wood the most soluble constituent at all stages of hydrolysis is the cellulose, the loss in cellulose reaching 12.8 per cent in two cases. The lignin, on the contrary, is very little affected by the hydrolysis, the lignin of the original wood being almost as soluble in alkali as the lignin in the hydrolyzed residues.

Remarks

Although the work here reported was not intended as a study of analytical methods for wood, yet it has been plainly shown that we must not rely too much on the absolute meaning of the accepted "determinations" of various wood components. Here we have a case where there is very evidently present in the partly decomposed wood a substance, probably a degradation product of the cellulose which is neither soluble in water nor isolated nor determined as cellulose, lignin, or pentosans. From the analytical results alone the presence of such a material might not have been suspected, and it was only the statistical data on the loss in weight and the composition of the original wood that threw a real light on the situation. A similarly undetermined material has been previously noted in partly decayed wood, and there again its presence was detected only because the analysis of the original wood was available and the loss in weight and the analyses of the partly decayed wood could be used in comparison. Frequently the loss of cellulose in partly decayed woods is considerably greater than the total loss in weight due to decay.[4]

A further example of the unsatisfactory condition of our analytical methods for wood is the fact that paper pulp

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[5] Ritter, This Journal, 15, 1264 (1923).

prepared by the alkali process, when bleached, shows an increase in the lignin determination, although it is quite evident that the bleaching process cannot manufacture lignin from some other constituent of wood pulp.[6] Another instance of a mistaken conclusion which might be made from comparative determinations of cellulose is found in the pulping of wood with neutral sodium sulfite.[7] On cooking aspen wood with sodium sulfite solution at low temperatures, the amount of cellulose based on the weight of the original wood is actually increased, if one is to credit the evidence afforded by the chlorination method of cellulose determination.

Summary

1—Although the principal effect of decay on wood, so far as removal of constituents is concerned, is apparently the same as a hydrolysis, yet these two processes differ in their effect on the alkali-solubility of the residue.

2—The total alkali-solubility of partly decayed wood is much greater than that of wood which has been hydrolyzed to the same extent (as shown by equal loss in weight).

3—The solubility of the lignin in alkali is very slightly increased by partial hydrolysis, whereas decay may render the lignin 50 per cent soluble.

4—The solubility of the residual cellulose is considerably increased by partial hydrolysis, but probably not to the same extent as it is by decay.

5—There is in partially hydrolyzed wood a material, probably a degradation product of the cellulose, which is not determined as cellulose, lignin, or pentosans. This material is soluble in 1 per cent sodium hydroxide.

[6] Hawley and Wise, *op. cit.*, p. 259.

[7] Rawling and Staidl, *Paper Trade J.*, **81**, No. 8, 49 (1925).

Manganese Interference in the *o*-Tolidine Test for Available Chlorine[1]

By Edward S. Hopkins

Department of Public Works, Bureau of Water Supply, Baltimore, Md.

It is an established fact that manganese salts produce the characteristic yellow chlorine color with the *o*-tolidine reagent. Buswell and Boruff[1,*] state that salts of this metal in as concentrated a solution as 11 p. p. m. manganese do not produce color. Solutions of a concentration of 100 p. p. m. manganese will not produce color provided the salt used is a stable one, such as sulfate or chloride, as any easily reduced salt of this and other metals will produce color with this reagent. As a matter of record a concentration of 0.01 p. p. m. manganese as potassium permanganate will give a color intensity corresponding to 0.03 p. p. m. chlorine and this color will increase in direct proportion to the concentration of the salt.

Two mols of potassium permanganate in alkaline solution produce 3 mols of available oxygen and, since chlorine is a univalent element and oxygen a bivalent one, 1 mol of potassium permanganate will equal 1.5 mols of oxygen or 3 mols of chlorine. Plotting the intensity of color produced, mol for mol in terms of chlorine readings, as in Figure 1, it is seen that this ratio is true and that the color is in direct proportion to the loosely bound oxygen. Such a condition would be expected from the studies of Ellms and Hauser.[2] This would indicate by analogy that the chlorine reaction is a similar one and is not a question of a color produced under definite pH conditions.

If a non-color-producing solution of manganese, sulfate, for example, is converted to the hydroxide by addition of a base, upon acidifying and adding the *o*-tolidine reagent 0.07 p. p. m. manganese will produce color. This phenomenon is true for all stable salts of manganese by actual experiment.

Experimental

Remembering the reaction involved in the Winkler[3] method for the determination of dissolved oxygen, it seemed quite likely that the absorption of oxygen by the manganese hydroxide was to be expected and that the reduction of these loosely bound oxides to manganous hydroxide or a stable compound by the *o*-tolidine produced the color. To prove this theory, manganous hydroxide was prepared with air excluded and the usual white precipitate was produced. By carefully keeping this precipitate under anaerobic conditions it was not possible to produce color with the *o*-tolidine reagent. Oxygen was absorbed very rapidly, the slightest addition of air changing the white hydroxide to a yellow hydroxide with subsequent production of color with the reagent.

Oxidation of this white precipitate with slight amounts of hydrogen peroxide gave color increase in proportion to the amount of oxygen present. Excessive amounts of oxygen produced a heavy black almost insoluble precipitate of hydrated manganese oxides containing excess oxygen. Upon addition of the reagent to these precipitates an intense yellow color was produced. In other words, the more oxygen absorbed the greater yellow color produced by the *o*-tolidine.

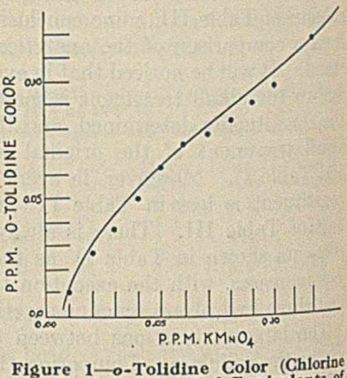

Figure 1—*o*-Tolidine Color (Chlorine Scale) Produced by Mol Equivalents of Oxygen from Alkaline Potassium Permanganate

Owing to the rapid oxidation of the manganese hydroxide by air, it was not possible to weigh accurate amounts and present quantitative data. A second experiment was performed using the same amounts of reagent as above, but the hydrogen peroxide and manganous hydroxide were allowed to stand together for 10 minutes. A greater color was produced and a heavier precipitate obtained after this time of contact than in the previous experiment.

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[1] Received January 28, 1927. Presented before the Division of Water, Sewage, and Sanitation at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

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

Manganese dioxide suspended in water will produce color with *o*-tolidine, which color can be also obtained in the clear filtrate from such an acidified suspension. Oxidation of this compound to MnOOH by chlorine gave an increase in color greater than that obtained from the salt originally.

It seemed desirable to learn if manganic hydroxide would produce color. This salt was carefully prepared as described in a standard textbook[4] and tested with the *o*-tolidine reagent, color being produced. On dissolving this hydroxide in sulfuric acid (1 to 4) and converting to manganous hydroxide by addition of sodium hydroxide, a greater intensity of color was produced than from the original manganic hydroxide owing to the absorption of oxygen from the air. This condition is shown in Figure 2. These curves are somewhat inaccurate since varying drops of the precipitate were placed in the *o*-tolidine solution and no exact weight could be obtained. Considering this condition and remembering that the curves in Figure 2 are plotted on a logarithmic scale, they agree very well with the one obtained from the carefully controlled potassium permanganate solution shown in Figure 1.

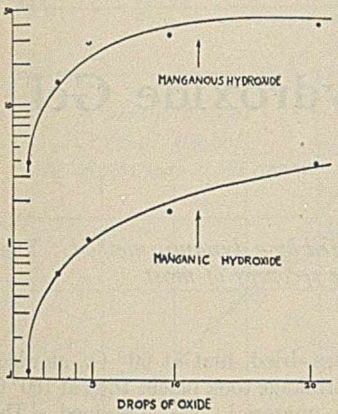

Figure 2—*o*-Tolidine Color (Chlorine Scale) Produced by Absorbed Oxygen in Manganous Hydroxide

It was noted that if hydrogen peroxide was added in excess to either the manganous or manganic hydroxide precipitates, these compounds were promptly reduced by the process of double oxidation to a stable compound and no color could be obtained with *o*-tolidine.

To conform with data obtained in relation to chlorine color[1] the pH's of all solutions were kept between 3.0 and 8.0, this test being made before the addition of the acid *o*-tolidine reagent.

It is of interest to note that the maximum intensity of color, measured quantitatively, developed by the manganese oxides was produced within 10 minutes and faded after 20 minutes. This corresponds with results obtained from chlorine tests.

To be certain that the color intensity was not affected by any possible production of chlorine from use of hydrochloric acid as a solvent for the *o*-tolidine, the solution was made with an equivalent amount of sulfuric acid since comparative tests produce similar color for the same amount of manganese compounds.

It is fairly evident that hydrated oxides of manganese containing more oxygen than manganous hydroxide are easily reduced and that the oxygen is loosely bound.[5] What form of manganese containing more oxygen than manganous hydroxide is necessary to produce this color?

Since chemical compounds combine in definite ratio, the first consideration was to vary the sodium hydroxide equivalents for forming the hydrated manganese oxides in order to learn if a complex oxide was formed. Two mols of sodium hydroxide combine with 1 mol of manganese to form 1 mol of manganous hydroxide, which upon standing 10 minutes gave color reading of 3.3 p. p. m. on the chlorine scale. A concentration of 50 mols sodium hydroxide to 1 mol Mn did not increase the color obtained, which shows that it is produced by oxygen absorption in the manganous hydroxide and is not a complex compound.

Discussion

Various formulas have been assigned to the hydrated manganous hydroxide precipitate when used as an oxygen absorbent. Studies of the Winkler method for the determination of dissolved oxygen by Theriault[6] present three separate formulas. Other textbooks—Smith,[4] Scott,[7] Dennis and Whittelsey[8]—assign different combinations. They all agree that the formulas indicate easily displaced oxygen atoms. This is confirmed by the experimental data obtained, and the reduction of such an oxide by the *o*-tolidine produces color.

One characteristic was noted. Upon acidifying the manganous hydroxide only those solutions giving a slight pink color, brown with some acids, or those containing definite brown or black particles, produced color with *o*-tolidine. When these particles were present they were insoluble in dilute sulfuric acid. On testing these colored solutions in a diffusion cell, it was found that they were colloidal solutions. That such a precipitate could be expected is shown by Bancroft[10] and Anargyros.[11]

Since it is known that the higher oxides of manganese are insoluble in sulfuric acid [7] and that it is possible for manganous hydroxide to "rapidly oxidize to a hydrated Mn_3O_4 and then be slowly converted to a colloidal hydrated Mn_2O_3,"[9] the theory may be advanced that the form of hydrated manganous hydroxide is the usual one present in natural waters.

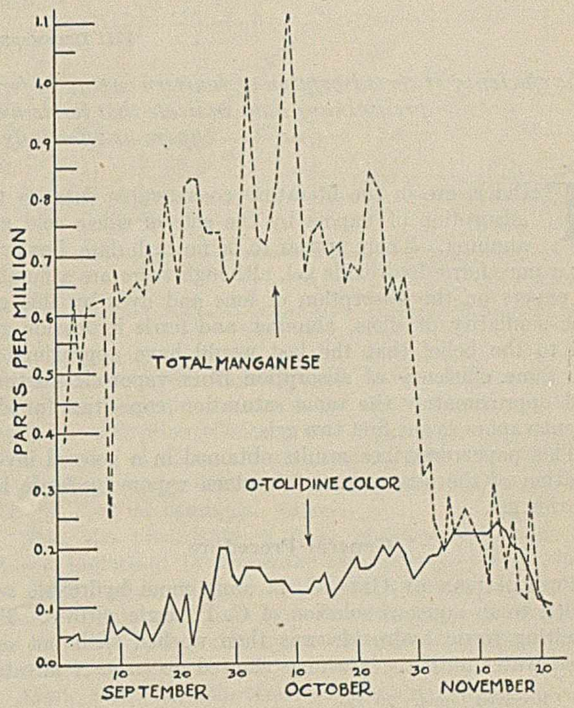

Figure 3—Plant Data—1925

Knowledge of these hydrated manganous oxides is essential to water purification, for Baylis[12] has shown the conditions under which manganese may occur in a water supply. Another factor would be the presence of manganous carbonate, which is soluble in free carbon dioxide. This was determined by test in the laboratory and confirmed by Robinson, Gardner, and Holmes.[13] This soluble manganese would be converted to the hydrated oxide by the action of air or dissolved oxygen in the water and produce color with *o*-tolidine, giving a false chlorine reading in the raw water. Such a condition is always present in this plant, the color ranging from a minimum of 0.02 to more than 0.3 p. p. m. Figure 3, showing the total manganese content of the raw water and the color resulting from same, is plotted from plant data for 1925. Since there is no relation between the trend of these curves it shows that the manganese is present as a combination of stable and unstable salts.

Even after filtration soluble manganese will be present from such a supply. Upon addition of alkali to reduce pipe corrosion by water containing free carbon dioxide, this manganese is promptly converted to the hydroxide with production of color by *o*-tolidine. This condition will give higher readings for chlorine than actually exists and therefore indicate security from a chlorine residual test, when as a matter of fact the actual amount of free chlorine present may be negligible.

Such a condition may easily exist in a small purification plant, with meager or no laboratory facilities, where greater reliance is placed upon the residual chlorine test than in the larger ones under constant bacteriological control. To call attention to these possibilities is the object of this paper.

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Adsorption of Vapors by Ferric Hydroxide Gel[1]

By J. H. Perry

1211 Delaware Ave., Wilmington, Del.

The efficiency of the adsorption of fourteen vapors by ferric hydroxide gel has been studied by a dynamic method. These preliminary data indicate that ferric hydroxide gel can be used for the recovery of most vapors as effectively as alumina and silica gels.

THERE are in the literature considerable data on the adsorption of vapors by the gels of silicic acid and alumina. There appear to be no such data, however, for a pure ferric hydroxide gel, although there are a number of papers on the adsorption of ions and dyes by this gel. The similarity of silica, alumina, and ferric hydroxide gels led to the belief that the last would have approximately the same efficiency of adsorption from vapor-air mixtures and approximately the same saturation capacities for different vapors as the first two gels.

This paper describes results obtained in a general investigation of the adsorption of fourteen vapors by ferric hydroxide gel.

General Procedure

PREPARATION OF GEL—C. P. ammonium hydroxide was added to an aqueous solution of C. P. ferric nitrate. The resulting ferric hydroxide was then washed with hot distilled water until the washings showed no trace of nitrates. The washed precipitate was dried, first at 60° C., at which temperature most of the shrinkage took place; then at 100° C. until a hard, glass-like material was obtained. This was broken up and screened. The material used for this series of experiments was 10–12 mesh.

ACTIVATION—Unless otherwise stated the gel was activated by passing through it dry carbon dioxide-free air heated to 230° C., the gel being heated in the same bath as the air. During the cooling from 230° to 25° C. no air was allowed to come in contact with the gel until the vapor-air mixture was started through it. This activation was repeated after each experiment, until the gel returned to its original weight, before being used in the adsorption experiments with another vapor. The duration of the activation varied but little after each experiment and was about 2 hours.

ADSORPTION—The general method of the experiments was the same as that described in a previous paper[2] and consisted in passing a vapor-air mixture at a definite rate (50 cc.

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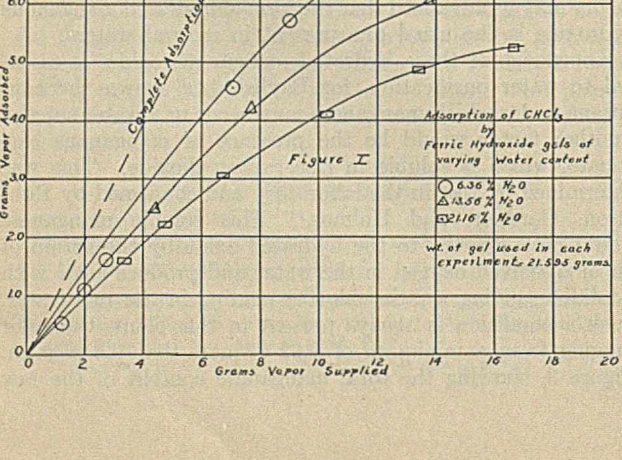
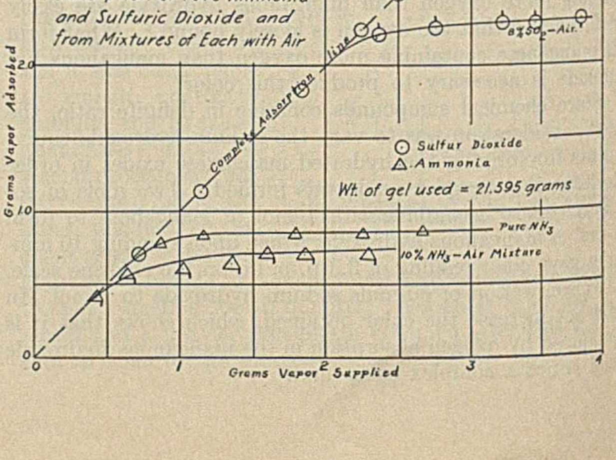
[1] Received January 20, 1927.

[2] Perry, *J. Phys. Chem.*, **29**, 1462 (1925).





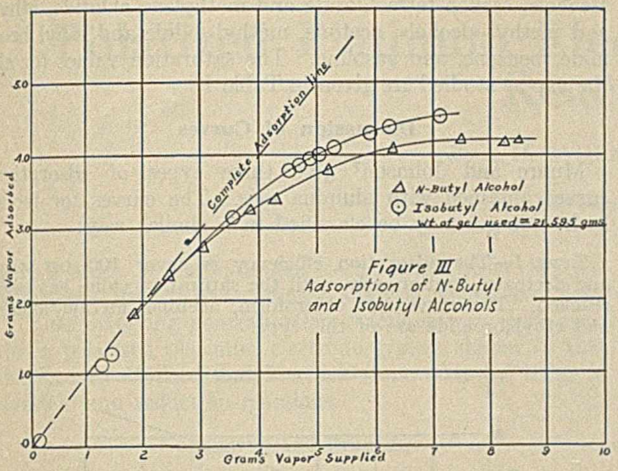


Figure III
Adsorption of N-Butyl and Isobutyl Alcohols

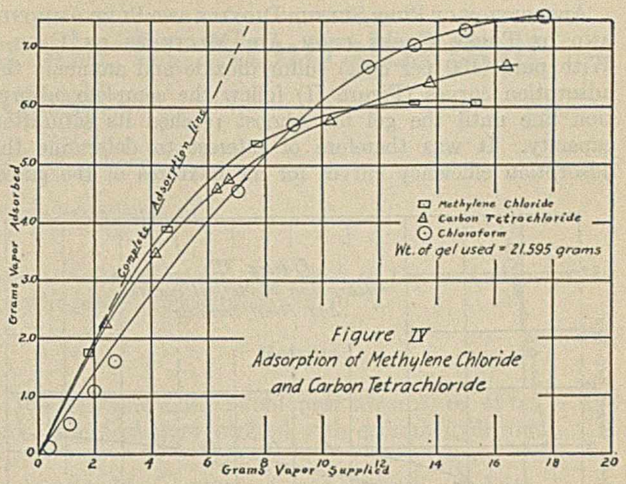


Figure IV
Adsorption of Methylene Chloride and Carbon Tetrachloride

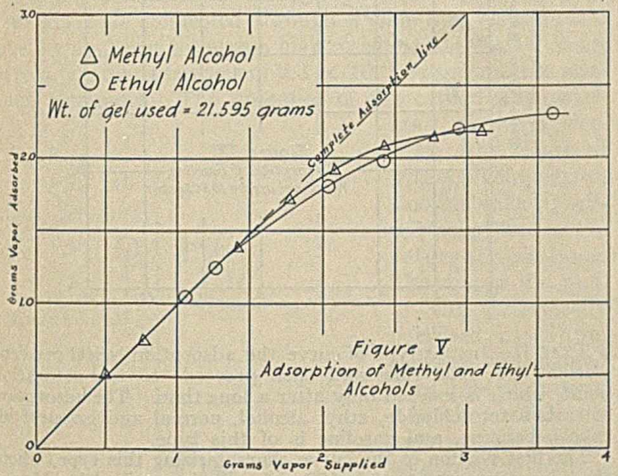


Figure V
Adsorption of Methyl and Ethyl Alcohols

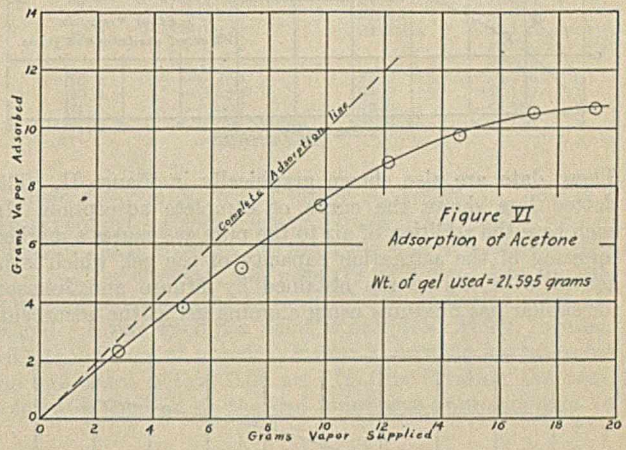


Figure VI
Adsorption of Acetone

per minute) through a U-tube containing a known weight and known apparent volume of the activated gel, which was thermostated at 25° C. The process of the adsorption was followed by weighing the saturator tubes and the U-tube containing the gel at frequent intervals. The vapor-air mixtures were prepared by passing dry, carbon dioxide-free air through two spiral saturating tubes (Vanier type) slowly enough to assure saturation of the air steam. The flow of air was controlled by a capillary flowmeter inserted in the line before the drying and carbon dioxide-removal tubes.

All chemicals were of C. P. grade and were not purified further unless otherwise stated. The temperature in each experiment was 25° C.

Results

Adsorptive Power of Ferric Hydroxide Gel as a Function of Its Water Content—The adsorptive power of a gel for vapor depends among other things upon its water content. Patrick and McGavack[3] measured the adsorption of sulfur dioxide by silica gels containing varying amounts of water and obtained the maximum adsorption capacity with gels containing from 4.86 to 9.97 per cent of water. In agreement with these results, Miller[4] has stated that the optimum water content of silica gel is from 5 to 7 per cent. Geldard[5] found that the amount of water in alumina gel had no effect on its adsorptive capacity. Dover and Marden[6] came to the same conclusion. Munro and Johnson,[7] however, have proved quite conclusively that the water content of alumina gel does influence markedly both its adsorption efficiency and final saturation capacity. The studies of these authors lead to the conclusion that the optimum water content of alumina gel is between 4.5 and 7.5 per cent of combined water.

With the precedents of both alumina and silica gels, it was important to determine the optimum water content of ferric hydroxide gel. Experiments similar to those of Munro and Johnson have been carried out using chloroform-air mixtures with ferric hydroxide gels containing various amounts of water.

Most, if not all, chloroform that can be bought, including the purest, contains ethyl alcohol, which retards or prevents decomposition. The chloroform used in this work was purified by agitation with concentrated sulfuric acid until the acid was no longer colored. It was washed with sodium carbonate, then successively with alkaline permanganate and distilled water, dried over sodium, and distilled.

Figure I shows the amounts of chloroform adsorbed from chloroform-air mixtures by three ferric hydroxide gels with varying water content.

The saturation values of these gels for chloroform are as follows:

Per Cent Water	Grams/10 Grams Gel
6.36	3.57
13.56	3.24
21.16	2.47

Unless otherwise specified, all experiments that follow were carried out using a ferric hydroxide gel containing 6.36 per cent of water.

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[3] *J. Am. Chem. Soc.*, **42**, 946 (1920).

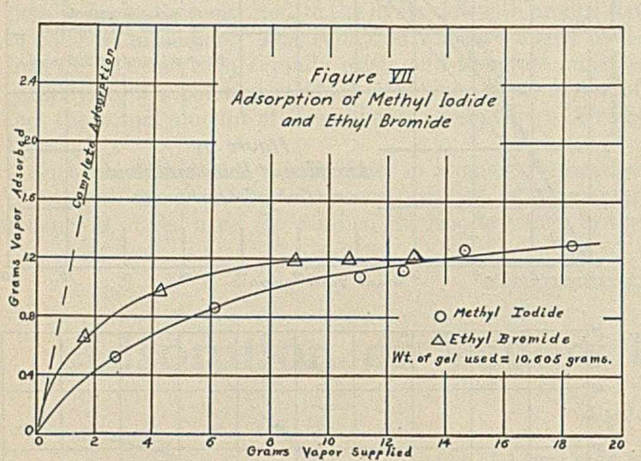
[4] *Chem. & Met. Eng.*, **23**, 1155 (1920).

[5] This Journal, **17**, 89 (1925).

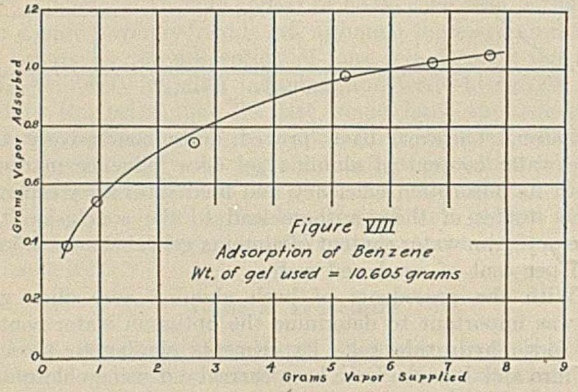
[6] *J. Am. Chem. Soc.*, **39**, 1609 (1907).

[7] This Journal, **17**, 88 (1925).

ADSORPTION OF PURE SULFUR DIOXIDE AND PURE AMMONIA AND OF THESE GASES FROM AIR MIXTURES OF EACH—With pure (100 per cent) sulfur dioxide and ammonia the adsorption curves (Figure II) follow the complete adsorption line until the gel has almost reached its saturation capacity. It was therefore of interest to determine the adsorption efficiency curves for air mixtures of the gases.



These data are also shown graphically in Figure II. The dotted line shows the curve of complete adsorption. In each case the addition of air to the pure gas causes a marked lowering of the saturation capacity of the gel, which is in accord with the results obtained by Munro and Johnson for similar gas mixtures using alumina gel as the adsorbent.



ADSORPTION OF WATER VAPOR—The adsorptive capacities of both silica and alumina gels are much greater for water than for any other substance so far studied. This is also true of ferric hydroxide gel. This gel adsorbs about 15 per cent of its weight with 100 per cent efficiency, after which the efficiency slowly falls off from the complete adsorption curve until a saturation value of about 18 per cent of its weight is reached.

Table I—Saturation Values
(Gel contains 6.36 per cent water)

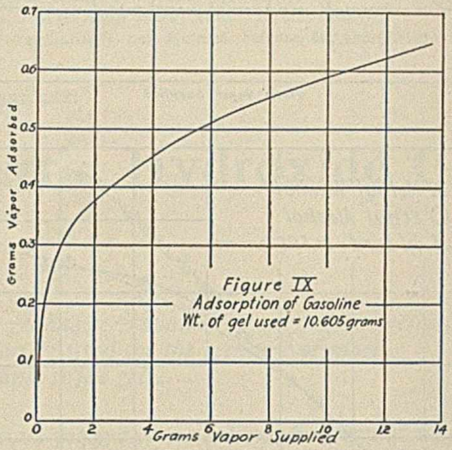
VAPOR	GRAMS VAPOR PER 100 GRAMS GEL	VAPOR	GRAMS VAPOR PER 100 GRAMS GEL
Acetone	50.9	Ethyl alcohol	10.8
Ammonia:		Ethyl bromide	11.5
Pure NH_3	4.36	Gasoline	6.7
NH_3-air mixture	3.5	Methyl alcohol	10.2
Benzene	10.1	Methyl iodide	12.6
Butyl alcohol (normal)	29.4	Methylene chloride	28.2
Isobutyl alcohol	21.3	Sulfur dioxide:	
Carbon tetrachloride	33.3	Pure SO_2	13.0
Chloroform	36.0	SO_2-air mixture	10.9

OTHER VAPORS—Adsorption data for the following vapors are given in Figures III to IX: Normal butyl and isobutyl alcohols, carbon tetrachloride and methylene chloride, ethyl and methyl alcohols, acetone, methyl iodide and ethyl bromide, benzene, and gasoline. The saturation values for all the vapors studied are given in Table I.

Discussion of Curves

Munro and Johnson[7] give three types of adsorption curves obtained with alumina gels. The curves for ferric hydroxide gel may be classified in a similar way:

TYPE I—The adsorption efficiency is never 100 per cent and decreases continuously until the saturation value has been reached. The curves for chloroform, acetone, methyl iodide, and ethyl bromide are of this type.



TYPE II—In this type of curve the adsorption is 100 per cent efficient for some time and then proceeds to the saturation point, which is reached only after a long time. The adsorption of carbon tetrachloride, ethyl alcohol, normal and isobutyl alcohols, benzene, and gasoline is of this type.

The first portion of the curve characterizing this type, where the adsorption efficiency is 100 per cent, is ascribed by Munro and Johnson to what Langmuir has called primary adsorption. The second part of the curve, where the adsorption gradually approaches zero efficiency, is ascribed to a combination of events—i. e., secondary adsorption, capillary condensation, and diffusion into the gel. In the light of our present knowledge regarding adsorption and attendant phenomena this is probably as accurate an explanation as is possible. Where the adsorption curve shows a sharp break, as in those of sulfur dioxide and ammonia (Figure II), the causes of the secondary phenomena are for the most part absent.

TYPE III—According to Munro and Johnson this type of curve is due to a chemical reaction. Here the adsorption is never 100 per cent efficient. The curves proceed in a straight line until the saturation value is nearly reached. This type of curve is represented in these experiments by the adsorption of methylene chloride and methyl alcohol.

It should be noted that there is an initial lag in the adsorption curves of chloroform and isobutyl alcohol. No adequate explanation for this phenomenon has yet been suggested.

New Fabric to Wrap Wool Bales

Wool merchants and textile manufacturers of the Bradford District in England have for some time past been working on a material to replace jute fabric as an outside wrapper for wool bales. A fabric has now been designed to overcome the difficulties resulting when jute fibers get into the wool.

The new fabric is composed of strands of paper twisted around a strand of unusually strong steel wire. The project has passed the experimental stage and will shortly be placed before the wool growers of the colonies for consideration. It is stated that this fabric can be manufactured in large quantities and at prices which compare favorably with the cost of jute.

A representative of the British concern expects to visit the United States shortly to interest American textile manufacturers.

Polarized Platinum Electrode in Neutralization Reactions[1,2]

By A. H. Wright and F. H. Gibson

WASHINGTON AND JEFFERSON COLLEGE, WASHINGTON, PA.

IN A study of the hydrogen electrode and other electrode systems used in electrometric analysis, a number of titrations involving neutralization reactions were performed with a polarized platinum electrode system similar to that described by Willard and Fenwick[3] and used by them in oxidation and reduction reactions.

Apparatus and Procedure

Figure 1 illustrates the arrangement of the apparatus used. Two dry cells connected through a slide-wire resistance to give 2 volts, then through a high resistance of 460,000 ohms, gave a polarizing current of 2.3×10^{-5} amperes at the platinum electrodes. The potential of the cathodically polarized platinum electrode was measured with a potentiometer, a normal calomel half-cell being used as the reference electrode. The change of e. m. f. of the cathodically polarized platinum electrode was followed during the progress of a titration where the hydrogen-ion concentration of the solution was changing. The rate of change of the e. m. f. at the end point for strong acids was found to be large and the titration curves gave good flex points. For weak acids the curves had a more gradual slope at the end point. The titration curves compare favorably with the reference curves for the hydrogen electrode given by Davis, Oakes, and Salisbury.[4]

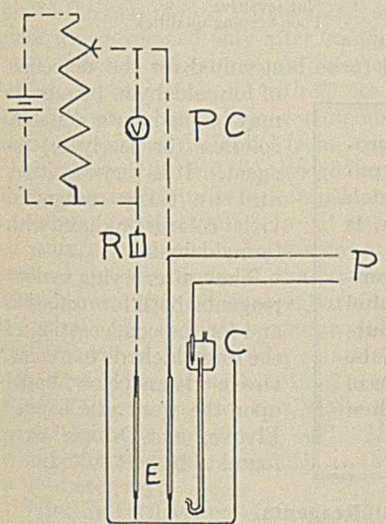


Figure 1—Polarized Platinum Electrode System

E—Platinum electrodes
PC—Polarizing circuit
P—To potentiometer
V—Voltmeter
R—High resistance
C—Calomel half-cell
Mechanical stirrer not shown

The end point breaks in successive titrations do not always occur at exactly the same potential in every case, but they do occur at the same hydrogen-ion concentration. Frequent treatment with cleaning solution and ignition to white heat before each titration helps give more consistent curves. The electrode reaches equilibrium in from 1 to 2 minutes and titrations can be completed much faster than with a hydrogen electrode.

The electrode is positive with respect to the calomel half-cell while in an acid solution and becomes negative when in an alkaline solution. When titrating a strong acid with a base the change occurs very close to the neutral point, or a hydrogen-ion concentration of 10^{-7}.

Results

The following data are obtained when 20 cc. of 0.5 *N* hydrochloric acid were titrated with sodium hydroxide:

Cc. of NaOH	*Volts*	*Cc. of NaOH*	*Volts*
0.0	+0.200	21.6	+0.055
5.0	+0.140	21.65	−0.023
10.0	+0.122	21.75	−0.100 Phenolphthalein end point
15.0	+0.120	21.8	−0.140
20.0	+0.106	22.0	−0.159
21.0	+0.094	23.0	−0.180
21.5	+0.081 Methyl orange end point	25.0	−0.190

These data are plotted in Curve *A*, Figure 2. This is a typical curve for strong acids and bases. The methyl orange indicator changed while the electrode was still slightly positive, but the electrode was negative with respect to the calomel half-cell when the phenolphthalein indicator color appeared. A very good flex point is produced which, together with the change of polarity, makes it possible to determine the end point within 0.05 cc. In this titration the total volume of solution at the end point was approximately 75

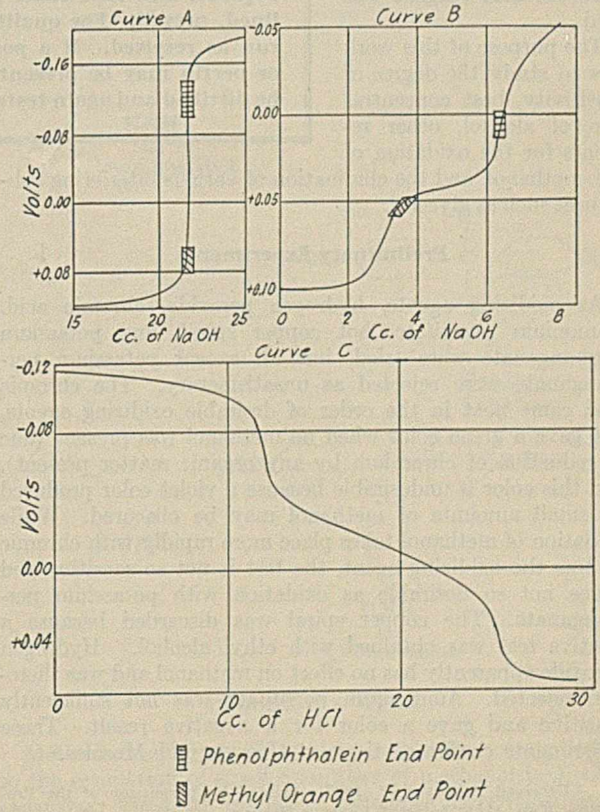


Figure 2

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[1] Received December 8, 1926.

[2] Abstract of a thesis submitted by F. H. Gibson in partial fulfilment of the requirements for the degree of master of science in chemistry at Washington and Jefferson College.

[3] *J. Am. Chem. Soc.*, **44**, 2504 (1922).

[4] THIS JOURNAL, **15**, 182 (1923).

cc. and but 0.3 cc. of titrating solution was required to give all the end-point phenomena.

From a similar procedure Curve *B* was produced by titrating dilute phosphoric acid with sodium hydroxide. This curve has the two characteristic flex points.

Curve *C* resulted when sodium carbonate was titrated with hydrochloric acid and gives two flex points.

Perhaps the greatest advantage of this electrode system is the fact that titrations involving oxidation and reduction reactions may be performed in the same apparatus. Hence, any laboratory having electrometric apparatus may, by adding an auxiliary electrode with the polarizing circuit, perform a number of titrations ordinarily requiring the hydrogen electrode.

Comparison of Sensitivity of Various Tests for Methanol[1]

By Leslie O. Wright

U. S. Internal Revenue Bureau, Branch Laboratory, Buffalo, N. Y.

A survey has been made of the various methods proposed for detection of methanol. Oxidation with potassium permanganate to form formaldehyde, which in turn is detected by reduced rosaniline solution, is the method adopted.

It is recommended for standard work, where comparisons are desired, that solutions of 5 per cent alcohol be used, and that other standard conditions, as outlined, prevail. For qualitative work, samples may be run as received. If a positive test is found, glycerol or pectin may be present and the sample must then be distilled and again tested.

NEARLY all of the numerous proposed tests for methanol depend upon the same principle—oxidation of the methanol present to formaldehyde, to formic acid, and in some of them to carbon dioxide and water. Georgia and Morales[2] report that the oxidation to formic acid or carbon dioxide is unsatisfactory, so that the generally accepted method is by oxidation to formaldehyde and the subsequent detection of this product by a suitable reagent.

The adequacy of the test implies, first, the efficiency of the oxidation of methanol, and second, the use of a sensitive reagent to detect formaldehyde by producing a compound giving an easily recognized color. For this second reaction a rosaniline-sulfurous acid reagent was used.

The purpose of this work was to study the degree of sensitivity, best concentration of alcohol, other reagents for the oxidation of the methanol, and the elimination of various interfering substances such as glycerol.

Preliminary Experiments

As oxidizing agents, hydrogen peroxide, chromic acid, ammonium persulfate, hot copper spiral, and potassium permanganate were tried, but all except potassium permanganate were rejected as unsatisfactory. The chromic acid came next in the order of desirable oxidizing agents, but gave a green color when no methanol was present (due to reduction of chromium by any organic matter present), and this color is undesirable because a violet color produced by small amounts of methanol may be obscured. While oxidation of methanol takes place more rapidly with chromic acid as the oxidizing agent, the test is not so sensitive and hence not so desirable as oxidation with potassium permanganate. The copper spiral was discarded because a positive test was obtained with ethyl alcohol. Hydrogen peroxide apparently has no effect on methanol and was therefore rejected. Ammonium persulfate was not sufficiently sensitive and gave a color for a negative result. These experiments confirmed those of Georgia and Morales.[2]

Reagents which were used to condense the formaldehyde to a color, with reasons for their rejection, are as follows:

Reagents	Why Discarded
Fuchsin bisulfite	Less sensitive than rosaniline
Morphine sulfate	Can be used only in concentrated acid
Codeine	Not sensitive
Apomorphine	Poor keeping qualities

Rosaniline was found to be best suited for the detection of formaldehyde because it may be made into a stable, colorless (or nearly so) reagent. It is very sensitive, and an easily recognized violet color is produced with formaldehyde.

Thus, after trying various reagents, both for oxidation and for the condensation of the formaldehyde to a color, those given below, based upon the work of Chapin,[3] Elvove,[4] and Deniges[5] were found to be best suited.

Reagents

(1) *Potassium Permanganate.* Dissolve 3 grams of potassium permanganate in 100 cc. of water previously distilled over potassium permanganate, and containing 15 cc. of phosphoric acid. By using water previously distilled from potassium permanganate solution, this reagent can be kept for a long time.

(2) *Oxalic Acid Solution.* Dissolve 5 grams of oxalic acid in a solution made by diluting 50 cc. of sulfuric acid (1.84) to 100 cc.

(3) *Schiff's Reagent* (*modified*). Dissolve 0.2 gram of rosaniline, or an equivalent weight of its salt, in 120 cc. of hot water, cool, and add this to a solution of 2 grams sodium bisulfite in 20 cc. of water. Finally add 2 cc. of concentrated hydrochloric acid and dilute the whole to 200 cc. This solution should become colorless or nearly so after standing. If it is protected from the air no deterioration results. A very pure rosaniline base was used in these tests, but a product of lesser purity may be used, giving a somewhat colored reagent, which is, nevertheless, satisfactory.

Determination

Place 2 cc. of the sample in a test tube and add 1 cc. of potassium permanganate solution. Allow to stand for 10 minutes; decolorize by adding 1 cc. of the oxalic solution, followed by 2 cc. of the modified Schiff's reagent and mix. The solution must be mixed thoroughly. If methanol is present a violet color is developed. With traces of methanol the color is not.

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[1] Received February 28, 1927. Printed by permission of the Prohibition Unit, U. S. Internal Revenue Bureau.

[2] This Journal, **18**, 304 (1926).

[3] This Journal, **13**, 543 (1921).

[4] *Ibid.*, **9**, 295 (1917).

[5] *Compt. rend.*, **150**, 823 (1910).

developed for an hour. Glycerol or pectin in sufficient amounts will produce a like color and for that reason if a positive reaction is obtained the test should be made on the distillate.

No specific alcoholic percentage is recommended, for while the test is somewhat more sensitive in dilute solutions, it is sufficiently sensitive in any concentration for qualitative work, as is shown in Table I.

Table I—Color Developed with Various Amounts of Methanol in Alcohol

Methanol by Volume	Ethyl Alcohol, Per Cent by Volume 1	5	10	25	50	75	95
Per cent							
0.00	0	0	0	0	0	0	0
0.0025	1	0	0	0	0	0	0
0.005	2	1	1	0	0	0	0
0.01	3	2	2	1	0	0	0
0.03	4	3	2	1	1	0	0
0.05	4	4	3	2	1	1	0
0.08	4	4	4	3	2	2	1
0.10	4	4	4	4	3	2	2

0—No color
1—Very slight color
2—Slight color
3—Fair color
4—Good color

Conditions Necessary for Standard Work

Alcohol Concentration—As is shown in Table I, for a given amount of methanol the color developed was very much stronger with weak alcoholic liquors than with stronger ones. The color is usually developed in a few minutes, but in the case of only 0.01 per cent methanol the maximum color was developed only after standing for 2 hours. Thus, while this test is best run on 5 per cent solutions or less, it will show positive results with 95 per cent alcohol, providing the methanol content is correspondingly higher. In reducing a sample of alcohol from 95 per cent to 5 per cent, the methanol content is also reduced and any advantage of greater sensitivity is counterbalanced.

Amount of Sulfuric Acid—It was found that the amount of sulfuric acid could be somewhat reduced and by this method the sensitivity of the test increased with no interference from other substances, but since the test is sufficiently sensitive this is not recommended. By using one-half the amount of acid (oxalic solution) a sample containing only 0.000048 cc. of methanol in 2 cc. of a 5 per cent alcoholic solution gave a positive test, while the blank gave no color using the same amount of acid. However, this reduction is not recommended inasmuch as this degree of sensitivity is not necessary.

Time of Oxidation—In a separate set of standard solutions containing 0.03 per cent methanol and 1 per cent ethyl, the time of oxidation was increased from 1 minute to 8 minutes, and the samples showed only a small difference between the color produced after oxidation for 1 minute and that oxidized for 8 minutes. To cover all cases of high percentages of alcohol and all variations in temperature, however, the oxidation should be allowed to continue for at least 10 minutes. The same test was run using 10 per cent ethyl and 0.03 per cent methanol, with the results showing much less color than in the former set using only 1 per cent ethyl, but the same small difference in color between that sample oxidized for 1 minute and those oxidized for 8 minutes as in the previous case.

Temperature—A study was made of the effect of variations in temperature of the solution during oxidation. The samples run contained 0.1 per cent methanol and 5 per cent ethyl alcohol. The temperatures were 3°, 20°, 60–70°, and 100° C. The results showed that variations in temperature had very little effect on oxidation except in the last case, which developed less color than the other samples. This, it is believed, is due to the continued oxidation of the formaldehyde to formic acid. Using the same strength of methanol, a study was made of temperature variations on the formaldehyde-condensation-to-color solution, at 3° and 100° C. At 3° C. no appreciable color developed and evidently no condensation takes place at this low temperature. After raising to 20° C., however, the color developed normally. After a color is formed, if the solution is raised to 100° C. the violet color is discharged. Variations of normal room temperature have no effect on intensity of color formed.

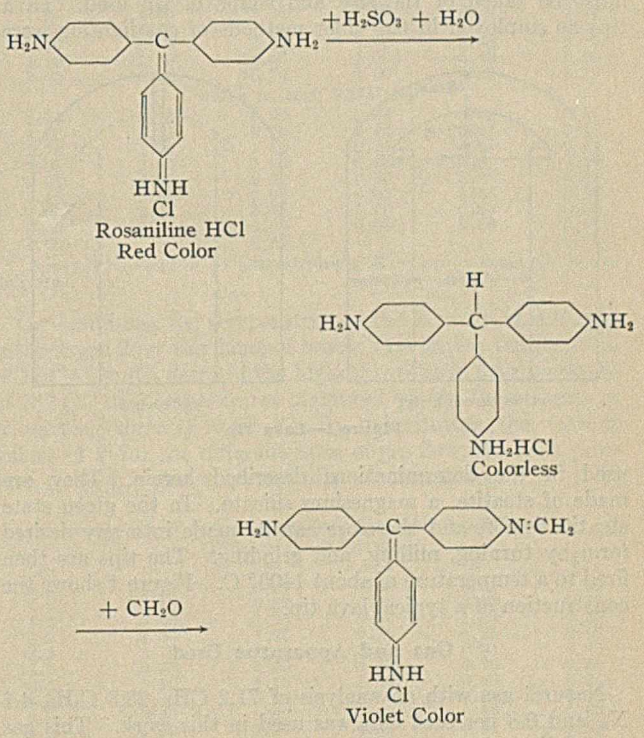
Tests in Presence of Glycerol

The only way found for eliminating a positive test in the absence of methanol and the presence of glycerol or pectin was by distillation, but glycerol was found to give only one-tenth of the amount of color given by an equivalent volume of methanol. Thus, when a sample has been reduced from 40 per cent to 5 per cent alcohol, the interference is only noticed when 4 per cent or more of glycerol is present in the original sample, this being a higher percentage than is usual. Several workers found that apple juice gave a positive reaction with most methods. This, it is believed, is due to the fact that pectin is present in fruits in the form of unstable methyl esters of pectic acid.

The following tests were made to determine how fruit juices could be analyzed in order to eliminate a positive reaction in the absence of methanol: The first was run on a dilute solution of pectin direct; the second, by distilling 150 cc. of diluted pectin to 100 cc.; the third, by distilling the diluted pectin solution containing sodium hydroxide solution, and the last, by using sodium carbonate. In the first and last two cases a positive reaction was obtained. It is, therefore, necessary that the sample be distilled slowly from a solution free from alkali.

Reaction

The mechanism of the reaction involved is probably as follows:



Quantitative Tests

Methods based upon physical constants are not applicable to the estimation of small quantities of methanol in alcohol because of the small margin of difference in physical properties. This method, however, by colorimetric comparison, is applicable to the estimation of even the smallest amounts of methanol. Using 5 per cent ethyl alcohol solution, the standards recommended for comparisons are: 0.00, 0.01, 0.05, 0.1, 0.2, and 0.4 per cent of methanol. It is quite necessary that standard conditions prevail—namely, (1) 5 per cent alcohol; (2) the same kind and amount of reagents; (3) 10 minutes for oxidation with potassium permanganate; (4) uniform temperature (room temperature is satisfactory, since both samples and standards will be at whatever temperature prevails); (5) length of time (20 minutes) in making comparisons after the addition of the modified Schiff reagent.

Acknowledgment

The writer is indebted to John F. Williams of this laboratory and to E. Raymond Riegel of the University of Buffalo for advice and assistance.

Flat Luminous Flames[1]

By D. S. Chamberlin and W. E. Thrun[2]

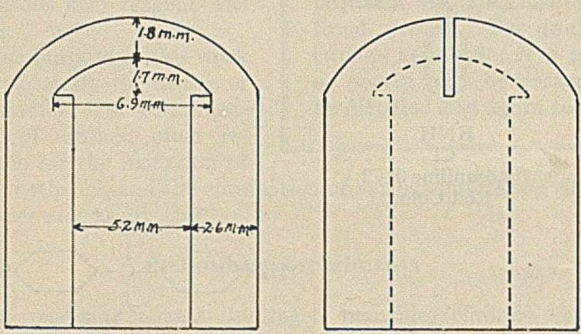
Lehigh University, Bethlehem, Pa.

A formula has been adapted from the Poiseuille equation for the flow of gases through a narrow slit as exhibited in the lava tip. A comparison of the flow of different gases from such tips in an ignited and an unignited condition develops various factors that are studied in this paper.

The shape and size of the lava-tipped flame was studied by photographic methods. The differences in gas flow from the tips in ignited and unignited conditions are discussed. It was found that the wider slotted tips did not conform to the same principles as those of narrower slotted tips.

LITTLE has been recorded concerning the burning of combustible gases in secondary air from slotted tips. Several investigators[3,4,5] have made investigations on the various types of luminous flames as they burn from lava tips in the shape of fishtails, batwings, etc., but such data on the shape and size of flames, flow rates, temperatures, and pressures that can be applied to the laws for the flow of gases are rather incomplete.

In the fundamental study of flat luminous flames, account must be taken of the size and shape of tip used. Lava tips as employed in the older methods of gas lighting were used in the determinations described herein. They are made of steatite, a magnesium silicate. In the green state steatite is soft and therefore can be made into any desired form by turning, milling, and grinding. The tips are then fired to a temperature of about 1400° C. Figure 1 shows the construction of a typical lava tip.



Section through slot

Side view

Figure 1—Lava Tip

Gas and Apparatus Used

Natural gas with an analysis of 71.2 CH_4, 23.3 C_2H_6, 4.7 N_2, and 0.8 per cent CO_2 was used in this work. This gas was delivered at a uniform pressure from a gas holder.

An ordinary differential flowmeter was constructed with a pressure gage attached as shown in Figure 2.

The arms of the meter were kept parallel by two or three wooden blocks of the same length. The zero position of the menisci was controlled by a bolt that could be screwed vertically through a nut. The nut being soldered to the gage holder, a slight motion of the bolt quickly adjusted the levels to the desired zero. At high rates of gas flow a movement of 1.0 cm. corresponded to a change in gas flow of 0.03 liter per minute; at the lower rates of flow 1.0 cm. movement corresponded to a change in flow of 0.68 liter per minute.

Pressure-Rate Relations

The data given in Table I were taken from a number of series of experiments that were performed under constant conditions. The gas escaping through a tip was lighted and the flow rate adjusted for a definite flowmeter reading. The pressure was then read. The flame was then blown out and the gas allowed to escape into the room. After a 3-minute interval the pressure and flow rate were again observed. On igniting the gas the initial readings were checked. These data were plotted and the results showed that:

1—The pressure-rate curves were not straight lines. When the gas was burning, the curve approached a straight line more nearly than when the jet was unignited.

2—The difference in pressure of burning and unignited jets rose with increasing flow rates to a maximum and then receded. It receded approximately to a zero value, as was found in several other runs. These runs are not shown.

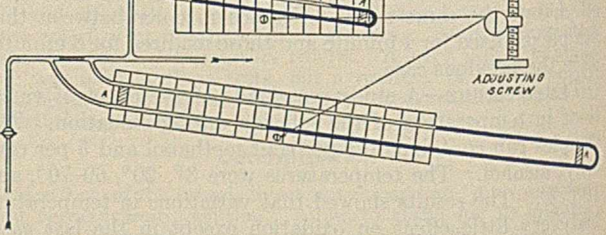


Figure 2—Flowmeter with Pressure Gage

In the investigation of the factors that controlled these flames, it was found quite generally that there was a maximum point in the flicker of the flame,[6] its shape, and tempera-

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[1] Received January 4, 1926; revised manuscript received March 23, 1927.

[2] Columbian Carbon Fellow, Lehigh University.

[3] Matake Kurokawa, *J. Soc. Chem. Ind.* (*Japan*), **29**, 139 (1926).

[4] King, "Treatise on Gas."

[5] *Bur. Mines, Bull.* **192**.

[6] Chamberlin and Thrun, *Gas Age-Record*, **57**, 41, 52 (1926).

ture. In order to explain this apparent "back pressure" on unignited jets, an equation which holds for the flow of gases through circular orifices was adapted to lava-tipped jets.

The equation[7]

$$h = \frac{K\rho R^2}{d^4}$$

as adapted from the formula of Poiseuille, applied to the flow of gas through circular orifices. This formula could be applied to the narrow slit opening by dropping the d^4 (diameter) and including this slit-opening factor in the term K, where h is the pressure in millimeters of water, ρ the density of the gas in grams per liter, and R the rate of gas flow in liters per minute, for the equation $h = K\rho R^2$.

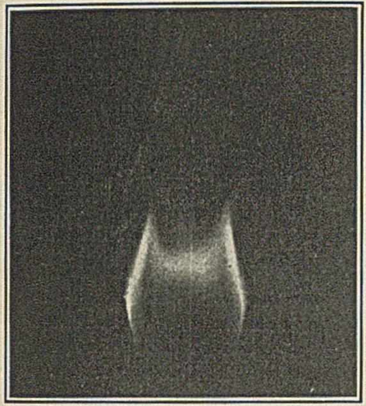

Figure 3

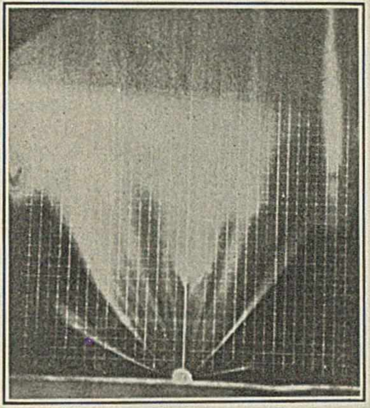

Figure 4

Table I—Pressure-Rate Data, Using Natural Gas
(Barometer, 748.0 mm. Hg; temperature, 24.0° C.)

Rate of Flow Liters per minute	Pressure Gas burning	Gas unignited (1 unit = 0.05 mm. H_2O)	Difference
	Width of slit, 0.381 mm.		
0.18	4.5	3.0	1.5
0.37	11.0	7.0	4.0
0.50	19.0	12.5	6.6
0.82	35.0	25.0	10.0
1.08	50.5	41.0	10.5
1.17	58.0	47.0	11.0
1.28	64.0	53.0	11.0
1.47	75.2	67.0	8.2
1.62	89.0	81.0	8.0
1.72	96.0	88.5	7.5
	Width of slit, 0.634 mm.		
0.50	8.0	7.0	1.0
0.82	17.0	15.0	2.0
1.08	26.0	22.5	3.5
1.28	34.0	30.0	4.0
1.47	42.5	38.0	4.5
1.62	50.0	45.0	5.0
1.76	56.0	51.0	5.0

Three gases were compared as to the value of the constant K, under the same conditions and at flow rates above one liter per minute. The value of K for carbon dioxide was 2.01, air 1.99, and natural gas 1.97. On plotting the values for h and R for natural gas on logarithmic paper, the curve was a straight line for all values of R above one liter per minute.

In Table II are shown values of h, R, and K for two different slit widths of tips. In order to compare the two tips at different rates, about twenty values of h and R were plotted on logarithmic paper and a straight line was drawn through these points. The values for comparative rates were selected from these curves and the value of K computed from the equation. A study of the data shows:

1—The value of K for the standard tip tends to decrease as R increases.

2—The value of K for the wide slotted tip increases with increase in R.

3—The value of K when the gas is burning is larger than when the gas is unignited—that is, K is always larger than K'.

4—The increase in h required to force the gas through the jet when it is burning, finally reaches a constant value $(h - h')$ for W_2.

5—Let W_1 = the standard tip width, W_2 the wide tip width, $P_1 = (h - h')$ for W_1, and $P_2 = (h - h')$ for W_2. Since $W_1/W_2 = 0.60$, then $P_2/P_1 = 0.60$. The increase in pressure is inversely proportional to the slit width.

6—For all narrow slotted tips there is a maximum value for the difference in pressure between the burning and unignited tips. This maximum difference, $h - h'$, occurs at the gas-flow rate of 1.2 liters per minute.

Effect of Temperatures on Value $(h-h')$

When the jet was burning, the gas was not measured at the temperature at which it escaped from the tip but at a lower temperature. The tip becomes heated and some of the heat is absorbed within the tip by the gas. In the equation ρ would have a value too large and R a value too small. Let T be the absolute temperature of the gas as measured and $T - t$ the temperature of the gas as it escapes.

$$\text{Then } h_1 = K\frac{T}{T+t}\left(R\frac{T+t}{T}\right)^2, \text{ or}$$

$$h_1 = K\,R^2\frac{T+t}{T}$$

$$\text{Therefore} \quad h_1 = h\frac{T+t}{T}$$

Table II—Comparison of Pressure and Rate of Flow for Two Different Slit Widths (Natural Gas)

R	h	h'	$h - h'$	K	K'
		Width of slit, 0.381 mm.			
0.50	1.32	0.57	0.75	6.35	2.74
0.80	2.35	1.23	1.12	4.40	2.31
1.00	3.15	1.80	1.35	3.77	2.16
1.25	4.30	2.80	1.50	3.29	2.15
1.50	5.40	4.10	1.30	2.87	2.18
2.00	8.30	7.30	1.00	2.48	2.19
2.50	12.50	11.50	1.00	2.40	2.20
3.00	16.70	15.70	1.00	2.23	2.10
		Width of slit, 0.634 mm.			
1.25	0.74	0.40	0.34	0.57	0.31
1.50	1.15	0.70	0.45	0.61	0.40
1.75	1.70	1.15	0.55	0.67	0.45
2.00	2.25	1.65	0.60	0.68	0.50
2.25	2.90	2.30	0.60	0.68	0.55
2.50	3.55	2.90	0.65	0.68	0.56
3.00	5.10	4.50	0.60	0.68	0.60
3.50	6.90	6.30	0.60	0.68	0.62
4.00	...	8.40	...	...	0.63

h = gas burning; h' = gas unignited; K = gas burning; K' = gas unignited.

On examining the temperature of the lava tip at different rates of gas flow, the flame of lowest rate gave a temperature of 110° C. and a flame of the highest rate gave a temperature of 75° C., the temperatures measured within these limits of R varying directly with R. By substituting the various values of T for the different rates of gas flow, the back pressure $(h - h')$ was only partially accounted for.

Table III—Pressure-Rate Data for Hydrogen Flame
(Width of slit, 0.381 mm.)

R	h	h'	$h - h'$	K	K'
0.5	1.70	0.25	1.45	6.30	1.00
1.0	2.60	0.72	1.88	2.60	0.72
1.5	3.55	1.25	2.30	1.58	0.57
2.0	4.60	1.90	2.70	1.15	0.48
2.5	5.70	2.50	3.20	0.91	0.40
3.0	6.80	3.20	3.60	0.76	0.36
3.5	8.10	4.10	4.00	0.66	0.34
4.0	9.40	5.10	4.30	0.59	0.32
4.5	10.60	6.00	4.60	0.52	0.30
5.0	11.80	7.00	4.80	0.47	0.28
5.5	13.40	8.40	5.00	0.44	0.28
6.0	14.80	9.70	5.00	0.41	0.27

The natural-gas flame from the standard tip was compared with a hydrogen flame under the same conditions. In Table III the value $(h - h')$ becomes constant at high rates of hydrogen flow, the highest rate of hydrogen flow for the

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[7] Benton, This Journal, **11**, 623 (1919).

standard tip being the value of R at which the velocity of gas flow from the tip begins to exceed the velocity of flame toward the tip. At rates at which the back pressure is constant, a temperature correction of the gas as it leaves the tip will make the pressures h and h' equal. At lower rates the difference between h and h' not made up by a temperature correction is due to a back pressure caused by the velocity of flame toward the tip opening.

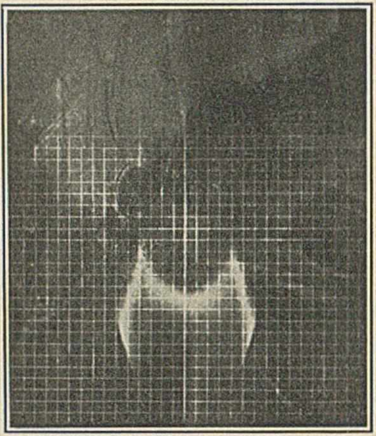


Figure 5

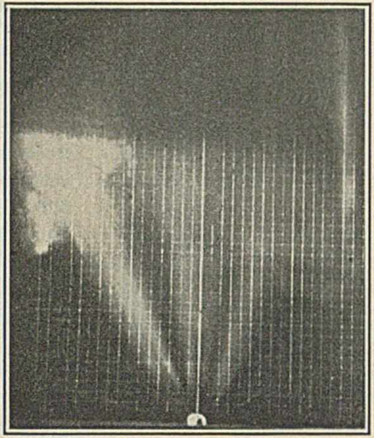


Figure 6

In a hydrogen flame burning in secondary air, at low rates the mantle of inflamed gas hugs tightly around the tip, heating it greatly. As the rate of gas flow increases this mantle lifts some from the tip but not entirely. This characteristic of a hydrogen flame over other flames is due to its wide limits of inflammability and its high flame speed.

Shape and Size of Lava Tip Flame

In order to produce a steady flame, the burner was placed in a cubical asbestos box. This box was provided with the proper vents and a glass door through which photographs of the flame could be obtained. The size of the flame at any rate of gas flow was obtained by taking first an exposure of the flame and then a second exposure on the same film of a black cardboard marked with white cross sections. This cardboard was placed in the same position as occupied by the flame.

A comparison was made of the gas jet as a flame and of the gas in an unignited state. The presence of unignited gas was made visible by allowing a small quantity of freshly made ammonium chloride to be picked up by the gas. At low rates of gas flow the unignited gas exhibited three very distinct bands. As the rate increased the three bands broke up into several distinct fingers, and at rates above where $(h - h')$ is a maximum the lateral fingers started to disappear and the bands grew together and took a nearly vertical position.

When the gas was lighted and burned at the flow rates as indicated above, the flames at low rates had no regular shape but were narrow and long. As the rate increased the flame took a regular form (Figures 3 and 4) and the visible part of the flame became confined. At rates above the maximum back pressure the flame became wider and less confined (Figures 5 and 6 and Table IV).

There is a definite lateral tendency in the gas flow as it leaves the unignited tip. On observing a lighted tip from above, the lateral fingers finally turn upward and the two luminous edges are folded over in a flange-like manner. The hot gases are lifted from their lateral tendency by the inrush of air and folded up and back against the flame. The higher the rate of flow, the greater the horizontal tendency of the gas before the inflamed gas is folded and confined. The change in the shape of the flame with increased flow rate for any one tip does not change the luminous area, as the ratio of flame area to the rate of flow is practically constant for a flame of regular structure.

Table IV—Change of Size and Shape of Flame with Rate of Flow
(Slit opening, 0.381 mm.)

RATE OF FLOW	MAXIMUM WIDTH	HEIGHT AT CENTER	HEIGHT OF FLANGES
Liters per minute	*Cm.*	*Cm.*	*Cm.*
0.50	2.60	5.30	6.00
0.82	4.20	5.00	6.50
1.08	5.00	5.60	7.75
1.28	5.90	5.75	7.75
1.47	6.75	6.50	8.50
1.62	7.25	7.50	9.10

The photographs of flames and jets from a wide slotted tip show a narrower but higher flame than from a narrow slotted tip at the same flow rates. As less pressure is necessary to cause the flow of gas from the tip, there is relatively more lifting of the lateral parts of the jet and consequently the luminous edges are higher. As the wider slotted tip flame changes much more slowly than the narrow flame, there is no simple relation between the size of flame and slot width.

Surgeon General Warns against Harmful Drugs in Cosmetics

Potent drugs of harmful nature are contained in improperly prepared cosmetics, although widely sold and advertised as absolutely harmless, Surgeon General Hugh S. Cumming recently declared. His warning was, in part, as follows:

> There is probably more interest in beauty preparations at the present time than there has ever been. The American Medical Association has been active in trying to bring to the attention of the public the dangers of improperly prepared cosmetics, advertised to beautify the complexion and at the same time showing a wanton disregard for human health and human life.
>
> Of course, no one will deny that irritant, and even caustic, drugs applied as cosmetics have a legitimate and important field of usefulness; but the abuse of these drugs because of the misleading claims made in connection with many of the so-called cosmetics involves a menace to health that should be guarded against. * * *
>
> The dangerous character of wood alcohol is so well established that it would appear almost incredible that anyone would dare offer a preparation containing wood alcohol for use on the human body. Wood alcohol is, however, but one of the many poisonous drugs that have been found in so-called cosmetics.
>
> Many writers and investigators have from time to time called attention to the possible harmful effects of preparations that are sold as beautifying agents, but up to the present time the problems involved have not been given the attention which they properly deserve.
>
> Of the potent drugs of a possible harmful nature that are used in so-called hair restoratives, there are lead acetate, silver nitrate, *p*-phenylenediamine, and resorcin. The beauty washes and face enamels contain an even more impressive array of dangerously potent drugs, including flake white or lead carbonate, lead plaster, corrosive sublimate or mercuric chloride, calomel, white precipitate or ammoniated mercury, pearl white or bismuth subnitrate, zinc white or zinc oxide, Chinese or commercial zinc oxide, and zinc soap.
>
> * * *
>
> It appears strange, therefore, that many of these substances are offered and are widely sold as cosmetics with the claim that the preparations containing them are absolutely harmless. The salts of heavy metals are easily absorbed and their toxic properties when so absorbed have been known for many years.
>
> It has also been observed that females are more susceptible to the action of metallic poisons than are males. Many scientists think that this is due to the harmful effects of lead upon the blood and the blood-making organs of the body and the greater dependence of females on a normal blood supply. For this same reason no doubt, young women are more susceptible to lead poisoning than are those more advanced in years.

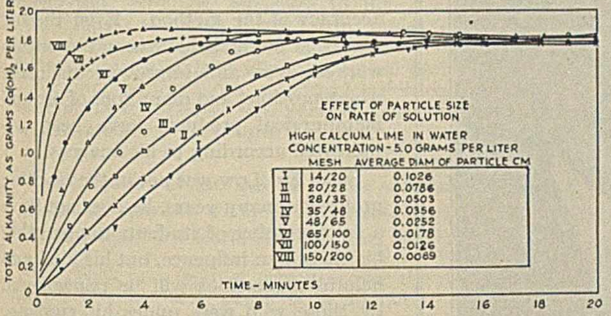
A Further Suggestion to Authors

In our "Suggestions to Authors" the following specifications are outlined for drawings that accompany manuscripts: All drawings should be made with India ink, preferably on white tracing paper or cloth. If coördinate paper is used, a blue-lined paper must be chosen as all other colors blur on reproduction.

In order that authors may understand why it is necessary to transmit their illustrations in this form, cuts have been prepared from a drawing on the various kinds of paper that are submitted to us. It is at once evident that the only satisfactory figure is No. 1, which was drawn on blue cross-section paper. The same results are obtained when white tracing paper or cloth is used. Suitable blue cross-section paper can be obtained from Keuffel & Esser Co., 127 Fulton St., New York City: No. 330, 5 × 5 lines to the inch, No. 332, 8 × 8 to the inch, and No. 331, 10 × 10 to the inch; also from Eugene Dietzgen Co., 218 East 23rd St., New York City, No. 377, 4 × 4 to the inch, No 376, 8 × 8 to the inch, and No. 375, 10 × 10 to the inch.

Lettering should be plain and large enough to reproduce well when the drawing is reduced to the width of a single column (3¼ inches) of This Journal or, less frequently, according to the shape and amount of detail, to 2 or 6¾ inches in width. Most figures can be advantageously drawn for a linear reduction to one-half or one-fourth. Coördinate lettering should be included within the chart.

Care should be taken not to waste space, as this means greater reduction and a less satisfactory illustration. Often it is possible to combine several curves in one figure and thus not only save space but enable the reader to make comparisons at a glance. Again, as shown in the accompanying illustrations, legends can often be included within the chart and thus effect a considerable saving in space.



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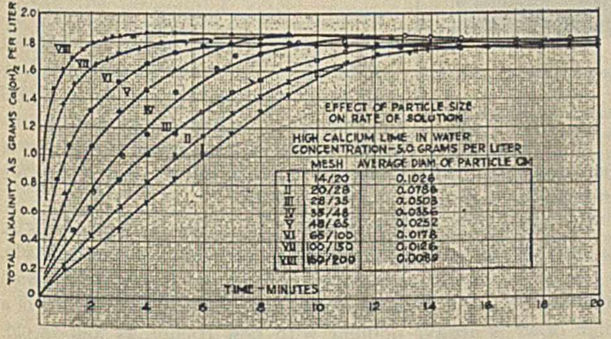

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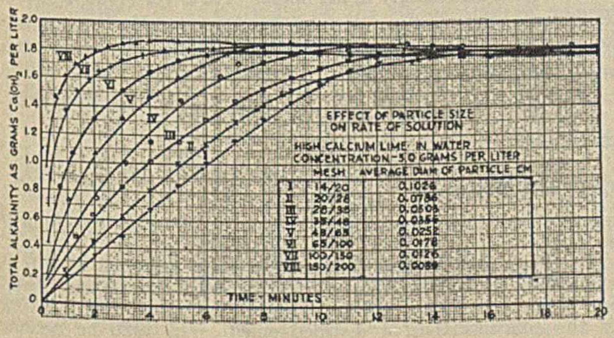

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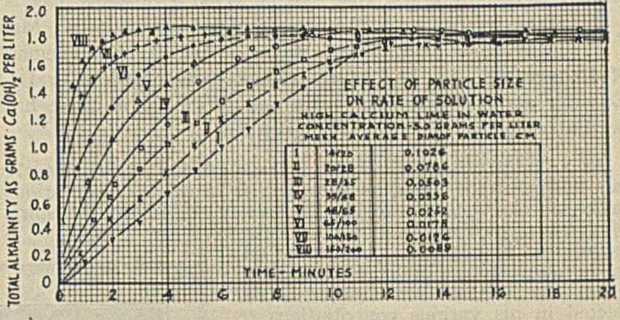

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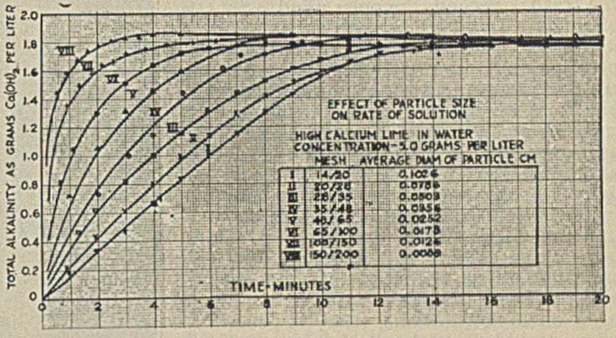

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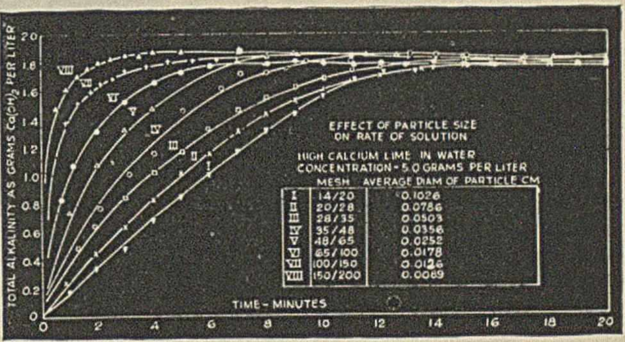

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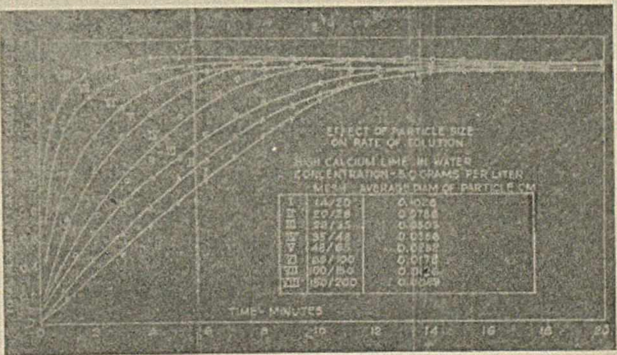


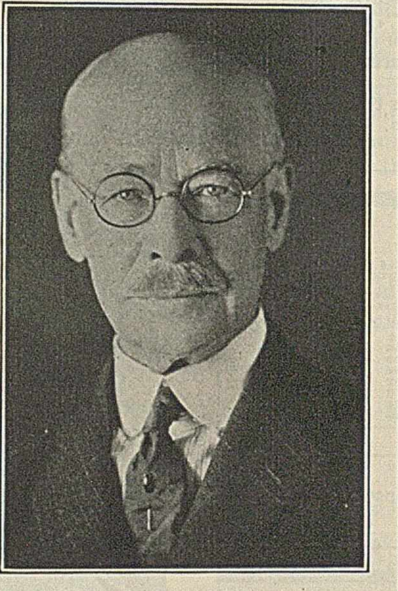
No. 7—Blueprint

AMERICAN CONTEMPORARIES

Albert H. Low

THE highest praise that can be given a business man is that he has won the esteem of his competitors. Mr. J. W. Root, a prominent assayer and metallurgical chemist of Denver, who has had a professional acquaintance with Dr. Low for about twenty-five years and for many of these has been a competitor in business, speaks thus of him:

> As a competitor in business, I always found him eminently fair and courteous, and as a co-worker in solving the various problems of our profession he has always displayed the spirit of a true scientist. This spirit he has manifested in many ways, but the following seem to embody the whole field: First, the spirit of investigation as reflected in his various contributions to scientific research, through all of which runs the dominant note of a seeker for the truth. Second, the open mind. So often have I and others noted this quality, seeing how little the prejudice and preconceived notions and conclusions arrived at after long work and study deter him from casting them aside utterly for a better and more logical answer, either as a result of his own work or that of another. Third, the spirit of helpfulness—this the most human of all. Coming to Denver over twenty-five years ago, knowing little of the business end of our mutual calling, and much more, I am afraid, of the technical side, I have always found Mr. Low ready to stop work on his own affairs, ready to listen to my troubles with kindly interest, and always ready to be generously helpful with suggestions for their solution.



A. H. Low

Dr. Albert H. Low was born in Chelsea, Mass. He received the B.S. degree in chemistry at the Massachusetts Institute of Technology in 1876. After holding the position of assayer and chemist at the Boyd smelter, Boulder, Colo., for several months, he was assistant during the next year in the chemistry department at M. I. T. He then accepted a position as chemist at the Silver Spring Dye Works at Providence, R. I. Ill health caused him to resign this position. After regaining health he went back to M. I. T. for the remainder of the school year as assistant in the laboratory. He then opened an office as assayer and chemist in Leadville, Colo., assisting in the erection of the smelter at Red Cliff, Colo., and helping to manage the California smelter at Leadville. Following this he came to Denver, Colo., as assayer and chemist at the Argo Works of the Boston and Colorado Smelting Company. After four years he became a member of the firm of Von Schultz and Low, Assayers and Chemists, Denver, Colo. During the war he was technical manager of the potash works at Antioch, Nebr. In 1919 Dr. Low accepted a position as head of the chemistry department of the Colorado School of Mines at Golden, Colo., where he remained until September, 1926. This school conferred upon him the honorary degree of doctor of science in 1922. Upon leaving the Colorado School of Mines, Dr. Low took up research work with a carbon company in Denver.

He is the author of two books, "Technical Methods of Ore Analysis" and "Notes on Technical Ore Analysis." The first of these is well known and has been used in many technical plants and in schools giving a course in ore analysis. He also contributed numerous papers to scientific journals.

He has been noted as an accurate analyst. His methods have received a very thorough test in his own laboratory. Many "phony" ores with a known composition, containing all the interfering elements, have been analyzed to test the accuracy of the method. Even the old and tried methods have been thoroughly worked over and improvements made where possible, and many tons of ore and metallurgical products have been adjudicated according to his analysis.

Since Dr. Low was not in the teaching profession many years, he does not have a great number of students to remember his classroom influence, but his kind and helpful suggestions will be remembered by those who were under his guidance the past few years. Many superintendents and managers of technical plants, however, have become thoroughly acquainted with his accurate work of analysis. When one thinks of Dr. Low he thinks of the ore and metallurgical industries. He was a pioneer of the development of the technical analysis of ores, and practically grew up with the development of the ore industry of Colorado.

He was a long time member of Colorado Scientific Society, and is at present a member of the Teknik Club of Denver, Colo.

Dr. Low has always remained young and is as straight as an arrow. He is the life of a social gathering and with his wit of a high order is always popular with new friends as well as old. With Mrs. Low, a most cultured and highly educated woman, he entertains charmingly in his home. He is very fond of games and amusements and is a genuine good sport. He has a generous and lovable nature, and I never heard him say a disrespectful word about anybody.

L. D. ROBERTS

Doran Heads Prohibition Bureau

J. M. Doran has been appointed Commissioner of Prohibition. He is particularly well qualified for this post because of his long government service and his intimate knowledge of the work of the Bureau of Prohibition. This promotion, the Secretary of the Treasury announced, is in accordance with a sound principle of administration to be followed wherever possible as the best means of developing experienced administrators and offering a real inducement to able men to enter the government service.

Dr. Doran entered the Bureau of Internal Revenue in 1907 as a chemist. He became head of the Industrial Alcohol and Chemical Division in 1920, having charge of and completing the work of the concentration of distilled spirits. In 1926 he became head of the Technical Division of the Prohibition Unit.

BOOK REVIEWS

Handbook of Chemistry and Physics. By Charles D. Hodgman and Norbert A. Lange. A Ready-Reference Pocket Book of Chemical and Physical Data. 11th edition. 1011 pages. Chemical Rubber Publishing Co., Cleveland, Ohio, 1926. Price, $5.00.

This handbook embraces such a variety of data as to make an adequate review impossible in the space at our disposal. The authors have assembled an amazing lot of useful information on both physics and chemistry, so that the chemist will find much that the average chemical handbook fails to provide.

Mathematical tables, which occupy 62 pages, are of increasing usefulness in chemical work. These are followed by an extensive series of general chemical tables which, in addition to the numerical data usually found in such handbooks, include a qualitative analysis scheme with proper references to the preparation of reagents, etc., a useful table of indicators, ionization constants, and an elaborate series of specific gravity tables. Under Properties of Matter are found tables of density, elasticity, coefficient of friction, resistance to crushing, tensile strength of metals, modulus of rupture, hardness, surface tension, viscosity, diffusion, and osmotic pressure of aqueous solutions. The tables on heat are equally inclusive. There is a section of hygrometric and barometric tables, a section on sound, one on electricity and magnetism, extensive reference to light, measures and units, with handy conversion factors, wire tables, a section on definitions and formulas, a group of miscellaneous tables, and a section dealing with methods of solving chemical problems.

We find the handbook a valuable addition to our library and recommend it to those who prize a collection of useful data in concentrated, compact form.

Mineral Waters of the United States and American Spas. By William Edward Fitch. 799 pages. Lea & Febiger, Philadelphia and New York, 1927. Price, $8.50.

This book is a distinct advance over the older works on the subject. It has 200 pages of introductory and general text relating to mineral waters and their uses, including chapters on certain topics by other recognized experts. Descriptions of natural conditions in the several states, with analyses of spring waters and information as to accommodations at the springs, make up the next 510 pages; the last 43 pages contain illustrated descriptions of seventeen resorts.

The author emphasizes the known real curative properties of mineral waters, but also states:

> When the astute physician of the present day reads of the wondrous water and more marvelous cures in an imposing list, as set forth in divers attestations from rejuvenated preachers, restored politicians, and renovated bobbed-haired suffragettes, persons unqualified by study or experience to give valuable testimony, and then carefully studies the analysis and finds that it contains only an infinitesimal amount of lime salts in parts per 1,000,000, is it any wonder that he tosses it into the waste-basket in disgust, and assuages his enraged intelligence with an expletive objuration on charlatanry in general, and the mineral spring mountebank in particular?*** A spring or spa exploiting a really meritorious mineral water, which has hopes for continuous patronage and endorsement of the profession, has no need to resort to exaggerated hyperbole nor to the use of superlatives.

The chapter by E. E. Smith on the classification of mineral waters is along the usual lines for the chemical classification, but gives a medicinal classification which is new. Dr. Smith has also given for each analysis throughout the book a medicinal classification of the water. E. H. S. Bailey prepared the chapters on the ingredients of mineral waters. The chapter on radioactivity is by John C. Hemmeter. Guy Hinsdale furnished the chapters on hydrotherapy.

The book contains descriptions of 425 active spring areas, with analyses of 871 waters. Mention is made of 424 springs from which water is sold and of 240 which were once popular resorts but have been abandoned.

The analyses are reported in hypothetical combinations in parts per million. The source of each analysis is indicated. Many are taken from published reports of state or federal bureaus. The names of the analysts and publications assure a high standard of accuracy for the analyses. The descriptions of many of the springs contain statements relating to medicinal properties that border on the style condemned by the author in the introduction.

W. D. Collins

The Microbiology of Cellulose, Hemicelluloses, Pectin, and Gums. By A. C. Thaysen and H. J. Bunker. Humphrey Milford, publisher. Oxford University Press, London, 1927. 363 pages. Price, 25 s.

In the preface the book is described correctly as a comprehensive compilation, from published sources, of the discussions of "microbiological changes" occurring in hemicelluloses, pectin, gums, and cellulose. The material is gathered from more than six hundred papers widely scattered in botanical, bacteriological, chemical, and technological literature.

In Part I the products are described as chemical entities, and the importance of biological agencies in their degradation is emphasized. Part II presents the *Schizomycetes* (bacteria), *Actinomycetes*, and *Eumycetes* (fungi in general), taking up organism by organism only the species cited by special workers in this field as active in producing changes. Descriptions of these organisms taken from standard sources are rewritten in the authors' language, with critical comment in the authors' own field. In other groups the rewritten descriptions are supposed to simplify the terms used, but lack of critical acquaintance with organisms and synonymy is evident. Part III, in seven chapters, presents the forms of decomposition reported in gums and pectin, hemicelluloses and cellulose, ensilage, peat and coal, cellulose fibers and fabric, wood and wood pulp, and industrial applications. The chapters dealing with products and processes present an abstract of the literature which puts the present status of research in these fields into compact, accessible form. The relation of abstractors rather than reviewers is fairly rigorously maintained, except in their personal field, in which first-hand knowledge is at once evident.

Tested by the reviewer's yardstick—a book sound and accurate in the reviewer's own field may be assumed to be dependable elsewhere—this book brings to the worker's table a key to the literature of this important group of microbiological activities and a reliable abstract of the investigations cited. It will therefore be a very useful and time-saving addition to his reference table.

Charles Thom

Physico-Chemical Metamorphosis and Some Problems in Piezochemistry. By Ernst Cohen. 181 pages. McGraw-Hill Book Co., New York, 1926. Price, $2.50.

As indicated by the title, this book really consists of two books, on closely related subjects, bound under one cover. The subject matter is essentially that contained in a course of twenty-two lectures given at Cornell University under the George Fisher Baker Non-Resident Lectureship in Chemistry during the second semester of the year 1925–1926.

Somewhat elementary in treatment and dealing with a restricted range of subjects, it is nevertheless a book which will be of value to all students and teachers of chemistry. The introductory lecture is devoted largely to a discourse on the philosophy of education, done in Professor Cohen's own charming style. The book as a whole belongs to that select class which may properly be called readable.

Part I treats of polymorphism in certain metals and compounds, the experimental methods which are applied, and the results obtained. Not the least valuable feature of this part of the book are the carefully planned experiments which are well adapted for lecture-room demonstration. Professor Cohen carefully develops the thesis that polymorphism is much more common than has ordinarily been supposed, and he sums up Part I by the statement (page 94) that "most, if not all hitherto determined physical-chemical constants of solid substances are in need of a revision, since it is very probable that the present values refer not to physically and chemically pure modifications, but to physically impure and metastable mixtures which contain the respective forms in unknown proportions. This state of affairs opens up an immense field of research to scientists and investigators, and one which may yet have many a surprise in store for us."

In Part II there is given, first, a description of the author's high-pressure apparatus. This is followed by a discussion of the effects of pressure on reaction-velocity and on solubility. Finally, the various electrical methods which may be used for studying inversions and the affinity of reactions under pressure are treated in considerable detail. The striking advantages of the electrical cell in physical-chemical investigation are emphasized, and by a study of this section the reader may obtain a demonstration of the accuracy, directness, and convenience of such methods.

The author's erudition and his broad knowledge of the subject are shown by the numerous apt quotations in English, German, French, Italian, and Latin.

L. H. Adams

The Law of Chemical Patents. By Edward Thomas. 358 pages. D. Van Nostrand Company, Inc., New York, 1927. Price, $6.00.

This work deals with what has become to a very considerable extent a distinct branch of the patent law, and one in which there has been a real need for a comprehensive and reliable work dealing with its principles and practice. Mr. Thomas' book well supplies this need. It is written on the assumption that the reader is interested in such practical matters as the patentability of new processes, compositions, and chemical apparatus and equipment, the adequate protection of such inventions, the validity and scope of chemical patents and how to realize on them, rather than the philosophy or the technicalities of procedure of the patent law.

As the author states, the courts are the final arbiters of the patent law, and in this work the law of chemical patents is set forth in the language of the courts with just sufficient explanation to make the matters considered clear to the layman.

The text consists chiefly of verbatim quotations from opinions of the courts arranged in numerous chapters, each provided with a short introductory section designed to enable those unfamiliar with the technicalities of patent law to grasp the principles involved in the rulings which follow, and to add greatly to the interest and value of the book to the reader. The grouping of the quotations under numerous subheadings and the provision of a table of contents by chapters, a table of cases, and a very complete index make the work particularly convenient and valuable for use as a reference book.

The author points out that a large proportion of the patents which become involved in litigation are poorly drawn. This is particularly true of chemical patents, and Mr. Thomas' work should be studied by patent solicitors who undertake the protection of chemical inventions and can be read with profit by all having to do with inventions along chemical lines.

C. L. Parker

Chemical Specifications Yearbook 1927. M. N. Conklin, Editor. 1st Edition, 142 pages. Compiled by Chemical Specifications, Inc., New York. Price, $5.00.

This attractively bound book is well printed on excellent paper, and appears to have few typographical errors. It lists about one hundred and seventy-five important chemicals, mentions their nature and manufacture, and gives "detailed specifications." Less than a dozen of the "specifications" include directions for tests, or references to places where the tests are described. Some "detailed specifications" are, in full: "Barium stearate contains theoretically 16.3 per cent metallic barium;' "Carbon dioxide—not less than 99.8 per cent;" "Carbon tetrachloride—99.7 per cent also chemically pure;" and "The sodium bicarbonate used in baking soda and the manufacture of baking powders must be of the very purest grade. For other uses lower grades may be used." A number of the "specifications" are merely typical analyses. About ninety requirements for special uses of various chemicals are also given. "An average grade" of ammonium oxalate, "an average sample" of barium chloride, "a typical analysis" of ammonium thiocyanate, "general requirements" for hydrochloric and nitric acids and for sodium oxalate are practically identical with the requirements suggested by the Committee on Analytical Reagents [This Journal, **17**, 756 (1925)] for "reagents to be used in careful analytical work." Such chemicals would be very expensive for some of the uses listed.

The book also contains a list of manufacturers, jobbers, and importers for each item. Only those who responded to inquiries regarding their products are included. Thus, several well-known producers of lime are omitted. No firm is listed as importing filter paper from England, France, Germany, or Sweden, where some of the filter paper used in the United States is manufactured. The listed manufacturers of this product are the J. T. Baker Chemical Company, of Phillipsburg, N. J., Morana, Inc., and the Palo Company of New York City.

The list of "more important chemicals" includes only thirteen of the seventy sodium compounds given in the Condensed Chemical Dictionary. Zinc cyanide is the only entry under "Z." The list of seven chemicals under "H" includes hydrogen peroxide and henna leaves, but omits hydrofluoric acid. This and other omissions can be cared for in the second edition, which is already in preparation and is expected to include "as many chemicals again as the present volume contains."

W. D. Collins

Chemistry and the Home. By Harrison E. Howe and Francis M. Turner, Jr. 355 pages. Charles Scribner's Sons, New York, 1927. Price, $1.50.

The home has been called the center of our American life. As such it necessarily influences every phase of life and is influenced by it. This is evidently the view held by the authors of this book, for in its eighteen chapters they have given valuable and interesting information upon a wide variety of topics.

Chemistry and the home have furnished the center about which this material is grouped. The chemist is called "the modern Marco Polo" and many of his discoveries are set forth. "Our civilization is to a high degree the product of research in the chemical laboratory."

The entire book contains almost countless items of interest that make a decided appeal. The chapters on silk, rubber, and illumination are especially well done. The emphasis upon research is dominant, as it should be. Striking statements are frequent, thus: "It would take fifty Mexicos to supply our full requirements of vanilla flavoring if it were all made from beans." Again, "Like every other haunt of men today, the barber-shop has been brought under the sway of chemistry."

We wonder, however, about this statement, though we cannot question its truthfulness:

> As a nation we don't yet listen to chemists. We listen to politicians and lawyers, occasionally to doctors and preachers. We are even beginning to listen to engineers, but not yet to chemists. The chemists don't charge enough for their advice to be regarded as of any value—a disadvantage which they share with the clergy alone.

In bringing about a better understanding of the work of the chemist and the value of his labors this book will be a powerful factor. It should be in every public library and would make splendid collateral reading for students in general chemistry and in home economics. We are indebted to men of the ability and standing of the authors in giving us a readable and authoritative, but in no sense technical, book. The more widely it is read, the more clearly will the work of the chemist be understood, and this sympathetic understanding must lead to further progress.

Harrison Hale

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. VII—Ti, Zr, Hf, Th, Ge, Sn, Pb, Inert Gases. By J. W. Mellor. 977 pages. Longmans, Green & Co., Ltd., London, 1927. Price, $20.00.

The seventh volume of this series completes the work on the elements of the fourth group and includes the inert gases. The presentation follows closely the plan of the series, each element being treated as to history, occurrence, and the preparation and properties of the element and its compounds. As mentioned in reviews of the earlier volumes, Mellor does not attempt to present the material from a critical standpoint, but gives a very exhaustive report of all the work which has been done.

Titanium, zirconium, and thorium are thoroughly covered. The chapter on the newly discovered element, hafnium, is of special interest. It seems unfortunate, however, that Mellor neglects to mention the part played by the application of the Bohr theory of the structure of the atom in the discovery of this element. He makes considerable mention of celtium, but fails to bring up the important point made by Hevesy that, according to modern atomic theory, the element 72 could not possibly be a rare earth but must be very similar to zirconium. The successful search for hafnium in zirconium minerals and laboratory preparations follow. This points to the non-validity of the celtium claim of Urbain, who worked with the rare earth mixtures. The discovery of hafnium stands out as one of the important successes of the Bohr atomic theory and this deserves mention here.

The material on germanium is summarized thoroughly in 20 pages, although it is already incomplete on account of the amount of work now being done owing to the increased availability of this rare element. One is impressed by the tremendous amount of accurate results secured by C. Winkler, its discoverer. Practically all his work has been substantiated by later workers. Winkler, however, confused the chloroform, dichloride, and oxychloride, but later corrected this in part. Mellor is not at all clear about these compounds. In one place the oxychloride is mentioned as a liquid lighter than the chloroform, and subsequently it is considered a white solid. The two-liquid-layer system Winkler mentioned has been found to be due to the binary mixture of germanium tetrachloride and germanium chloroform, which are only partially miscible. The existence of the oxychloride has never been demonstrated and is highly problematical. A discrepancy in the boiling point of monogermane is explained by saying that it had been in contact with mercury overnight and hence had decomposed. Pure monogermane has been allowed to stand over mercury for months without showing any evidence of decomposition.

Tin is given 208 pages and lead 404. The treatment is very adequate and is especially complete for the metals and their alloys. The inert gases are covered in 62 pages.

The method of pointing out the compound or property under discussion by printing in heavy type so that it is easily found is very commendable.

Considering the encyclopedic nature of the book, Mellor has succeeded in making it amazingly easy and interesting reading. The research worker and student will find many a valuable suggestion in the historical development of each topic. This volume is a worthy member of the series which has been so warmly received.

A. W. Laubengayer

Home Preservation of Fruit and Vegetables. By Margaret J. M. Watson. 142 pages. Oxford University Press, London: Humphrey Milford, 1926. Price, $2.00.

This little volume has been prepared for the use of the housewives of Great Britain. For this reason the book contains considerable information that would not be of much interest to American housewives. On the other hand, some recipes, particularly those for English style orange marmalade and English jams, will be found very useful to American housewives and jam manufacturers as well. While the book is designed for housewives, most of the recipes call for certain weights of the various ingredients—e. g., "$^{1}/_{4}$ ounce of citric acid to every 4 pounds of fruit"—if given in the more familiar "cups and teaspoons" system of the American household the recipes would be more readily used by the average housewife. Cooking jams to a definite weight, as recommended by Miss Watson, is very commendable.

Preservation of fruit by dilute sulfurous acid solution and the use of such fruit in jams is well described and should prove of use to manufacturers. The hydrometer test for jellies is recommended; American jelly makers find a thermometer more convenient for determining the jellying point.

More and better illustrations would be desirable. In reading the book, American housewives might be somewhat confused by some of the English terms such as "pips" for seeds, "bottle" for fruit jar, etc. Sterilizing of canned fruits at 190° F. instead of the usual 212° F. is recommended and, although commendable, is difficult to conduct in the home kitchen.

The book in general is well written and should prove useful to housewives, especially those who like to attempt unusual recipes.

W. V. Cruess

1914–1924, Dix Ans d'Efforts Scientifiques, Industriels et Coloniaux, Volume II. Edited by Jean Gerard. Quarto, pages 1555–3060. Illustrated. *Chimie et Industrie,* Paris, 1926. Price, $12.00 for Volumes I and II.

Volume I of this monumental work was reviewed in This Journal, **18,** 876 (1926). The present volume begins with Part V, which describes the economic equipment of France. This includes descriptions of the developments in water and electric power, post and telegraphs, highways and transportation, banks, industrial establishments, and the economic trade balance of France. Part VI describes French colonial effort and includes chapters on the products obtained from the colonies of France. Part VII describes in great detail the industrial, agricultural, and economic development of each of the French colonies. Part VIII is composed of concise descriptions of some two hundred and sixty-five chemical and allied industrial establishments of France. This section really constitutes an industrial chemical catalog of the country.

There is thus brought together in these two volumes detailed information upon all phases of modern chemical industrial development in France and her colonies. It is a record of which France may well be proud—and an example which other nations will certainly desire to emulate.

Atherton Seidell

Standards Yearbook 1927, First Issue. Prepared by the National Bureau of Standards of the Department of Commerce. To be issued annually. 398 pages. 39 illustrations. Sold by the Superintendent of Documents, Government Printing Office, Washington, D. C. Price, $1.00.

The Standards Yearbook contains much more information than might be expected from the title. In addition to the descriptions of fundamental and derived standards of measurement, it takes up lines of activity relating to standard constants, standards of quality, standards of performance, and standards of practice. These and the research relating thereto can be made to cover nearly all lines of human endeavor. All activities of governmental and private agencies on standardization in a limited sense are well described. Much research outside the Bureau of Standards is omitted even though it may lead to standardization.

The character and scope of the book are indicated by the chapter and section headings which follow, with the number of pages in each section given in parentheses: Trend of standardization (6); International standardizing agencies, governmental (3); non-governmental (16); National standardizing agencies, outside the United States, (10); Fundamental and working standards of the United States of America, from acidimetry to thermometry (23); Federal standardizing agencies, aside from the National Bureau of Standards, (96), including a list of federal government research and testing laboratories (4); National Bureau of Standards (137); Municipal (3) and state (7) agencies; General standardizing agencies, A. S. T. M. and others, (12); Standardizing activities of technical societies and trade associations (80), listing over two hundred organizations with the name and address of the secretary or other executive officer of each; Testing and certification for the consumer (5).

The book is the only general record of progress in standardization up to 1927 and is necessary to those who wish to know what has been done, is being done, and is planned with reference to standardization and related research. Future annual editions will carry the advances from year to year and changes in officers and work of the organizations engaged in standardization. Much of the material, however, can be reprinted each year without change.

W. D. Collins

Four Thousand Years of Pharmacy. An Outline History of Pharmacy and the Allied Sciences. By Charles H. LaWall. 665 pages. 64 illustrations. Octavo. J. B. Lippincott Co., Philadelphia, 1927. Price, $5.00.

In this interesting volume Professor LaWall has given us a bird's-eye view of the development of pharmacy over a period of forty centuries. The story of the development of drugs and their application to the treatment of disease involves, to a large extent, the history of chemistry and medicine as well as other sciences upon which the art of pharmacy is based. To endeavor to cover forty centuries of this development in one volume of rather large type limits the story to what may be called the "high-lights," and the reviewer must take the broad viewpoint of what has been written in order to be fair in his estimate of the task that has been performed.

In the introduction it is stated that "the primary function of pharmacy is to prepare medicines for those who require them. It is, therefore, a highly specialized calling which may rise to the dignity of a true profession or sink to the level of the lowest commercialism, according to the ideals, the ability, and the training of the one who practices it." The historical data collected by the author bear this out.

The author has given us a very good description of the activities of a number of individuals who, in various periods in the history of the world, have in one way or another influenced the development of pharmacy, medicine, alchemy, and chemistry, but he has not gone into great detail on any particular phase of the development of pharmacy, probably for the very good reason that this was impossible in a volume of such a limited size.

The chronological table will be of considerable value to the student of contemporaneous history. One finds, however, comparatively few references to pharmacy itself, and many references to events in the history of medicine and science generally which have at best a decidedly remote bearing on the development of pharmacy. For example, one wonders what effect the passage of the first Meat Inspection Act in Germany in 1875 or the institution of the School of Mines at Columbia University in 1864 have to do with pharmacy.

The bibliography will be of considerable value to any student of pharmaceutical history or the history of allied sciences.

While it cannot be claimed that the author has written a thorough history of pharmacy, he has presented a very readable and interesting outline which will occupy in the field of history of pharmacy a place comparable to that occupied by Wells's "Outline of History" in the field of world history. Undoubtedly, this book will create a greater appreciation of the part that pharmacy has played in the development of medicine and chemistry, and it may act as a stimulus to others interested in the history of pharmacy to develop volumes which will portray in greater detail each one of the periods which LaWall has pictured to us so entertainingly.

How to Apply for a Position. By Letter and Interview. By Maurice H. Weseen. 73 pages. College Book Store, Lincoln, Neb., 1927. Price, 50 cents.

The author of this booklet, associate professor of business English at the University of Nebraska, has given a very good analysis of the problem which confronts anyone who applies for a position, whether in person or by correspondence. Most of the space is devoted to suggestions on writing letters of application. The average letter writer, whether seeking a position or not, could profit by reading it, and those who are interested in the more practical side will find many helpful suggestions in the numerous examples of letters written by men seeking employment. Perhaps the most useful pages are those devoted to "Application Don't's" and "Application Do's." Altogether, the book should find its proper niche in business literature.

NOTES AND CORRESPONDENCE

Successive Potentiometric Titration of Copper and Iron in Metallurgical Products

Editor of Industrial and Engineering Chemistry:

In their article under this title,[1] the authors maintain that the potentiometric estimation of copper according to Zintl and Wattenberg[2] gives irregular results with marked positive and negative errors up to 6 per cent.

The method of Zintl and Wattenberg is as follows:

> The copper solution, containing 4 to 8 per cent free hydrochloric acid, is reduced with excess titanous chloride solution, the concentration of which need not be known, and is then titrated potentiometrically with potassium bromate or dichromate. During the titration the oxygen must be carefully excluded by passing carbon dioxide through the vessel. The oxidizing agent first oxidizes only the excess of titanous chloride, then a potential jump is noticed, which indicates the beginning of the oxidation of cuprous to cupric salt. A second potential jump indicates the end point. The solution used between the two jumps corresponds to the copper present.

Buehrer and Schupp usually find their values much too low. They do not exclude atmospheric oxygen by passing in an indifferent gas, but cover the solution with kerosene.

On different occasions we have also tried to work under a layer of kerosene or toluene, to protect from oxidation a solution to be titrated, but without success.[3] Even if the layer of kerosene is several inches thick and the stirring is slow, atmospheric oxygen penetrates through it and, for example, in the titration of hot cupric salt solutions with titanous chloride, especially near the end point, the potential never becomes constant. If one waits long enough, titanous chloride can be added *ad lib.* without reaching an end point. A second source of error is also noticeable if the tip of the buret dips only into the protective layer. The drops of the titrating liquid leaving the buret often remain for a long time inside the kerosene layer before penetrating into the aqueous solution, and if these are not noticed large errors may result. For this reason we have avoided the use of a liquid protective layer and perhaps the poor results of Buehrer and Schupp may be thus explained.

Buehrer and Schupp conclude from their results that the reduction of cupric salt by titanous chloride must be incomplete in hydrochloric acid solution, in agreement with the fact that the normal potentials of Cu^{++}/Cu^{+} (0.17 volt) and Ti^{++++}/Ti^{+++} (0.00 volt) lie near together.

This conclusion is erroneous. The difference between normal potentials indicates the possibility of titration only when no appreciable complex formation takes place in the solution.[4] A complex ion is formed, however, in the case of cuprous salt in hydrochloric acid solution. The potential of a cupric-cuprous electrode is markedly shifted to the positive side by chloride. A solution of cupric and cuprous salts in equal proportions in 5 per cent hydrochloric acid gives a potential of about 0.49 volt against the hydrogen electrode, whereas in chloride-free solution the normal potential should be 0.17 volt. That the reduction of cupric salt in 5 per cent hydrochloric acid is complete with titanous chloride is seen from the fact that during titration at the first jump one drop of the titrating solution shifts the potential at least 58 millivolts—i. e., increases the concentration of the cupric ions tenfold.

The statement of Buehrer and Schupp that Zintl and Wattenberg found direct titration of cupric salt with titanous chloride impossible is entirely erroneous. Zintl and Rauch[5] have not only used the direct titration for estimating copper, but also for standardizing titanous chloride.

E. Zintl

Bayer Academy of Sciences
München, Germany

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Editor of Industrial and Engineering Chemistry:

In reply to the comments of Professor Zintl, it may be pointed out, first, that the writers rigorously excluded oxygen, not only by means of a layer of kerosene 1 to 2 inches deep, but also by the use of purified nitrogen bubbled through the solution. The nitrogen would be equally as effective in preventing oxidation of cuprous ion as carbon dioxide, and the kerosene we have also found very satisfactory in other titrations. Since the solutions were titrated hot, not only would the solubility of oxygen be less in the kerosene, but the kerosene vapors constantly rising would tend to prevent access of air to the protecting layer. The difficulty of enclosed droplets of solution in the kerosene layer was avoided by having the tip of the buret extend through the

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[1] Buehrer and Schupp, This Journal, 18, 121 (1926).

[2] *Ber.*, 55, 3366 (1922).

[3] See also Hempel, "Gasanalyt. Methoden," p. 33, Braunschweig, 1913.

[4] Zintl, "Elektrometrische Massanalyse, Handbuch der Arbeitsmethoden in der anorganischen Chemie, Vol. II, p. 984.

[5] *Z. anorg. Chem.*, 146, 281 (1925); Zintl, *Ibid.* 152 35 (1926).

kerosene layer and well into the solution. Furthermore, the stirring by even rapid rotation of a glass rod as a rule did not agitate the layer appreciably, so that suction of air into the solution was not able to occur. It is very significant that our results were in most cases too low, whereas if atmospheric oxidation of the cuprous ion formed had occurred the results would have been high. We therefore believed ourselves to be justified in the conclusion that the low results were due to incomplete reduction of the copper.

The second question concerns the Cu^+/Cu^{++} potential, and Professor Zintl's point here is well taken. No doubt both the Cu^+/Cu^{++} and the Ti^{+++}/Ti^{++++} potentials shift greatly with change in concentration of H^+ and Cl^-. Granting that the potential difference is sufficient to warrant the conclusion that the reaction would go to completion, we must recognize that the copper is largely in the form of the chloro-complex ion, which is known to react very slowly with certain ions, and this may also be true of its reaction with titanous ion. It is probably a question of speed as well as of equilibrium in this titration. Our experiments have not given evidence that the reaction goes to completion under the conditions of the titration.

The last point relates to the direct titration of cupric ion with titanous chloride. We regret the error on page 124 of our paper, in which we state that "Zintl and Wattenberg[2] find that direct titration cannot be made." These authors did not report any work on the direct titration, but only on the indirect determination—namely, by adding excess titanous chloride and titrating back with either dichromate or bromate. Kolthoff[6] reported that direct titration with titanous chloride alone does not give accurate results for copper. Since our observations confirmed those of Kolthoff and since the reference to Zintl and Rauch,[5] which Professor Zintl quotes, was unknown to us at the time our paper was accepted for publication, we naturally assumed that Zintl's results for the direct titration were in agreement with ours. Further work will be done in this laboratory to clarify this question.

T. F. Buehrer
O. E. Schupp, Jr.

University of Arizona
Tucson, Ariz.
April 18, 1927

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[6] *Rec. trav. chim.*, **43**, 820 (1924).

Kjeldahl Digestion Apparatus

Editor of Industrial and Engineering Chemistry:

We have read, with much interest, the article by E. G. Hastings, E. B. Fred, and W. H. Peterson [This Journal, 19, 397 (1927)] with reference to a Kjeldahl digestion shelf being operated in the laboratory of the Department of Agricultural Chemistry of the University of Wisconsin, Madison, Wis.

The idea of a fume tube with nipples on the side that go into the neck of a Kjeldahl flask and some means for furnishing a positive draft, such as an exhaust fan, was patented in September, 1924, and assigned to The Duriron Company, who have since been making up and marketing them.

The first Duriron tubes were made and installed a year or more before application was made for patent papers. Duriron proved so very satisfactory for the construction of these tubes and exhaust fans, gas ducts, etc., that a complete digestion shelf was designed including not only the tubes, exhaust fan, exhaust pipe, and condensate removers, but supporting frames, burners, etc., and made part of The Duriron Company's standard product.

Duriron spray nozzles are sometimes used to replace the Duriron exhaust fan, and in small installations it has been found that these spray nozzles perform the dual service of furnishing the necessary draft, at the same time condensing the gases so that they may be discharged to a sewer.

Although The Duriron Company holds the patent rights to such type apparatus, they have, of course, no objection to its use by the University of Wisconsin. We merely call attention to the patent features to guard against the manufacture of such equipment for sale or for general use by others.

W. H. Scott

The Duriron Company, Inc.
Dayton, Ohio
March 23, 1927

Note on the Radiation from Luminous Flames

In This Journal, 19, 4 (1927), R. T. Haslam and M. W. Boyer, in discussing the radiation from luminous flames, mention a scheme proposed by Lent [*Wärme*, **49**, 145 (1926)] to increase the radiation from relatively nonluminous flames by adding an illuminating agent to the gas so as to produce particles of carbon to serve as radiation centers.

A similar proposal was made and tried out in 1913 by Walter A. Schmidt, of the Western Precipitation Company, with the coöperation of Buckner Speed. These gentlemen had been puzzled as to why the heat requirement for portland cement burning was greater when oil was used as a fuel than when powdered coal was so used. They suspected that when powdered coal was used, the ash particles remaining enhanced radiation from such flames and that the absence of similar particles in the flame from oil might cause the lower efficiency.

A series of tests was consequently undertaken at the plant of the Riverside Portland Cement Company to investigate this point. In these tests very fine dust was blown into the front part of the kiln so as to mix with the combustion gases, and the output and fuel consumption of the kiln, with and without such added dust, were noted.

The results of these tests were inconclusive, which, however, is not surprising in view of the well-known uncertainties about kiln production in the ordinary plant and the unduly large excess of fuel which always is used in connection with cement burning. It might be expected, however, that as the art of cement burning is improved and the fuel consumption approaches more nearly the theoretical limit, it will be possible to demonstrate that one actually can improve the efficiency of an oil-fired kiln by some such means.

Evald Anderson

Western Precipitation Company
Los Angeles, Calif.
April 4, 1927

Calendar of Meetings

American Chemical Society—74th Meeting, Detroit, Mich., September 5 to 10, 1927.
  Division of Colloid Chemistry—Fifth National Colloid Symposium, University of Michigan, Ann Arbor, Mich., June 22 to 24, 1927.
  Institute of Chemistry—State College, Pa., July 4 to 30, 1927.
  Division of Organic Chemistry—Second National Symposium on Organic Chemistry, Columbus, Ohio, December 29 to 31, 1927.
First International Congress of Soil Science—Washington, D. C., June 13 to 22, 1927.
American Leather Chemists' Association—Cincinnati, Ohio, June 15 to 17, 1927.
American Society for Testing Materials—Annual Meeting, French Lick, Ind., June 20 to 24, 1927.
American Electrochemical Society—Fall Meeting in the form of an excursion through the Northwest, September 4 to 20, 1927.
11th Annual Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 26 to October 1, 1927.

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 Education

An Outline of Methods of Research with Suggestions for High School Principals and Teachers. *Bulletin* 24, 1926. 31 pp. Paper, 10 cents.

Bureau of Foreign and Domestic Commerce

Important Demand for Insecticides for Tobacco Estates in Sumatra East Coast. *Special Circular* 171, Chemical Division. 8 pp. Issued April 23, 1927.

Palm-Oil Industry of Sumatra and West Africa. S. B. Redecker and Frank Messenger. *Trade Information Bulletin* 471. 17 pp. Paper, 10 cents.

Rayon Industry of Lucerne, Switzerland. *Semi-Monthly Bulletin* 19-J, Textile Division. 4 pp. Issued May 3, 1927.

The Chemical Industry in Baden. *Special Circular* 172, Chemical Division. 9 pp. Issued April 25, 1927.

Bureau of Mines

Accidents at Metallurgical Works in the United States during the Calendar Year 1925. W. W. Adams. *Technical Paper* 412. 40 pp. Paper, 10 cents.

Coal-Mine Fatalities in March, 1927. W. W. Adams. *Reports of Investigations* 2803. 7 pp. Issued April, 1927.

Consumption of Explosives in March, 1927. W. W. Adams. *Reports of Investigations* 2804. 9 pp. Issued April, 1927.

Copper in 1925 (General Report). C. E. Julihn and H. M. Meyer. *Mineral Resources of the United States, 1925.* Part I, pp. 347–408. Issued April 27, 1927. Paper, 10 cents.

Explosibility of Coal Dust from Four Mines in Utah. H. P. Greenwald. *Technical Paper* 386. 20 pp. Paper, 5 cents.

Methods and Tools for Removing Paraffin from Flowing Wells. C. E. Reistle, Jr. *Reports of Investigations* 2802. 4 pp. Issued April, 1927.

Petroleum in 1925. G. R. Hopkins and A. B. Coons. *Mineral Resources of the United States, 1925.* Part II, pp. 311–84. Issued April 20, 1927. Paper, 10 cents.

Production of Sponge Iron. C. E. Williams, E. P. Barrett, and B. M. Larsen. *Bulletin* 270. 175 pp. Paper, 35 cents.

Safeguarding Workmen at Oil Derricks. H. C. Miller. *Bulletin* 272. 111 pp. Paper, 40 cents.

Sand and Gravel in 1925. E. R. Phillips. *Mineral Resources of the United States, 1925.* Part II, pp. 281–303. Paper, 5 cents.

Some Economic Phases of the Carbon Black Industry. G. R. Hopkins. *Circular* 6033. 5 pp. Issued April, 1927.

Sources and Distribution of Major Petroleum Products: Atlantic Coast States 1925. E. B. Swanson. *Circular* 6031. 14 pp. Issued April, 1927.

Stop, Look, and Listen! The Roof Is Going to Fall. J. W. Paul. *Circular* 6032. 3 pp. Issued April, 1927.

Tests with Rock Dust for Extinguishing Fire. H. C. Howarth and H. P. Greenwald. *Reports of Investigations* 2801. 5 pp. Issued April, 1927.

The Manganese Situation from a Domestic Standpoint. J. W. Furness. *Circular* 6034. 21 pp. Issued April, 1927.

Zinc in 1925 (Smelter Report). Amy Stoll. *Mineral Resources of the United States, 1925.* Part I, pp. 329–46. Issued April 25, 1927. Paper, 5 cents.

Bureau of Standards

Standards Yearbook 1927. Compiled by the National Bureau of Standards. *Miscellaneous Publication* 77. 392 pp. Cloth, $1.00.

Thermal Expansion of Graphite. Peter Hidnert and W. T. Sweeney. *Technologic Paper* 335. 8 pp. Paper, 5 cents.

Bureau of the Census

Animal and Vegetable Fats and Oils: Production, Consumption, Imports, Exports, and Stocks by Quarters, Calendar Years 1925 and 1926. 16 pp. Paper, 5 cents.

Department of Agriculture

Annotated Bibliography on the Storage of Cottonseed and of Seed Cotton. Henry M. Steece. Coöperative Extension Work in Agriculture and Home Economics. 13 pp.

Effect of Soil Microörganisms on Paraffin Used as a Coating to Decrease the Injurious Action of Lead Arsenate on Plant Roots. W. E. Fleming. *Journal of Agricultural Research*, 34 (February 15, 1927), 335–8.

Relation of Soil Temperature and Soil Moisture to the Infection of Sweet Potatoes by the Stem-Rot Organisms. L. L. Harter and W. A. Whitney. *Journal of Agricultural Research*, 34 (March 1, 1927), 435–41.

The Determination of Organic Matter in Soils by Means of Hydrogen Peroxide. W. O. Robinson. *Journal of Agricultural Research*, 34 (February 15, 1927), 339–56.

The Nitrogen Compounds of the Rice Kernel as Compared with Those of Other Cereals. S. L. Jodidi. *Journal of Agricultural Research*, 34 (February 15, 1927), 309–25.

The Value of Beef Protein as a Supplement to the Proteins in Certain Vegetable Products. Ralph Hoagland and G. S. Snider. *Journal of Agricultural Research*, 34 (February 15, 1927), 297–308.

The Vitamin C Content of Fresh and Canned Pear. V. C. Craven and M. M. Kramer. *Journal of Agricultural Research*, 34 (February 15, 1927), 385–92.

Department of Commerce

Progress in the Elimination of Waste. Herbert Hoover. Extract from the Fourteenth Annual Report of the Secretary of Commerce. 29 pp.

Geological Survey

Contributions to the Geography of the United States, 1926. M. R. Campbell. *Bulletin* 790. 46 pp.

Geology of the Cat Creek and Devils Basin Oil Fields and Adjacent Areas in Montana. Frank Reeves. *Bulletin* 786-B. *Contributions to Economic Geology, 1926.* Part II, pp. 39–95. Paper, 30 cents.

Geology of the Upper Matanuska Valley, Alaska. S. R. Capps. With a Section on the Igneous Rocks. J. B. Mertie, Jr. *Bulletin* 791. 92 pp. Paper, 30 cents.

Surface Water Supply of the United States, 1924. Part IV—St. Lawrence River Basin. N. C. Grover, S. B. Soule, A. H. Horton, Lasley Lee, A. W. Harrington, and C. H. Pierce. *Water-Supply Paper* 584. 147 pp. Paper, 20 cents.

Pan American Union

Tropical Hardwoods with Special Reference to Their Uses in American Industries. *Forestry* 15. Reprinted from the March, 1927, *Bulletin of the Pan American Union.* 9 pp.

Public Health Service

Arsphenamine–Sodium Thiosulfate Treatment of Experimental Syphilis. Carl Voegtlin and H. A. Dyer. *Public Health Reports*, 42 (April 15, 1927), 1045–52.

Definitions of Pasteurization and Their Enforcement. L. C. Frank, F. J. Moss, and P. E. LeFevre. *Public Health Reports*, 42 (April 29, 1927), 1152–62.

Paris Green Applied by Airplane in Control of Anopheles Production. L. L. Williams, Jr., and S. S. Cook. Reprint 1140 from *Public Health Reports.* 22 pp. Paper, 10 cents.

Water Supplies on Canadian Great Lakes Vessels. G. H. Ferguson. *Public Health Reports*, 42 (April 22, 1927), 1097–1101.

New Books

Class-Book of Organic Chemistry. Vol. I. For First-Year Medical Students and Senior Science Students in Schools. J. B. Cohen. 344 pp. The Macmillan Company, New York. Price, $1.60.

Elements of Chemistry. Harry N. Holmes and Louis W. Mattern. 519 pp. The Macmillan Company, New York. Price, $1.80.

First Principles of Chemistry. F. W. Dootson and A. J. Barry. 339 pp. The Macmillan Company, New York. Price, $2.00.

Investigation of the Caking Power of Coal. J. T. Burdekin. Fuel Research, Physical and Chemical Survey of the National Coal Resources, No. 8, Department of Scientific and Industrial Research. 21 pp. H. M. Stationery Office, London. Price, 1 s. net.

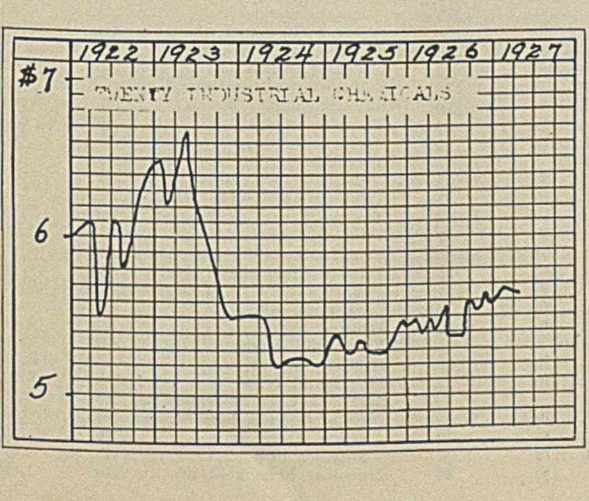
Methods of Analysis of Coal. 35 pp. Fuel Research, Physical and Chemical Survey of the National Coal Resources, No. 7, Department of Scientific and Industrial Research. H. M. Stationery Office, London. Price, 9 d. net.

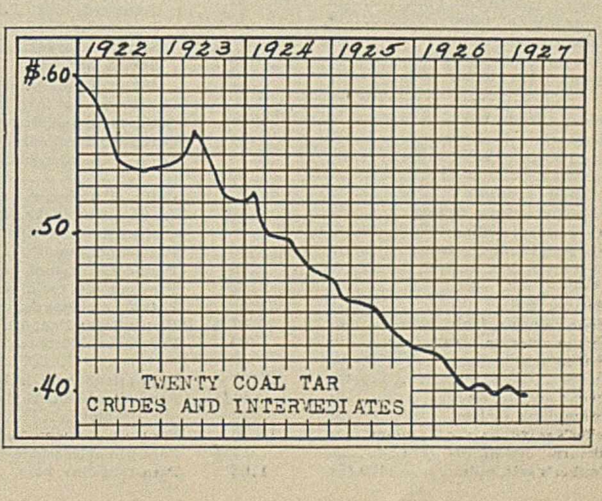
Selenium. A List of References 1817–1925. Compiled by Marion Foster Doty. 114 pp. New York Public Library. Price, 65 cents.

MARKET REPORT—MAY, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON MAY 15

Acetanilide, tech., bbls..........lb.	.27
U. S. P., bbls..............lb.	.35
Acetic anhydride, 92–95%, cbys..lb.	.29
Acetone, C. P., drums, wks.....lb.	.12
Acetophenetidine, bbls..........lb.	1.60
Acid, Acetic, 28%, c/1. bbls.100 lbs.	3.38
56%, c/1. bbls.........100 lbs.	6.09
Glacial, c/1. bbls......100 lbs.	11.47
Acetylsalicylic, bbls.......... lb.	.85
Anthranilic, 99–100%, drums..lb.	.98
Benzoic, tech., bbls..........lb.	.58
Boric, bbls...................lb.	.08½
Butyric, 60%, pure, 5-lb. bot..lb.	.55
Chloroacetic, mono-, bbls., wks....................lb.	.25
Di-, cbys.................lb.	1.00
Tri-, bbls.................lb.	2.50
Chlorosulfonic, drums, wks....lb.	.15
Chromic, pure, 98%, drums...lb.	.37
Chromotropic, bbls...........lb.	1.00
Cinnamic, 5-lb. cans..........lb.	3.25
Citric, U. S. P., kegs, bbls....lb.	.43½
Cresylic, pale, drums........gal.	.60
Formic, 85%, cbys., N. Y.....lb.	.10
Gallic, U. S. P., bbls.........lb.	.65
Glycerophosphoric, 25%, 1-lb. bot...................lb.	1.85
H, bbls., wks..................lb.	.55
Hydriodic, 10%, U. S. P., 5-lb. bot...................lb.	.65
Hydrobromic, 48%, cbys., wks.lb.	.45
Hydrochloric, 20°, tanks, wks.................100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks.. lb.	.06
60%, bbls., wks............lb.	.13
Hydrofluosilicic, 35%, bbls., wks.....................lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis........lb.	.36
Lactic, 22%, dark, bbls.......lb.	.05½
66%, light, bbls., wks.......lb.	.26
Metanilic, bbls...............lb.	.60
Mixed, tanks, wks........N unit	.06
S unit	.01
Molybdic, 85%, kegs..........lb.	1.25
Naphthionic, tech., bbls......lb.	.55
Neville & Winther's, bbls......lb.	.95
Nitric, C. P., cbys............lb.	.12
Nitric, 38°, c/l. cbys., wks. ....100 lbs.	5.50
Oxalic, bbls., wks............lb.	.11¼
Phosphate, bulk.............ton	9.50
Phosphoric, 50%, cbys.......lb.	.07
Picramic, bbls................lb.	.50
Picric, bbls. c/l..............lb.	.30
Pyrogallic, tech., bbls........lb.	.85
Salicylic, tech., bbls..........lb.	.37
Stearic, d. p., bbls. c/l.......lb.	.11
Sulfanilic, 250-lb. bbls........lb.	.15
Sulfuric, 66°, c/l. cbys., wks. ....100 lbs.	1.35
66°, tanks, wks............ton	15.00
60°, tanks, wks............ton	10.50
Oleum, 20%, tanks, wks...ton	18.00
40%, tanks, wks.........ton	42.00
Sulfurous, U. S. P., 6%, cbys..lb.	.05
Tannic, tech., bbls............lb.	.30
Tartaric, U. S. P., cryst., bbls......................lb.	.33
Tobias, bbls...................lb.	.85
Tungstic, kegs................lb.	1.00
Valeric, C. P., 10-lb. bot......lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.......................gal.	3.70
Amyl, 10%, Imp. drums.....gal.	1.40
Butyl, drums, c/l. wks.......lb.	.19¼
Cologne Spirit, bbls..........gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs.............gal.	.42
No. 1, Comp. denat., drs..gal.	.44½
Isobutyl, ref., drums.........lb.	...
Isopropyl, ref., drums........gal.	1.00
Propyl, ref., drums...........lb.	1.00
Wood, *see* Methanol	
Alpha-naphthol, bbls...........lb.	.65
Alpha-naphthylamine, bbls......lb.	.35
Alum, ammonia, lump, bbls., wks..................100 lbs.	3.15
Chrome, casks, wks......100 lbs.	5.25
Potash, lump, bbls., wks..100 lbs.	3.50
Soda, bbls., wks.........100 lbs.	3.25
Aluminum, metal, N. Y.........lb.	.26
Aluminum chloride, anhyd., drums.....................lb.	.35
Aluminum stearate, 100-lb. bbl...lb.	.23
Aluminum sulfate, comm'l bags, wks.............100 lbs.	1.40
Iron-free, bags, wks......100 lbs.	1.75
Amidopyrine, boxes............lb.	4.60
Aminoazobenzene, 110-lb. kgs...lb.	1.15
Ammonia, anhydrous, cyl., wks..lb.	.11
Ammonia water, 26°, drums, wks.......................lb.	.02¾
Ammonium acetate, kegs.......lb.	.34
Bifluoride, bbls..............lb.	.21
Bromide, 50-lb. boxes........lb.	.53
Carbonate, tech., casks.......lb.	.08¾
Chloride, gray, bbls..........lb.	.05¾
Lump, casks...............lb.	.12
White, bbls...............lb.	.05¼
Iodide, 25-lb. jars............lb.	5.20
Lactate, bbls.................lb.	.15
Nitrate, tech., cryst., bbls.....lb.	.21
Oxalate, kegs.................lb.	.35
Persulfate, cases.............lb.	.27½
Phosphate, dibasic, tech., bbls....................lb.	.18
Sulfate, bulk, wks........100 lbs.	2.40
Thiocyanate, tech., kegs......lb.	.40
Amyl acetate, tech., drums......lb.	2.00
Aniline oil, drums..............lb.	.15
Anthracene, 80–85%, casks, wks..lb.	.60
Anthraquinone, subl., bbls......lb.	.90
Antimony, metal...............lb.	.14
Antimony chloride, anhyd., drums.....................lb.	.17
Oxide, bbls..................lb.	.16¼
Salt, Dom., bbls.............lb.	.18
Sulfide, crimson, bbls.........lb.	.25
Golden, bbls...............lb.	.15
Vermilion, bbls.............lb.	.37½
Tartrolactate, bbls...........lb.	.45
Argols, red powder, bbls........lb.	.08
Arsenic, metal, kegs............lb.	.45
Red, kegs, cases.............lb.	.10½
White, c/l. kegs.............lb.	.03¾
Asbestine, bulk, c/l............ton	16.00
Barium carbonate, bbls., bags, wks......................ton	47.50
Chloride, bags, wks.........ton	58.00
Dioxide, bbls., wks...........lb.	.13
Hydroxide, bbls.............lb.	.04½
Nitrate, casks...............lb.	.08
Barium sulfocyanide, 400-lb. bbls.......................lb.	.27
Barytes, floated, 350-lb. bbls., wks......................ton	23.00
Benzaldehyde, tech., drums.....lb.	.65
F. F. C., cbys...............lb.	1.40
U. S. P., cbys...............lb.	1.15
Benzene, pure, tanks, mills.....gal.	.22
Benzidine base, bbls............lb.	.70
Benzoyl chloride, carboys.......lb.	1.00
Benzyl acetate, cbys...........lb.	1.30
Alcohol, 5-liter bot..........lb.	1.40
Chloride, tech., drums........lb.	.25
Beta-naphthol, bbls............lb.	.24
Beta-naphthylamine, bbls.......lb.	.63
Bismuth, metal, cases..........lb.	2.25
Bismuth nitrate, 25-lb. jars.....lb.	1.85
Oxychloride, boxes..........lb.	3.10
Subnitrate, U. S. P., 25-lb. jars......................lb.	2.20
Blanc fixe, dry, bbls...........ton	80.00
Bleaching powder, drums, wks. ....100 lbs.	2.00
Bone ash, kegs.................lb.	.06
Bone black, bbls...............lb.	.08¼
Borax, powd., bbls.............lb.	.04½





Bordeaux mixture, bbls..........lb.	.11
British gum, com., c/l......100 lbs.	4.37
Bromine, bot....................lb.	.47
Bromobenzene, drums..........lb.	.50
Bromoform, 5-lb. bot...........lb.	1.65
Butyl acetate, 100-gal. drums...gal.	1.45
Cadmium bromide, 50-lb. jars....lb.	1.20
Cadmium, metal, boxes..........lb.	.70
Cadmium sulfide, cs.............lb.	1.20
Caffeine, U. S. P., 5-lb. cans.....lb.	3.05
Calcium acetate, bags......100 lbs.	3.50
Arsenate, bbls..................lb.	.07½
Carbide, drums.................lb.	.05½
Chloride, drums, wks....100 lbs.	21.00
Lactate, tech., bbls............lb.	.35
Nitrate, bbls..................ton	52.00
Phosphate, monobas., bbls....lb.	.07
Tribas., bbls..................lb.	.11
Calcium carbonate, tech., bgs. 100 lbs.	1.00
U. S. P., precip., 175-lb. bbl....lb.	.06½
Camphor, Amer., bbls...........lb.	.72
Jap., cases.....................lb.	.66
Crude, cases....................lb.	.64
Camphor, monobrom, cs.........lb.	1.85
Caramel, bbls..................gal.	.63
Carbazole, bbls.................lb.	.15
Carbon bisulfide, drums.........lb.	.05½
Carbon black, cases.............lb.	.12
Carbon dioxide, liq., cyl.........lb.	.06
Carbon tetrachloride, drums.....lb.	.07
Casein, stand. gr., bbls..........lb.	.18
Cellulose acetate, kegs..........lb.	1.40
Cerium oxalate, kegs............lb.	.32
Chalk, pptd., casks..............lb.	.04¼
Charcoal, willow, powd., bbls....lb.	.06
China clay, imp., bgs......100 lbs.	15.00
Chloral hydrate, drums..........lb.	.60
Chloramine T., 5-lb. bot.........lb.	1.75
Chlorcosane, 5-lb. bot...........lb.	.55
Chlorine, liq., c/l., cyl..........lb.	.05½
Chlorobenzene, mono-, drums...lb.	.07
Chloroform, tech., drums........lb.	.20
Chlorohydrin, anhyd., drums....lb.	.75
Chromium acetate, 20° sol., bbls. lb.	.05½
Cinchonidine sulfate, 100 oz.....oz.	.35
Coal tar, tanks, bbls., wks......gal.	.07
Cobalt, metal, kegs.............lb.	2.50
Cobalt oxide, bbls...............lb.	2.00
Cod-liver oil, bbls..............bbl.	45.00
Collodion, drums................lb.	.23
Copperas, c/l., bulk............ton	13.00
Copper, metal, elec.........100 lb.	12.90
Copper carbonate, bbls..........lb.	.16¾
Chloride, bbls..................lb.	.28
Cyanide, drums.................lb.	.48
Oxide, red, bbls................lb.	.16½
Sulfate, c/l., bbls.........100 lb.	4.95
Cotton, soluble, bbls............lb.	.40
Cream tartar, bbls...............lb.	.24¾
Cyanamide, bulk, N. Y. ....Ammon. unit	1.80
Diaminophenol, kegs............lb.	3.80
Dianisidine, kegs................lb.	3.25
Dichlorobenzene, drums.........lb.	.06
Diethylaniline, drums............lb.	.55
Diethylphthalate, drums.........lb.	.25
Diethylsulfate, tech., drums.....lb.	.20
Dimethylaniline, drums..........lb.	.30
Dimethylsulfate, drums..........lb.	.45
Dinitrobenzene, drums...........lb.	.15½
Dinitrochlorobenzene, bbls......lb.	.15
Dinitronaphthalene, bbls........lb.	.32
Dinitrophenol, bbls..............lb.	.31
Diphenylamine, bbls.............lb.	.45
Diphenylguanidine, bbls.........lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.................100 lbs.	1.10
Ether, nitrous, bot...............lb.	.90
Ether, U. S. P., drums...........lb.	.14
Ethyl acetate, 99%, drums.....gal.	1.10
Bromide, drums.................lb.	.50
Chloride, drums.................lb.	.22
Methyl ketone, drums..........lb.	.30
Ethyl benzyl aniline, 300-lb. drs..lb.	1.05
Ethylene bromide, drums........lb.	.70
Chlorohydrin, anhyd., drums..lb.	.75
Glycol, c/l., wks...............lb.	.30
Feldspar, bulk..................ton	20.00
Ferric chloride, tech., bbls......lb.	.07½
Ferrous chloride, cryst., bbls.....lb.	.05
Ferrous sulfide, bbls.......100 lbs.	2.50
Fluorspar, 95%, bags...........ton	25.00
Formaldehyde, bbls..............lb.	.11¼
Formaniline, drums..............lb.	.38
Fuller's earth, bags, c/l., mines..ton	15.00
Furfural, 500-lb. drs., c/l.......lb.	.17½
Glauber's salt, bbls.........100 lbs.	1.05
Glucose, 70°, bags, dry.....100 lbs.	3.14
Glycerol, C. P., drums...........lb.	.27
G salt, bbls......................lb.	.50
Hexamethylenetetramine, U. S. P., drums...................lb.	.60
Hydrogen peroxide, 25 vol., bbls.......................lb.	.06½
Hydroquinone, kegs.............lb.	1.25
Indigo, 20%, paste, bbls.........lb.	.14
Iodine, crude, 200-lb. kgs.......lb.	4.20
Iodine, resubl., jars.............lb.	4.65
Iodoform, bot....................lb.	6.00
Iridium, metal..................oz.	110.00
Kieselguhr, bags................ton	60.00
Lead, metal................. 100 lb.	6.65
Lead acetate, bbls., white......lb.	.15
Arsenate, bbls..................lb.	.14
Oxide, litharge, bbls...........lb.	.09¼
Red, bbls.......................lb.	.10
Peroxide, drums................lb.	.25
White, basic carb., bbls........lb.	.10¾
Sulfate, bbls....................lb.	.10
Lime, hydrated, bbls.......100 lbs.	.85
Lime, live, chemical bbls., wks. ....100 lbs.	1.05
Limestone, ground, bags, wks...ton	4.50
Lithium carbonate, 100-lb. kgs...lb.	1.45
Lithopone, bbls..................lb.	.06⅛
Magnesite, crude................ton	36.00
Calcined, 500-lb. bbls., wks...ton	48.00
Magnesium, metal sticks, wks...lb.	.85
Magnesium carbonate, bags.....lb.	.06¾
Chloride, drums...............ton	37.00
Fluosilicate, cryst., bbls.......lb.	.10
Oxide, U. S. P., light, bbls....lb.	.42
Manganese chloride, casks......lb.	.08
Dioxide, 80%, bbls............ton	80.00
Sulfate, casks...................lb.	.07
Mercury bichloride, cryst., 25 lbs. lb.	1.58
Mercury, flasks, 75 lbs.........flask	124.00
Meta-nitroaniline, bbls..........lb.	.72
Meta-phenylenediamine, bbls....lb.	.90
Meta-toluylenediamine, bbls....lb.	.72
Methanol, 97%, tanks..........gal.	.82
Methyl acetone, drums.........gal.	.88
Salicylate, cases................lb.	.47
Methyl chloride, cylinders......lb.	.55
Michler's ketone, bbls..........lb.	3.00
Monoethylaniline, drums.......lb.	1.05
Naphtha, solvent, tanks........gal.	.35
Naphthalene, flake, bbls........lb.	.04½
Nickel, metal....................lb.	.35
Nickel salt, single, bbls.........lb.	.08
Double, bbls...................lb.	.08½
Niter cake, bulk................ton	4.50
Nitrobenzene, drums............lb.	.08½
Oil, castor, No. 1...............lb.	.14
China wood, bbls..............lb.	.25
Coconut, Ceylon, tanks........lb.	.08½
Cod, N. F., tanks.............gal.	.59
Corn, crude, tanks, mills......lb.	.07¾
Cottonseed, crude, tanks......lb.	.07¾
Lard, edible, bbls..............lb.	.15¾
Linseed, bbls...................lb.	.112
Menhaden, crude, tanks.....gal.	.47½
Neat's-foot, pure, bbls.........lb.	.12¾
Oleo, No. 1, bbls..............lb.	.11½
Olive oil, denat., bbls.........gal.	1.68
Foots, bbls....................lb.	.09¼
Palm, Lagos, casks............lb.	.08¼
Peanut, crude, tanks..........lb.	.10
Perilla, bbls....................lb.	.16¼
Rapeseed, bbls., English.....gal.	.90
Red, bbls.......................lb.	.09
Soy bean, crude, bbls.........lb.	.12¼
Sperm, 38°, bbls..............gal.	.85
Whale, bbls., natural winter..gal.	.76
Ortho-aminophenol, kegs........lb.	2.20
Ortho-anisidine, drums..........lb.	2.35
Ortho-dichlorobenzene, drums...lb.	.06
Ortho-nitrochlorobenzene, drums ....lb.	.32
Ortho-nitrophenol, bbls.........lb.	.85
Ortho-nitrotoluene, drums......lb.	.13
Ortho-toluidine, bbls............lb.	.27
Palladium, metal................oz.	80.00
Para-aminophenol, kegs.........lb.	1.15
Paraldehyde, tech., drums......lb.	.27
Para-formaldehyde, cases.......lb.	.55½
Para-nitroaniline, drums........lb.	.52
Para-nitrochlorobenzene, drums ....lb.	.32
Para-nitrophenol, bbls...........lb.	.50
Para-nitrosodimethylaniline, bbls.......................lb.	.92
Para-nitrotoluene, bbls..........lb.	.30
Para-phenylenediamine, bbls....lb.	1.20
Para-toluidine, bbls.............lb.	.38
Paris Green, 500-lb. kgs.........lb.	.19
Phenol, drums...................lb.	.16
Phenolphthalein, drums.........lb.	1.30
Phenylethyl alcohol, 1-lb. bot....lb.	7.00
Phosphorus, red, cases..........lb.	.60
Phosphorus trichloride, cyl......lb.	.45
Phthalic anhydride, bbls........lb.	.18
Platinum, metal.................oz.	95.00
Potash, caustic, drums..........lb.	.07⅞
Potassium acetate, kegs.........lb.	.29
Bicarbonate, casks.............lb.	.09
Bichromate, casks..............lb.	.08¼
Binoxalate, bbls................lb.	.16
Bromate, cs.....................lb.	.35
Carbonate, 80–85%, calc., casks.......................lb.	.05⅝
Chlorate, kegs..................lb.	.08½
Chloride.......................ton	34.55
Cyanide, cases..................lb.	.55
Meta-bisulfite, bbls............lb.	.11
Permanganate, drums..........lb.	.14½
Prussiate, red, casks...........lb.	.39
Yellow, casks.................lb.	.18½
Titanium oxalate, bbls.........lb.	.25
Pyridine, drums................gal.	1.25
Quinine bisulfate, 100 oz........oz.	.40
Sulfate, 100-oz. cans..........oz.	.40
Resorcinol, tech., kegs..........lb.	1.30
Rochelle salt, bbls., U. S. P......lb.	.21
R salt, bbls......................lb.	.45
Saccharin, cans..................lb.	1.75
Salt cake, bulk..................ton	19.00
Saltpeter, gran., bbls............lb.	.06
Silica, ref., bags.................ton	18.00
Silver nitrate, 16-oz. bot........oz.	.40⅞
Soda ash, 58%, light, bags, contract, wks.............100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.........100 lbs.	3.10
Sodium acetate, bbls............lb.	.04½
Benzoate, bbls.................lb.	.50
Bicarbonate, bbls........100 lbs.	2.00
Bichromate, casks.............lb.	.06¼
Bisulfite, bbls..................lb.	.08½
Bromide, bbls..................lb.	.48
Carbonate, sal soda, bbls., 100 lbs.	1.30
Chlorate, kegs..................lb.	.06¼
Chloride, bags................ton	12.00
Cyanide, cases.................lb.	.20
Fluoride, bbls..................lb.	.08¾
Hyposulfite, reg., crys., bbls...lb.	.02½
Metallic, drums, 12¼-lb. bricks lb.	.27
Naphthionate, bbls............lb.	.55
Nitrate, crude, bags, N. Y. ....100 lbs.	2.60
Nitrite, bbls.....................lb.	.08½
Perborate, bbls.................lb.	.21
Peroxide, cases.................lb.	.27
Phosphate, trisod..............lb.	.04
Picramate, kegs................lb.	.69
Prussiate, bbls.................lb.	.12
Silicate, drums, tanks, 40°, 100 lbs.	.75
Silicofluoride, bbls............lb.	.04¾
Stannate, drums...............lb.	.48½
Sulfate, anhyd., bbls..........lb.	.02¼
Sulfide, cryst., bbls...........lb.	.02½
Solid, 60%.....................lb.	.03½
Sulfocyanide, bbls.............lb.	.40
Tungstate, kegs................lb.	.85
Strontium carbonate, bbls......lb.	.08
Nitrate, bbls...................lb.	.08
Strychnine alkaloid, 100 oz., powd.........................oz.	.56
Sulfate, powder................oz.	.38
Sulfur, bulk, mines, wks........ton	19.00
Sulfur chloride, red, drums......lb.	.05½
Yellow, drums..................lb.	.03¾
Sulfur dioxide, commercial, cyl..lb.	.08½
Sulfuryl chloride, drums........lb.	.65
Thiocarbanilid, bbls.............lb.	.22
Tin, Amer., stand...............lb.	.69
Tin bichloride, 50% sol., bbls....lb.	.19½
Oxide, bbls......................lb.	.72
Titanium oxide, bbls., wks......lb.	.40
Toluene, tanks.................gal.	.35
Tribromophenol, cases..........lb.	1.10
Triphenylguanidine, drums......lb.	.69
Triphenyl phosphate, bbls......lb.	.75
Tungsten................WO_3 unit	10.50
Urea, pure, cases...............lb.	.18
Whiting, bags...................ton	18.00
Xylene, 5°, drums, mills.......gal.	.50
Xylidine, drums.................lb.	.37
Zinc, metal, N. Y.......... 100 lb.	6.75
Zinc ammonium chloride, bbls...lb.	.06¼
Chloride, granulated, drums...lb.	.06¼
Oxide, Amer., bbls.............lb.	.07⅜
Stearate, bbls..................lb.	.19
Zinc dust, bbls., kegs, c/l.......lb.	.09