

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume III

JUNE, 1911

No. 6

BOARD OF EDITORS.

Editor: M. C. Whitaker.

Associate Editors:

Geo. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, Wm. Brady, Wm. Campbell, F. B. Carpenter, Virgil Coblenz, Francis I. Dupont, W. C. Ebaugh, Wm. C. Geer, W. F. Hillebrand, W. D. Horne, Karl Langenbeck, A. D. Little, C. E. Lucke, P. C. McIlhiney, E. B. McCready, Wm. McMurtrie, J. Merritt Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, Geo. C. Stone, Ernst Twitchell, Robt. Wahl, Wm. H. Walker, W. R. Whitney.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered at the Post-Office, Easton, Pa., as Second-class Matter.

EDITORIALS

A SURVEY OF CYANIDATION IN 1911.

The advances made in the last ten years in the art of cyaniding ores of gold and silver have taken place so rapidly that few men are aware of the extent to which the field of application of the process has widened. Indeed, these changes and improvements have followed so fast on the heels of one another that even the men engaged in the practice of cyanidation are at times ignorant of the later developments. The change has been gradual, and one of the most striking things about it is the chemistry of the process which is little advanced today over what it was ten years ago. Essentially a hydrochemical process, all the improvements have been mechanical and though we may have a better knowledge of its chemistry, that knowledge is of little use to us in solving the problems connected with it. The essential advantage of cyanidation over other hydro-metallurgical processes is its chemical simplicity. Various workable processes have been devised that improve on the present cyanide process in theory, but in practice, the fact that they require a higher degree of metallurgical skill for their successful application, will always prove a bar to their adoption if cyanidation will do the work almost as well. There undoubtedly will be ores of gold and silver that cyanidation will not extract the values from and we can turn to other processes when that is so. The great variety of ores treated by cyanidation makes one feel that where a gold or silver ore is concerned, in at least nine cases out of ten, cyanidation will make a better extraction at a lower cost than any other process.

Cyanidation was first practiced on the sand or granular portion of the tailing, from mills treating quartzose, gold-bearing ores. It was not regarded as suited to silver ores at first but soon was found to be applicable to them, though it made only a 60 per cent. recovery, because it did so at such a low cost.

These first plants were percolation plants and could only operate when part, or all, of the slime, or colloidal portion of the ore, was run to waste. The decantation plants of South Africa were an effort to solve the problem of treating slime that never fully succeeded. The most marked advance in cyanidation began when the submerged suction filter was brought to such a state of mechanical efficiency that it was generally applicable. The two best known exponents of this principle in this country are the Moore and Butters filters, though I believe the idea was previously employed by Cassel in South Africa in a less efficient form.

The submerged suction filters not only made it possible to treat all the slime but even made it desirable to reduce as much of the ore as possible to nearly a slime condition. These new conditions created new demands and a host of clever mechanical appliances has been perfected to meet them. It was no longer possible to bring the finely ground ore in contact with cyanide solution by passing the solution through the ore, as in a percolation plant, so this was achieved by mixing the ore and solution together and keeping the ore suspended in the solution by means of agitation. Unconsciously the tremendous improvement in extraction possible through finer grinding has been learned until now cyanidation presupposes fine grinding, agitation and filtration.

At present, gold and silver ores varying widely in chemical composition, and in value from \$4 to \$35 in gold, and from a few ounces to thirty ounces in silver, are being successfully cyanided. Cyanidation has displaced pan-amalgamation. The cost of cyaniding is lower, the extraction better and pan-amalgamation only was suited to ores essentially of silver, whereas cyanidation extracts both gold and silver. Lixiviation, with the necessity of previous roasting, costs much more to practice, makes a poorer extraction

of silver and none of the gold. Chlorination likewise requires roasting of the ore and makes no extraction of the silver. Even where an ore is so rebellious that it must first be roasted, cyaniding has displaced chlorination and lately the ores of Cripple Creek and Cobalt, chemically complex and hitherto considered hard metallurgical problems, are now successfully treated in the raw state, when low grade, by cyanidation. The last field to be invaded, and one in which the possibilities have not been reached, is that of concentrate treatment. Hitherto the concentrate produced by gold and silver mills was always shipped to the smelters, in many cases an uneconomical proceeding—but now every few months adds another to the list of concentrates that can be successfully cyanided. Simple ore-dressing—that is, amalgamation and concentration—will hold its own for some time to come on the low-grade ores to which it is suited, because the preparation of the ores is less elaborate and the whole operation can be performed for about one-third of the cost of cyanidation. Even then, the concentrate will probably be treated by cyanidation and wherever the grade of the ore is high enough to justify the expense of making a higher extraction, cyanidation will be preferred.

Most of these processes require a high order of metallurgical skill, but cyanidation can be successfully practiced by men of no technical education and little knowledge of chemistry.

The development of the process has consisted purely in refinement. Cyanide mills are now elaborate structures in which there is a special device employed for every possible operation. This high efficiency has been attained at the cost of flexibility, and smooth continuous operation is essential to low cost. The tendency in mill practice is to relieve the operator of the necessity of exercising his judgment and to place more responsibility in the hands of the designer. The function of the mill-man now is to understand his machinery and keep it in operation, but the extraction that the mill makes depends on that machinery being properly adjusted in the design of mill.

The cost of mills has increased enormously. This has made it advisable to employ a better standard of materials in their construction and more care in their design. A degree of thoroughness is exercised in testing previous to design that was unheard of a few years ago. Then standard mill construction involved 850 lb. stamps, wooden mortar blocks and framing, and three tons per stamp per day was regarded as good practice; the rough approximation generally accepted for mill construction was \$1,000 per stamp. This was equivalent to a cost for construction of \$335 per ton of daily capacity. Later the increased cost of materials and labor and the increase to 1050 lb. in the weight of stamps, with the consequent daily capacity of five tons per stamp, made \$2,000 per stamp the figure, equivalent to \$400 per ton of daily capacity. Now, the advent of the fine-grinding, agitation and filtration plant has so added to the machinery installed in mills, that the role of the stamp has been altered so that it can no

longer be taken as a basis for estimation and \$1,000 per ton of daily capacity will often be found as the correct figure for mill construction. The variation in cost is greater, however, and an estimate must be gone into with more care than formerly was the case. The standards of construction have changed. A wooden mortar block now excites more comment than a concrete one did seven years ago. Steel framing, concrete floors, retaining walls and foundation all are common practice.

The mills all resemble one another so that they virtually conform to a type. Those that differ from the type remain different not because they are better but because it would cost too much to change them. Every modern cyanide plant now involves fine-grinding, settling of the pulp to greater density and removal of the surplus solution, agitation, further settling and filtration. Crushing, in the majority of cases, is performed wet. The reason for the wide-spread adoption of this process to the exclusion of all others and of this type of mill is found in the cost and the extraction. The cost of cyanidation seldom gets below 50 cents per ton, but it should never exceed \$1.50 per ton. The extraction of gold should always be from 90 to 95 per cent., and of silver from 88 to 92 per cent. These results, which are so frequently attained in practice that they can be expected, make cyanidation an art, with the wide-spread application of which every metallurgist should be familiar.

ARTHUR R. TOWNSEND.

THE GENERAL MEETING IN JUNE.

Those chemists who were fortunate enough to listen to the remarks of Charles F. Chandler during the banquet at the opening of the Chemists' Club last March will not soon forget the earnestness of his description of the growth of the coöperative idea among American chemists. Having been among the very first in this country to organize a small group of men interested in chemistry and having been one of the small number who met around Priestley's grave in Northumberland, Penn., August 1, 1874, which meeting resulted in the organization of the American Chemical Society, he spoke with authority. The chief tenor of his advice was to "get together," and those who know him well know that he as well as others of the pioneers in American chemical science have exerted their full influence throughout their lives to induce American chemists to get together for their own advancement and the advancement of the profession. The point cannot be too strongly emphasized, for its practical embodiment is seen in the remarkable growth of the American Chemical Society in the last twenty years and the wonderful influence it has had upon the development of chemical industry in America and upon the increase of individual knowledge and endeavor among American chemists.

The Local Sections of the Society afford means of personal contact with chemists in limited localities, and these Local Sections have done a great and good

work in developing the spirit of helpfulness and fellowship among their members. Altogether too few of the members of the Society, however, attend the general meetings which occur semi-annually. It is true that attendance at these meetings is rapidly increasing, but it has not yet reached the point that can reasonably be expected, and it is hoped that the members of the Society will carefully consider this point and make every endeavor to be present at Indianapolis and future gatherings of the general Society.

No member who has not been a regular attendant at the general meetings can realize the wonderful help they may be in the development of the individual. They give opportunity of meeting chemists in all kinds of work, thereby broadening the knowledge of the individual; they give opportunity of meeting chemists who are interested in the same lines of work and thereby frequently add to the specific facts which are important in special industries; they give opportunity of meeting the most successful chemists both in industrial and educational work and thereby add inspiration—they give opportunity for visiting special industrial works, adding to the practical knowledge of the visitor; they give opportunity for a summer or winter outing, for every Local Section does much to entertain its guests.

Many chemists feel that they cannot afford the time and expense of attending these meetings. Most of those who do attend, especially after they have been two or three times so that they become acquainted, realize that they cannot afford to stay away even if the distance is great and time is pressing. Especially the young or isolated chemist who has not the opportunity of frequent intercourse with his fellows, who is too apt to get into one line of thought, cannot afford to stay away, for the friendships made and the inspiration gained through knowledge of the work of others will make him a better chemist and is certain in the end to add to his material as well as to his mental advancement.

It is particularly pleasant to see the changing attitude of many of our most prominent firms towards attendance at the general meetings of the Society. A few years ago chemists complained that they found it difficult even to get the necessary leave of absence to attend the meeting. Now the case is quite often reversed. Firms have found that they gain so much by the presence of their chemists at these meetings that those who have had experience have almost invariably not only allowed the necessary time for attendance but in many instances now insist upon attendance and in an increasing number of cases pay all the expenses of the chosen individual. These cases are as yet altogether too few, but they are yearly increasing and it is indicative of a broader and more successful American chemical industry. It is certainly true that it is the most progressive and successful firms that require their chemists as a part of their work to attend the general meetings of the American Chemical Society.

Special efforts are being made to have the summer meeting in Indianapolis a great success, and definite

assurance can now be given that every member who attends the meeting will have unusual opportunity both for enjoyment and for professional development. The Entertainment Committee is planning an interesting program for the entertainment of ladies, and it is certain that they, too, will find the meeting unusually attractive. An especially amusing program is promised for the smoker on one evening; the following evening an automobile ride to the Country Club with lunch on the grounds, lawn fete, dancing, music, etc., is expected; on the third evening the usual banquet will be held. Two full days will probably be given up to the meetings of the Divisions, while the morning of the first day will be given to general addresses of interest to all chemists. One afternoon those present are to be especially entertained at the dedication of the new laboratories of the Eli Lilly Company, one of the largest pharmaceutical manufacturing companies in America. Saturday will probably be given up for the main part to visits to manufacturing plants.

Begin to plan now for the summer meeting. Remember the date is Wednesday, June 28th, to Saturday, July 1st; the place, Indianapolis. Let us all "get together" there!

CHARLES L. PARSONS.

ENDOWMENT FUND.

No organization which does a great and broad public service should be without the resource of available funds to promote and further the work.

On every hand we see a continual and worthy effort being made to stabilize and make sure of a continuous performance such endeavor.

Why the American Chemical Society should not take advantage of the very apparent opportunity is hardly understandable. Here awaiting us for action are to be found the ideal conditions under which a most successful effort can be undertaken. An organization composed of a body of men representing all classes, working for a great common good, namely, the advancement of chemical knowledge, with the best field for its application.

With an intangible valuable attribute to the goods to be delivered—working brains; a market for these same goods, which is boundless; an unsatisfied demand for the best obtainable execution measured by the ability of the individual and the effectiveness made possible by the organization as a unit, what more could be asked or could be offered which would appeal to the users and consumers of such a product, namely, the body corporate, The American Chemical Society? We who are of it should individually and all together determine upon a course which will enable the Industrials of this country to benefit by an open-minded, free-for-all research in all branches of chemistry, giving to the struggling young chemist inspiration by opportunity, and to the manufacturers at large an appreciation of unrestricted research, the benefit of which can be enjoyed by all to the great advancement of the industries of this country.

That an endowment fund would properly take care of this need is very apparent, and in one way only

can such a fund be made available—absolute and complete cooperation with a well defined plan of action carefully thought out and made the interest of every director, councilman, division chairman, sectional chairman and member.

In order to secure the opinion of the Society as a whole we take this opportunity to place an insert in this issue, and request your prompt reply to the questions of the Chairman of the Endowment Committee.

B. T. B. HYDE.

ORIGINAL PAPERS.

THE MICROSCOPIC EXAMINATION AND IDENTIFICATION OF CARBON.

By G. A. ROUSH.

Received March 28, 1911.

The remarkable success which has in the last few years attended the application of microscopic methods to the examination of the structure and properties of metals and alloys suggested an attempt to apply the principles of metallography in the examination of carbon. The carbons of commerce are made up of small particles of one or more of the different varieties of amorphous carbon cemented together by means of a binder, usually tar or pitch. The object of this investigation was, if possible, to develop some distinguishable difference in the appearance under the microscope of these ultimate particles of carbon, by which they could always be recognized, in order that the composition of unknown materials might thus be determined.

The wide-spread uses to which carbon is being put nowadays, and the variety of raw materials which may enter into the composition of carbons of different classes and grades has made desirable a method for the differentiation of various raw materials which may have been used, and an approximate analysis of the composition of any particular sample. The principal commercial uses of carbon are for arc light electrodes of various kinds, electrodes in furnace and electrolytic processes, electrodes for dry and wet batteries, brushes for dynamos and motors, contacts and resistance material in electrical apparatus and machinery.

Such a wide scope of uses as are shown here necessarily implies a considerable number of available raw materials which may be used to give the carbons the distinctive properties best suited for their particular uses. The list of available materials includes the following:

Lampblack
Retort Carbon
Petroleum Coke

Graphite	{	Natural	{	Powdered
		Artificial		Flake
Coal Coke	{	Bituminous	{	Bee Hive
				By product
		Anthracite		Gas

Coal coke is at present used very little, if any, on account of its high ash content, but it is a possible available material for future use, provided some process can be devised to remove the ash, or for some use where the presence of the ash is not detrimental. Lampblack is used most in the high-grade arc carbons, and to a small extent in some grades of motor and dynamo brushes. Electrodes are mainly of petroleum coke, sometimes of retort

carbon and sometimes of a mixture of these two. Motor and dynamo brushes may be composed wholly of retort carbon, petroleum coke or one of the varieties of graphite, or of mixtures of two or more of these materials, with occasionally a small percentage of lampblack, as stated above.

Heretofore there has been no means of even approximately estimating the composition of products of this kind, except by judging from appearance, and comparing with trial mixtures. Hence the determination of the composition, or the duplication, of a sample of unknown composition was a matter of considerable difficulty, which, it is hoped, will be somewhat lessened by the results of this investigation. The results here described are not as full and complete as might be desired, but those obtained are given as a step in the right direction, with the hope of adding to them in the future.

Methods.—The methods are simply those used in the examination of a sample of a metal or alloy to determine its internal structure. These can be found in full in any standard work on metallography, and so will be given only briefly here. The method in general consists in selecting a suitable sample of the material in question, grinding on one side a flat surface by means of an emery wheel, and then bringing this flat surface to a smooth polish by rubbing it successively on emery papers of increasing fineness. After a perfectly smooth polished surface is obtained, the structure of the material is developed by etching the surface by means of some suitable etching medium, and the prepared surface is then ready for examination under the microscope, the object being, as stated before, to develop some distinguishable difference in the appearance of the particles of which the material is composed, by which they can be recognized and distinguished.

Preparation of the Samples.—The samples should be selected so as to be as representative as possible, and several different sections should be prepared so that the results obtained may represent a fair average of the material in question. In order to accomplish this, the samples examined should include sections, the polished surfaces of which were originally perpendicular to each of the three principal axes of the original sample, since the orientation of the particles of carbon varies with the shape of the particle and with the shape of the die through which they are forced.¹ The samples to be examined are best removed from the entire mass by means of a hack saw. The surface to be prepared is first flattened by touching to an emery wheel or dressing with medium rough file. The further polish-

¹ Those not familiar with the manufacture of carbon are referred to the writer's article on this subject in *THIS JOURNAL*, May, 1909.

ing of the sample then consists in removing the scratches left on the surface by one grinding medium with a succeeding one of finer grit. The emery or file can be followed by rubbing on an emery paper of No. 1 or No. 0 grade, and this is followed by successive grades of Crocus paper from No. 0 to No. 0000. The sample should be rubbed on each paper so that the scratches produced are at right angles to those produced by the preceding paper, since by this means it can be most easily determined when all the scratches of the preceding paper have been eliminated. A few rubs over the surface of the No. 0000 Crocus paper usually suffices to fill the grit of the paper with finely divided carbon from the sample in hand so that the surface is given a more or less mirror-like polish, which is the result desired. The steps necessary to obtain such a polish vary widely with the different materials. In some cases only two or three of the different polishing papers are required, and with others one may have difficulty in obtaining the desired results at all. Some samples give satisfactory results at first trial, while others require repeated attempts before they finally give a surface that can be examined with any satisfaction. It is a matter that can be learned only by experience, since every individual piece requires its own individual treatment.

After the specimen is polished, it has to be given a further treatment in order that the structure may be distinguished. The surface must be treated in such a manner that the softer parts of the material are worn away more than the harder, so that in this manner the structure of the material is left in outline. This may be accomplished in one of two ways: the sample may be heated to a red heat so that the air attacks and oxidizes the polished surface, leaving the denser and more resistant parts in outline, or the surface may be still further polished on a soft, yielding material such as chamois skin or broadcloth, so that the softer parts are worn away more rapidly than the hard, thus leaving the outlines in relief. In the further descriptions the former is known as "heat etching" and the latter as "relief polish." These two different ways of finishing the specimen give a somewhat different final appearance, and the question as to which is the more suitable for a given sample can be decided only by trial. It is often of benefit to prepare samples in both ways and compare them with each other. No set rule can be given as to the amount of etching necessary, as this varies with the different samples, but usually, if heat-etched, it should not be more than just enough to destroy the gloss of the polished surface. The specimen should be heated to a red heat in a blast lamp and allowed to oxidize in the open air until the gloss from the polished surface has just disappeared, when the entire sample should be cooled below a red heat as quickly as possible by holding it in a blast of cold air. It is often more difficult to get good results with the relief polish than with the heat etching. The specimen should be examined frequently with the microscope during the polishing operation, and as soon as a good relief is obtained the polishing should be stopped, for a relief once developed can be easily de-

stroyed by polishing a little too long. In some cases the relief polish might be followed to good advantage by the heat etching, giving better results than could be obtained from either used alone.

After a specimen has been etched sufficiently, and has been shown by a preliminary examination under the microscope to be in the condition in which it is desired, it should be mounted permanently on a slide. The etched surface is very delicate, and if it is attempted to preserve the specimens loose, even though they are packed in cotton, the liability of damage to the etched surface is great. They are best preserved by mounting them on a regular microscope slide by means of sealing wax. In order that the entire surface of the specimen may be in focus, it is necessary in mounting that its surface be kept perfectly parallel with the surface of the slide on which it is mounted. This is done by means of the device shown in Fig. 1, which can be

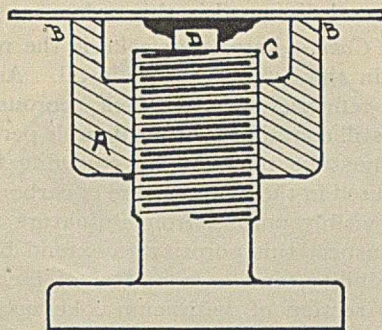


Fig. 1.—Mounting device for specimens.

made in any machine shop. By turning the circular ring A, the surfaces B and C can be separated any distance desired and yet always remain parallel to each other, if the instrument has been properly made. The specimen D is laid polished surface down on the face C, the ring A is turned until a slide laid on B just clears the specimen, a few drops of hot wax are then dropped on the back of the specimen or on the center of the slide, and the slide is pressed down against the face of B until the wax is cold.

After the preparation and mounting of the specimen it is ready for examination under the microscope. For this purpose any microscope can be used which can be supplied with an apparatus for vertical illumination, descriptions of which can be obtained from any standard work on metallography. The instrument used in this investigation was the Leitz metallograph, supplied with eye-pieces and objectives giving magnifications of 65, 200, 325 and 550 diameters. Practically all of the work was done with the two lower magnifications, the larger ones being used only occasionally when a sample was found in which the raw materials had been ground exceedingly fine.

Whenever possible the samples should be filed away for future reference, but where this is impossible, or where records are wanted for any other purpose, recourse may be had to photography, which will reproduce the appearance of the samples in all of their detail. In some ways the photomicrograph is of more value

than the original sample as a record, since it makes easy the comparison of one sample with another, or different magnifications of the same sample. The details of this process can be obtained from some book on photography or metallography.¹

A carbon treated in this manner and viewed under the microscope has an appearance similar to Figs. 2 and 3. In these the individual grains can be distinguished readily, the former being magnified 65 diameters and the latter 200 diameters. The problem now before us is to find some means of distinguishing between the different individual grains when some are of one material and some are of another. This was accomplished by studying pure samples of the different raw materials that enter into the make-up of the carbons. As has been shown in the list of raw materials, the most important of these are petroleum coke, retort carbon, artificial graphite and natural graphite, varying in importance in the order named. These will be taken up and discussed in this order.

Petroleum Coke.—Petroleum coke is the residue left in the still in the refining of crude oil. As obtained from the oil refineries, it is a black, porous carbonaceous mass, still containing a considerable percentage of oil, which must be removed by calcining before the coke can be used in the manufacture of carbons. While the mass is visibly porous, from its nature and origin one would suspect this porosity to extend beyond the limits of visibility, and as a matter of fact, it does. Fig. 4 is a section of petroleum coke magnified 65 diameters. This shows to good advantage the large pores in the mass, and the cellular nature of the finer part of the structure. Fig. 5 shows the same section under a magnification of 200 diameters. Here it can be seen that the porosity of the material still persists up to the limits of this magnification, giving the surface a peculiar striated appearance, due to the numerous fine pores throughout the mass of the material. This striated appearance is characteristic of petroleum coke, and can easily be detected and recognized wherever this material is found. Numerous samples of petroleum coke have been examined from different sources, that had received all sorts of different treatment, and none were found in which this peculiar characteristic striated appearance could not easily be developed and recognized.

Fig. 6 shows a section of a carbon rod known to be made from petroleum coke, magnified 65 diameters, showing the structure of the body of the carbon. Fig. 7 is the same section under a magnification of 200 diameters, showing the characteristic striated appearance developed in the particles of petroleum coke. Figs. 8 and 10 compared with Fig. 6 show what varied appearances may be met in the shape of the individual grains and the structure of the body of the carbon, yet all, under the higher magnification, show the same characteristic appearance of petroleum coke, as seen in Figs. 7, 9 and 11.

¹ For greater detail concerning the apparatus and operations mentioned consult any of the following books: Gulliver, *Metallic Alloys*; Law, *Alloys and Their Industrial Application*; Osmond and Stead, *The Microscopic Analysis of Metals*; Howe, *Iron, Steel and Other Alloys*; Ruer-Mathewson, *Introduction to Metallography*.

Retort Carbon.—Retort carbon is the carbon deposited in the flues leading from the retorts in a coal gas bench. Most retort carbon is found as a heavy steel-gray mass with a granular structure. The mass may vary considerably in density and porosity in different parts, and may be contaminated with more or less soot, but it is of a fairly uniform granular structure throughout. A second form is found in the shape of nodules, which have been deposited in successive layers, and the grains of carbon are usually smaller than in the granular variety. Fig. 12 shows a section of granular retort carbon under a magnification of 65 diameters; Fig. 13 shows a section of nodular retort carbon under the same magnification. In the former the uniform body of the material is shown, while in the latter the successive layers from which the nodules are built up are readily distinguished. Under a higher magnification both varieties show practically the same structure, a somewhat roughened, finely pitted surface, apparently made up of very fine granules, as shown in Fig. 14, where the same sample as shown in Fig. 12 is shown under a magnification of 200 diameters. This structure is not changed at a still higher magnification as is shown in Fig. 15, which is a sample of retort carbon under a magnification of 325 diameters. This is the characteristic structure of retort carbon. As in the case with petroleum coke, wide variation may be met in shape of the individual grains and the structure of the body of the carbon, as can be seen in Figs. 16, 18 and 20, but under the higher magnification all show the characteristic pitted surface, as seen in Figs. 17, 19 and 21.

Graphite.—The presence of graphite in a carbon, if to any appreciable extent, can be detected by the general appearance of the carbon and by the specific gravity. Carbons made from petroleum coke and retort carbon are not liable to have a specific gravity higher than 2.05, and many do not go above 2.00, while graphite has a specific gravity of 2.25–2.30. The amount of ash in the sample is also an indicator. A carbon made from a good grade of petroleum coke should not exceed 0.25–0.75 per cent. of ash, the latter being a high figure. A good grade of retort carbon will run from 1.00 to 2.00 per cent., with occasionally 2.50 per cent. If artificial graphite be present in the carbon, these figures may not be changed very much, for the better grades of artificial graphite do not have a very high ash content. It is probable, though, that one of the lower grades would be used, which would result in an appreciable increase in the ash content. If natural graphite were used, the difference would be still more marked, unless an exceptionally pure graphite were used.

Artificial Graphite.—Artificial graphite, being a manufactured product obtainable from several different sources, does not show a distinctive structure such as characterizes petroleum coke and retort carbon. No samples of artificial graphite have been found thus far that possess any distinctive characteristic markings of their own. Fig. 22 shows a section from a block of Acheson graphite, presumably made from petroleum coke. Fig. 23 is a section from another

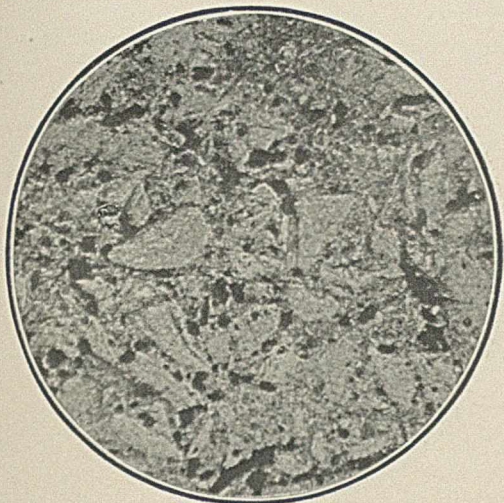


Fig. 2. $\times 65$.
Carbon sample showing structure and individual grains.
Heat-etched.



Fig. 3. $\times 200$.
Carbon sample showing structure and individual grains.
Heat-etched.

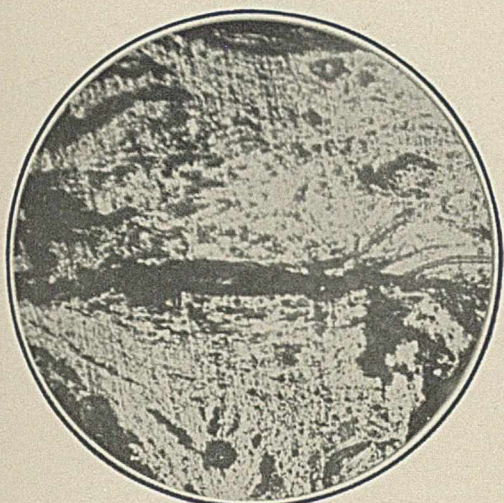


Fig. 4. $\times 65$.
Section of petroleum coke. Relief polish.

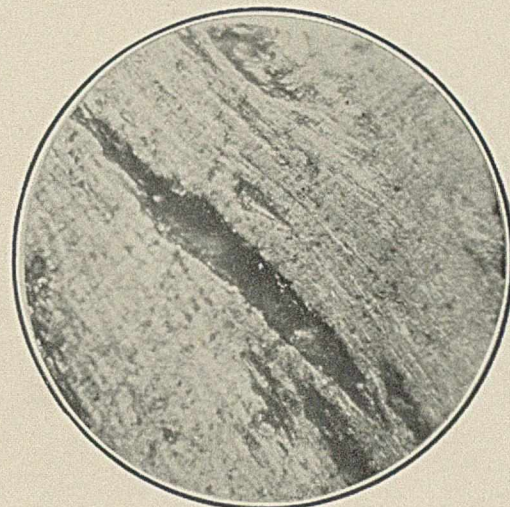


Fig. 5. $\times 200$.
Section of petroleum coke. Relief polish.

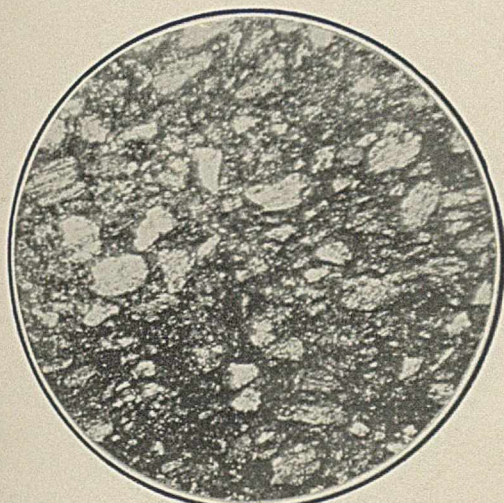


Fig. 6. $\times 65$.
Carbon rod showing individual grains of petroleum coke.
Heat-etched.

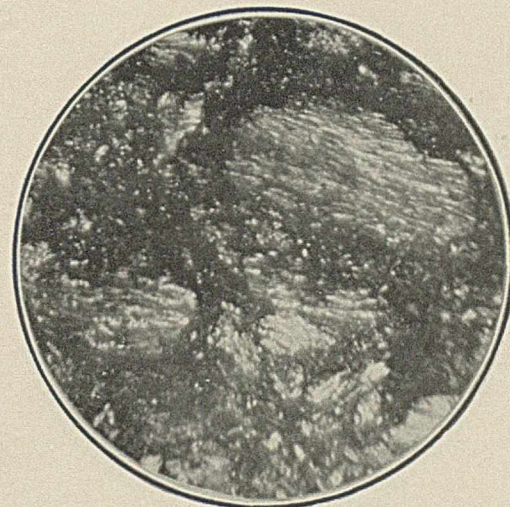


Fig. 7. $\times 200$.
Fig. 6 under higher magnification. Heat-etched.

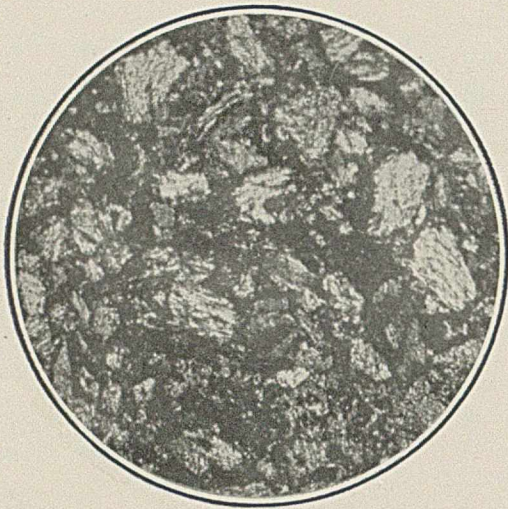


Fig. 8. $\times 65$.
Carbon rod showing individual grains of petroleum coke.
Heat-etched.

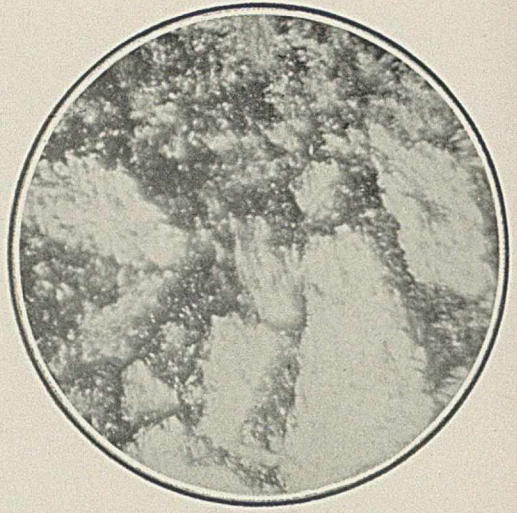


Fig. 9. $\times 200$.
Fig. 8 under higher magnification. Heat-etched.

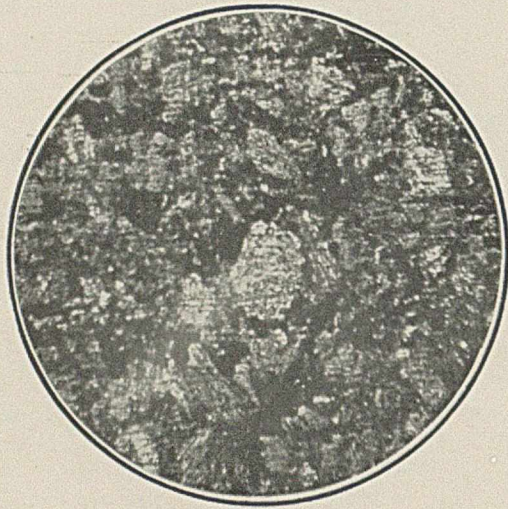


Fig. 10. $\times 65$.
Carbon rod showing individual grains of petroleum coke.
Relief polish.

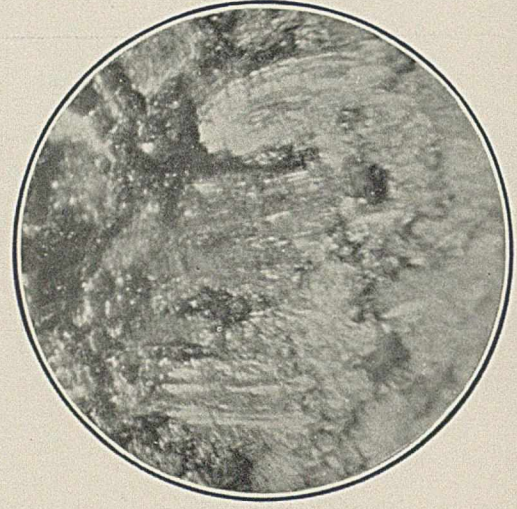


Fig. 11. $\times 200$.
Fig. 10 under higher magnification. Relief polish.

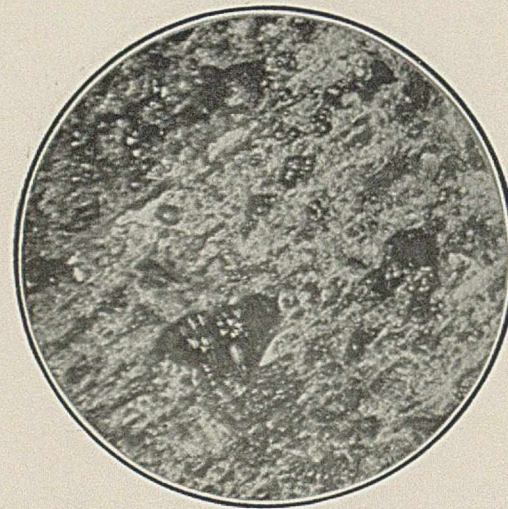


Fig. 12. $\times 65$.
Section of granular retort carbon. Relief polish.

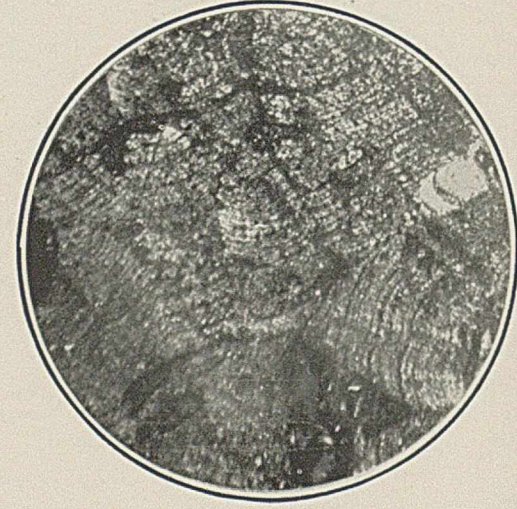


Fig. 13. $\times 65$.
Section of nodular retort carbon. Relief polish.

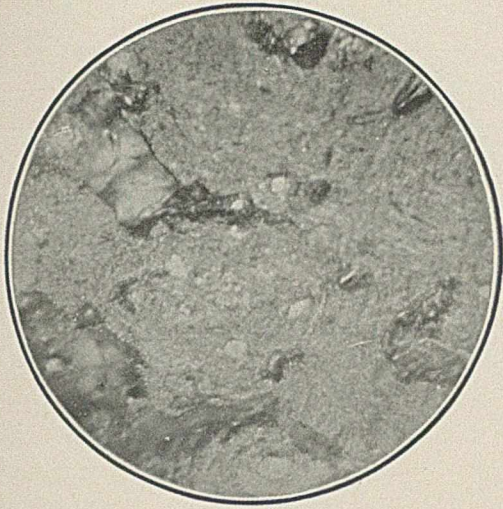


Fig. 14. $\times 200$.
Fig. 12 under higher magnification. Relief polish.

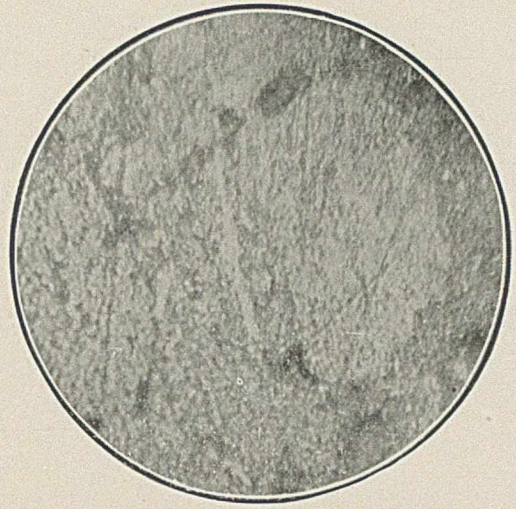


Fig. 15 $\times 325$.
Retort carbon under higher magnification. Relief polish.

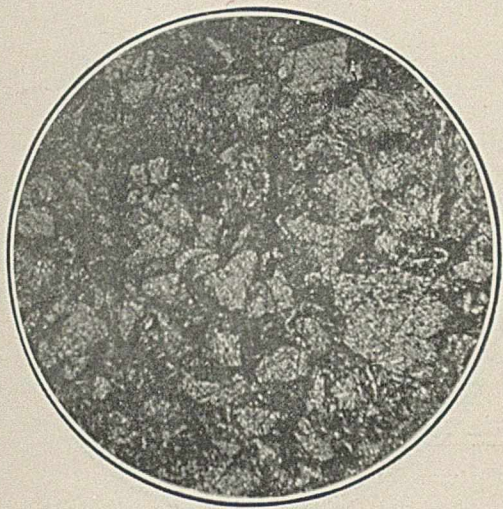


Fig. 16. $\times 65$
Carbon showing individual grains of retort carbon. Relief
polish.

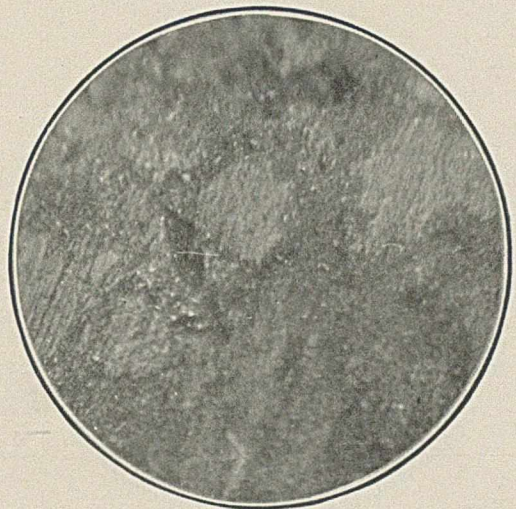


Fig. 17. $\times 200$.
Fig. 16 under higher magnification. Relief polish.

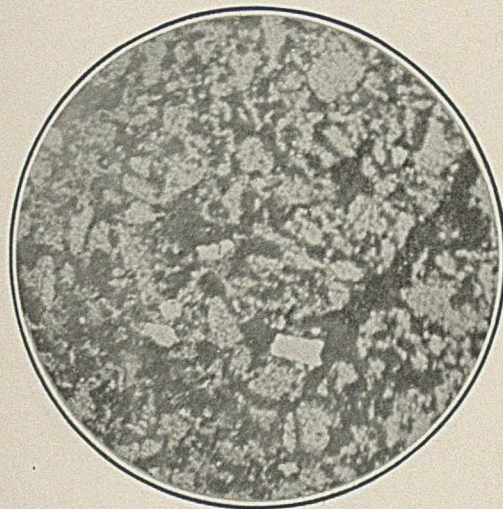


Fig. 18 $\times 65$.
Carbon showing individual grains of retort carbon. Heat-
etched.

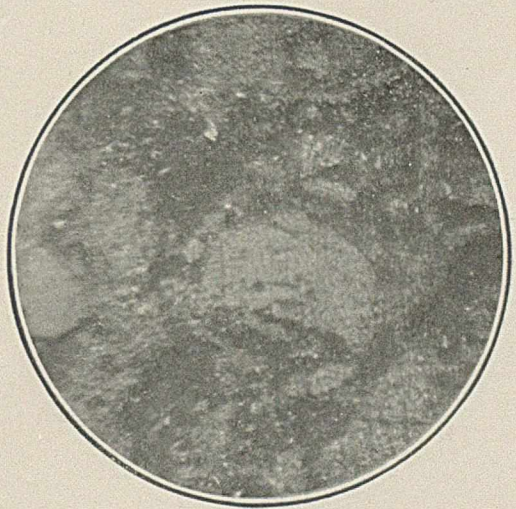


Fig. 19. $\times 200$.
Fig. 18 under higher magnification. Heat-
etched.

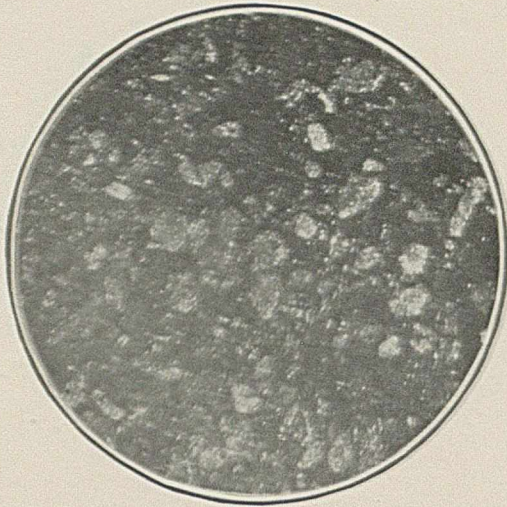


Fig. 20. $\times 65$.
Carbon showing individual grains of retort carbon. Heat-
etched.

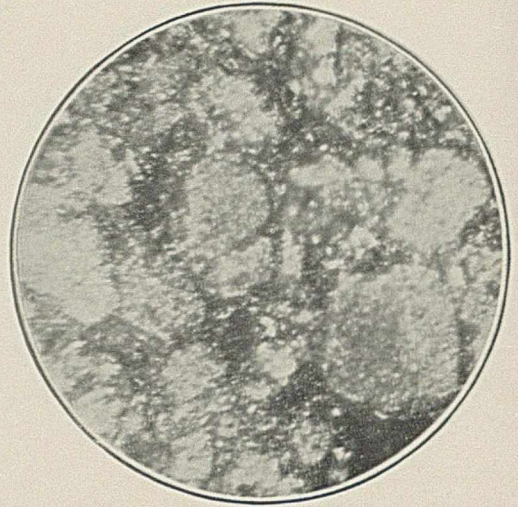


Fig. 21. $\times 200$
Fig. 20 under higher magnification. Heat-etched.

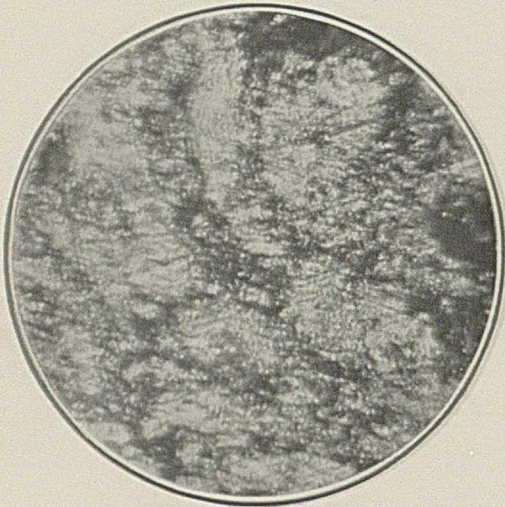


Fig. 22. $\times 200$.
Section of Acheson graphite. Heat-etched.

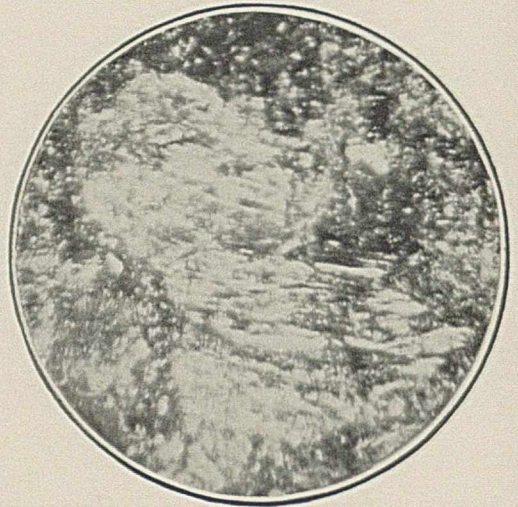


Fig. 23. $\times 200$.
Section of Acheson graphite. Heat-etched.



Fig. 24. $\times 200$.
Sample containing petroleum coke and artificial graphite.
Heat-etched.

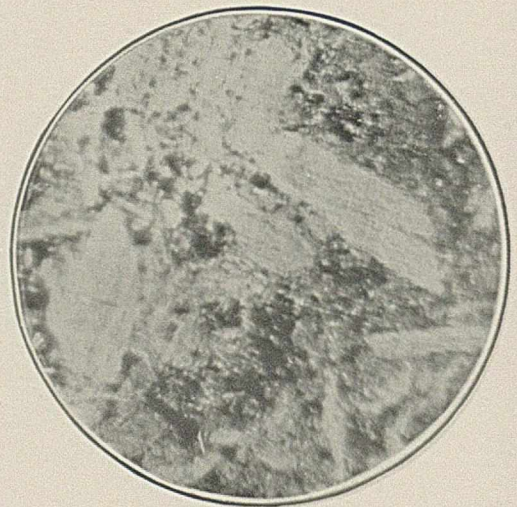


Fig. 25. $\times 200$.
Sample containing retort carbon and artificial graphite.
Relief polish.

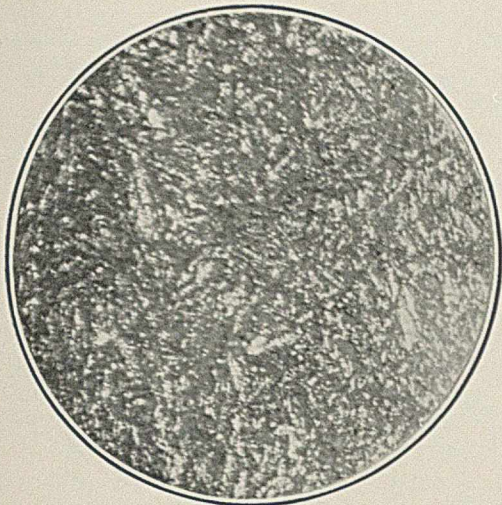


Fig. 26. $\times 65$.
Carbon from fine natural graphite. Heat-etched.

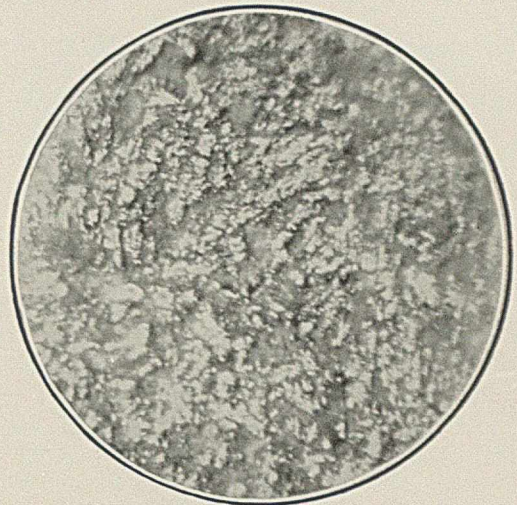


Fig. 27. $\times 200$.
Fig. 26 under higher magnification. Heat-etched.

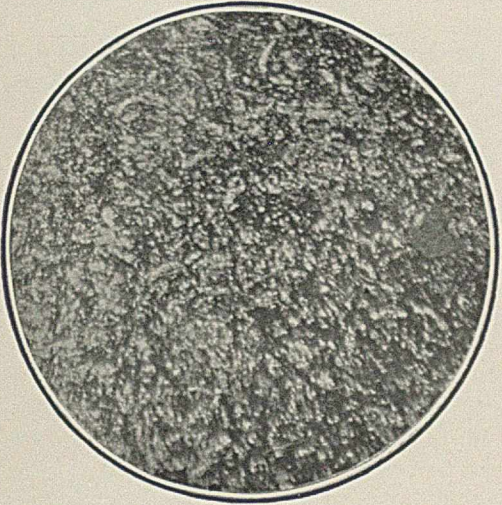


Fig. 28. $\times 65$.
Carbon from larger natural graphite. Heat-etched.

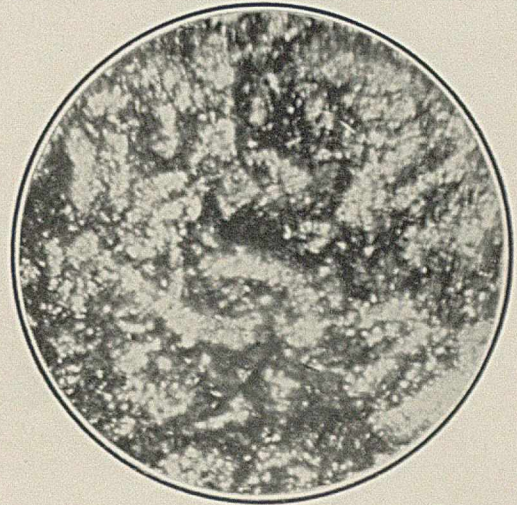


Fig. 29. $\times 200$.
Fig. 28 under higher magnification. Heat-etched.

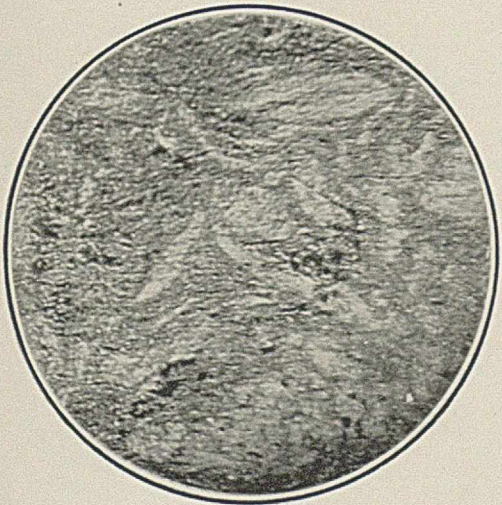


Fig. 30. $\times 325$.
Carbon from larger natural graphite. Relief polish.



Fig. 31. $\times 65$.
Carbon from coarse natural graphite. Relief polish.

piece of Acheson graphite that plainly shows its origin by its characteristic striated appearance. The question immediately presents itself, Why should one of these samples show no distinctive markings, and the other show them so plainly? Is this second sample a case of incomplete conversion, or is this retention of form analogous to a pseudomorphous crystal? Samples similar to the latter are not at all hard to find; as a matter of fact, they seem to be more numerous than the former.

So far, artificial graphite has shown no characteristics by which it can be distinguished from other materials under the microscope. The samples shown in Figs. 24 and 25 contain more or less graphite along with the other constituents, but one is not able to pick out the individual particles as can be done with the petroleum coke and retort carbon, and since, as is stated above, artificial graphite can be made from any of the different forms of amorphous carbon, we are liable to find samples of artificial graphite which still retain more or less of the appearance of any of the possible original materials. A full and careful study of the graphites obtained from the different commercial varieties of amorphous carbon will be required before one can say with any assurance that these forms of graphite can be identified, and distinguished one from another.

Natural Graphite.—The natural graphites are as a rule more or less of a flaky nature, with the flakes varying in size from an almost impalpable powder up to almost an eighth of an inch across. While the natural graphites do not have any very distinctive markings, after a little experience one can generally recognize them by the shape of the flakes. Figs. 26 and 27 show a sample of very fine natural graphite under magnifications of 65 and 200 diameters, respectively. Figs. 28 and 29 show a graphite with a slightly larger flake, under the same magnifications. Figs. 30 and 31 show flakes of still larger size, the former being enlarged 325 times, and the latter only 65 times. These last two samples are finished with the relief polish, while the other two are heat-etched. The different results produced by the two methods on similar materials is shown clearly.

Similarities and Differences.—Occasionally cases are found where particles of one material show an appearance similar to one of the other materials, and require considerable study and manipulation before they can be definitely identified as one or the other. The preparation of several specimens from each sample examined usually will enable one to avoid false conclusions in a case of this kind.

Anodular retort carbon, such as is shown in Fig. 13, may under some conditions appear very similar to the striated surface of petroleum coke. This can usually be detected by a higher magnification, which will develop to a greater extent the characteristic structure of the retort carbon, and will also aid in the identification by bringing out more clearly the almost perfect parallelism of the lines on the surface, which is much more perfect than is found in the striations of petroleum coke.

The striated appearance of the petroleum coke is

due to the presence of minute pores extending throughout the body of the material. If the section is cut so that its surface is perpendicular, rather than parallel, to the course of these pores, the surface will appear more or less pitted, similar to the characteristic structure of retort carbon, particularly under the lower magnifications. This can usually be detected without much difficulty by a higher magnification and specimens cut from other parts of the sample under examination.

A natural graphite in large flakes, if etched by heat, may show striations similar to petroleum coke, but this material can usually be detected by the shape of the flakes, as shown in Figs. 29, 30 and 31.

With a little experience, one can become familiar with these similarities and differences, so that the identification of the different materials can be accomplished without much difficulty.

Optical Analysis.—The next step after the identification of the constituents of the carbon is the determination of the quantities in which the different constituents are present. When the materials have been ground very fine, this is a difficult matter, but if the particles are not too small, so that their outlines can be definitely determined, fairly accurate results can be obtained. For this purpose, the methods of optical analysis used in petrography for the analysis of rocks can be used.

It has been determined¹ that the sum of the diameters of a large number of adjacent particles, measured in a straight line, bears the same ratio to the total length of the line from outside to outside of the first and last particles, as the volume of these particles is to the total volume of the material; in other words, the quotient obtained by dividing the total length of the line into the sum of the diameters of the particles touching the line and measured on the line, gives the percentage by volume of the whole, occupied by those particles. For this purpose the sample in question is put under the microscope at a magnification sufficient to clearly distinguish all of the individual particles, using a micrometer eye-piece, preferably one with cross hairs unless the scale of the micrometer has a line drawn lengthwise through it, as some do have. This will give the field an appearance like that shown in Fig. 32. The hair line serves as the straight line across the surface of the specimen, along which the measurements are to be made. Those portions of the line are measured which lie on the particles whose percentage is sought. Whatever may be the size or shape of the particles encountered, that portion of the line is measured that lies on the surface of all the particles under the scale of the micrometer, and note is made of the total length of the micrometer scale, and of the sum of all the diameters of the particles as measured along the straight line. Other portions of the specimen are then measured in the same way until the total distance measured over is at least 100 times the diameter of the largest particle encountered. The greater the total length measured, the greater the accuracy of the results, and,

¹ Rosiwal, *Verh. Wien. Geol. Reichsanstalt*, **32**, 143 (1898); Williams, *Am. Geol.*, **35**, 40-43 (1905); *Quantitative Classification of Igneous Rocks*, by Cross, Iddings, Pierson and Washington, 204.

if possible, several different specimens of the same material should be used in order to get a better average. When the desired number of measurements have been made, the sum of the diameters measured, times 100,

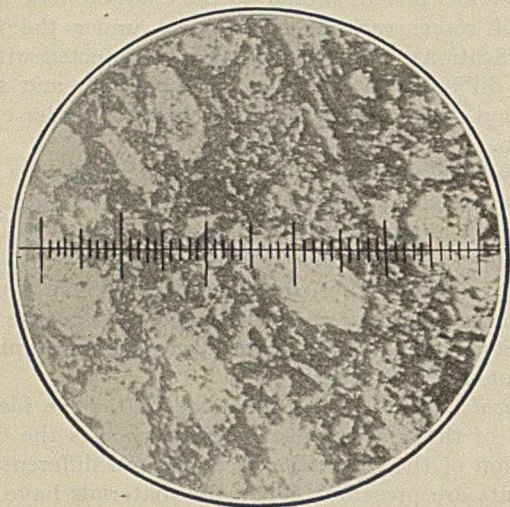


Fig. 32. $\times 65$.

Specimen under micrometer eye-piece ready for measurement.

divided by the total distance measured over gives the percentage by volume occupied by the particles measured. By this method, several different constituents may be determined at one time simply by having separate columns to add the diameters of the different particles measured. When the material is made up of two or more constituents, it requires more work to get the desired results, because it usually requires a higher magnification to distinguish one constituent from another by their characteristic markings than it does to simply distinguish the individual particles from each other; for this reason the apparent diameters of the particles as measured will be greater, and a greater number of measurements will be required in order to secure the desired accuracy.

When the percentage by volume has been determined the percentage by weight, if desired, can be calculated from the density of the whole mass and that of the material in question.¹

The accuracy of this method as applied to materials of this kind is not as great as might be desired, but with care, results can be obtained that have sufficient accuracy to make them of considerable value. The first precaution to be observed is to secure as fair an average as possible by making a large number of measurements from as many different samples of the material in question as can be obtained. The fineness to which the constituents entering into the carbon have been pulverized has considerable effect on the accuracy of the results, for if the particles are exceedingly small, it is difficult to obtain a polished section in which the outlines of the grains are clear and definite. For this reason, the results as obtained are always liable to be more or less below the true values, owing to the fact that it is difficult, in making the measurements, to find and include all of the very fine particles. Low results

¹ Methods for the determination of the density of carbon can be found in the article referred to in Note 1.

may also be expected to a certain extent if the section has been prepared by heat etching rather than by the relief polish, since the burning destroys to a greater extent the original outline of the grains.

Specimens of known composition have shown results differing from the calculated contents by only one per cent., while in other cases the difference was as high as four or five per cent., depending on the success with which the sections measured were prepared, the size of the grains, and the definiteness of their outline. The difficulties encountered with very small grains can be only partially avoided by higher magnification. This will of course make the grains more easily distinguished, but they will still lack definiteness of outline. As with all the other operations, a little experience will give one the ability to make the measurements fairly readily.

Conclusion.—These methods of identification and analysis should prove of some value to the manufacturers and users of carbons of various kinds, particularly so of dynamo and motor brushes, the manufacture of which must be very closely followed in order to secure a uniform product, and a systematic study of the structure and body of the different materials should lead to a marked improvement in their quality and wearing properties.

The outline of this subject as presented here still leaves much to be desired, but it is hoped that sufficient results have been shown to prove themselves of use, and it is hoped that the field may soon be broadened, and further results added to those already obtained.

MORGANTOWN, W. VA.

[CONTRIBUTION FROM RESEARCH DEPARTMENT, THE AMERICAN ROLLING MILL CO., MIDDLETOWN, OHIO.]

THE DETERMINATION OF OXYGEN IN IRON AND STEEL.

By ALLERTON S. CUSHMAN, Director of Institute of Industrial Research.

Received April 22, 1911.

The determination of oxygen in iron and steel has not received sufficient attention in the United States. The text-books on steel works analyses, which are in common use in this country, do not include methods of analysis for oxygen content of irons and steels. This is probably due to the fact that in the ordinary steel-making processes ferro-manganese can be freely used, so that it is assumed that the percentage of oxygen in the steel rarely reaches or exceeds the danger point. As a matter of fact, steel often carries much more oxygen than it should, as can be seen by referring to Table II.

In the manufacture of iron of very high purity in basic open-hearth furnaces the oxygen content has to be very carefully watched, or the product may be overburned and contain an excess of oxide and dissolved oxygen.

A number of methods for the determination of oxygen have been proposed, among which may be mentioned: (1) Heating the sample in a stream of dry chlorine; (2) dissolving the sample in special solvents such as copper sulphate or bromine; (3) combustion of the sample in the form of borings in pure dry hydrogen.

The latter method, which is due to Ledebur,¹ is the only one that has proved reliable. In Ledebur's original method, the sample is given a preliminary combustion in pure nitrogen in order to burn off the last traces of impurities and to get rid of all hydrocarbons, as well as adsorbed oxygen on the surface of the particles of the sample. If the preliminary heating in nitrogen is dispensed with, the results will be slightly higher, but it is probable that for general work sufficiently accurate results can be obtained if the sample is carefully prepared for the combustion in hydrogen.

SAMPLES.

The samples should consist of fine borings or shavings from a milling machine. The drill or machine tool should be scrupulously clean and free from all traces of oil or dirt, and should be geared to run slowly so as not to heat the sample while it is being cut. Lack of careful attention to this point will lead to high results, owing to surface oxidation of the fine particles of the drillings.

APPARATUS.

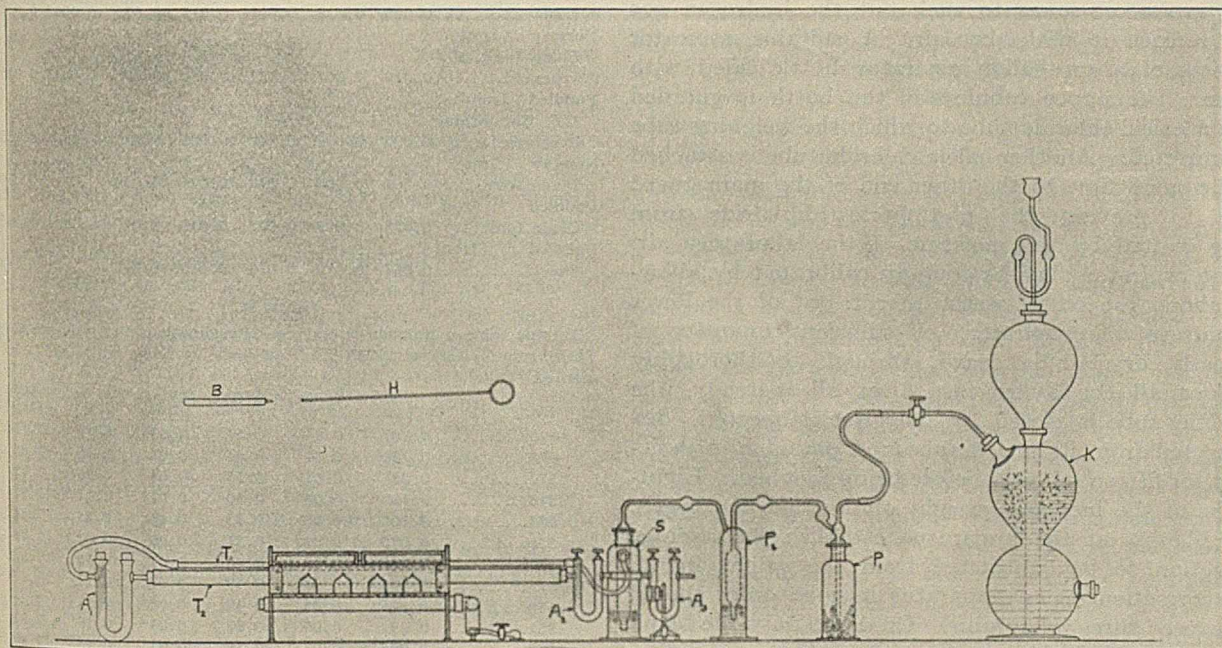
The apparatus used in making the oxygen determination is shown in illustration B-740.

A one-gallon Kipp generator is used for generating the hydrogen. It should be charged with drillings

as shown in the figure. It passes first over stick potash, and next through a 30 per cent. potash solution. This solution in the second bottle should be renewed as soon as it shows a tinge of yellow, due to the appearance of sulphides. The hydrogen next passes through concentrated sulphuric acid to dry it, and then enters a silica tube with $\frac{1}{4}$ " bore, 30" in length, which contains a 6" roll of platinum gauze. The $\frac{1}{4}$ " tube lies on top of a 1" \times 30" fused silica tube contained in a suitable 12" gas blast furnace.

The object of the preliminary heating over platinum foil is to free the hydrogen from the small quantity of oxygen which it always contains. If this precaution is not taken, the results will be too high. The water formed in the small-bore silica tube is caught in a "U" tube shown in the figure, which contains phosphoric anhydride opened up with glass wool. This drying tube has rubber stoppers. The connection is made with pure gum tubing and is permanent, the sample being introduced from the opposite end of the combustion tube.

Blanks should be run from time to time to make sure that the apparatus is in good order and everything working properly. Samples should not be introduced into or removed from the combustion tube when it is more than hand-hot, but silica tubes may be



Denotations:

- | | |
|--|---|
| K—Kipp generator. | A ₁ —U-tube phosphoric acid. |
| P ₁ —Potassium hydrate sticks. | A ₂ —U-tube phosphoric acid weighed. |
| P ₂ —Potassium hydrate solution. | A ₃ —U-tube phosphoric acid trap. |
| S—Sulphuric acid conc. | B—Platinum boat. |
| T ₁ — $\frac{1}{4}$ " bore silica tube. | H—Hook of $\frac{1}{8}$ " copper wire. |
| T ₂ —1" bore silica tube. | |

of pure iron or mossy zinc, and dilute hydrochloric acid (1:1). Steel turnings should not be used in the generator, as the object is to generate the purest possible hydrogen. Hydrochloric is preferable to sulphuric acid. After its formation the hydrogen is purified and dried by passing through the usual train

¹ "Leitfaden für Eisenhüttenlaboratorien," Vieweg und Sohn, Braunschweig, 6 Auflage, 1903, S. 122.

quickly cooled with perfect safety by turning off the gas and allowing the cold air blast to play on the tube.

METHOD.

Twenty to thirty grams of finely divided borings are weighed into a platinum or silica boat $\frac{1}{2}$ " \times $\frac{1}{2}$ " \times 6". The boat with its charge is quickly in-

serted in the combustion tube and pushed to the middle zone by means of a rod of suitable length. The stream of hydrogen should be passing freely when the tube is opened for the insertion of the sample. After the stopper is replaced, the weighing tube and guard tube are finally connected with pure gum tubing. The weighing tube is a 4" "U" tube, with ground glass stoppers, containing phosphoric anhydride opened up with glass wool. The guard or trap tube is similarly charged and is intended to prevent the drawing back of moisture from the air of the laboratory. After the apparatus is all connected and in good order, the pure dry hydrogen should be allowed to sweep through a few minutes until all air is removed from the entire system. The gas is then lighted, the blast turned on and the temperature quickly run up to a bright red heat, about 850° C. This heat is maintained for thirty minutes, while the hydrogen is passing through the apparatus at the brisk rate of about 100 cc. per minute. After the combustion is completed the gas is turned off the furnace, leaving the blast playing upon the hot tube. The stream of hydrogen should continue to pass until the tube is cool enough to bear the hand upon it.

Immediately after the tube is cool enough, the hydrogen is shut off and the weighing tube, with its guard tube, disconnected and connected with a suitable aspirator, so as to suck out the hydrogen gas and replace it with dry air. A suitable aspirator consists of a one-gallon aspirator bottle filled with water. The upper tubulure of the bottle is guarded with a calcic chloride tube to which the weighing tube is connected. Another calcic chloride tube is attached at the same time to the other end of the main guard tube to prevent the phosphoric anhydride from being wetted by the moisture of the laboratory air.

The aspirator may be roughly calibrated by allowing about 500 cc. of water to run out of the lower tubulure of the aspirator. A sufficient quantity of perfectly dry air is drawn through to thoroughly displace all the hydrogen. After all is ready, the weighing tube is closed by its glass stopcocks, disconnected from its guard tube and placed in a desiccator for fifteen minutes before being weighed. Eight-ninths of the increased weight of the tube is oxygen. The blanks on the apparatus establish the average correction to be subtracted from the weight found. The correction on an apparatus in good order should not exceed three milligrams. On damp days the blank is usually a little higher than when the air is dry.

In charging the weighing tube with phosphoric anhydride and glass wool, take care to remove any specks of phosphoric acid from the upper portions of the tube. The following points should be given careful attention in order to attain the highest degree of accuracy.

Samples must be clean, absolutely dry and free from oil. They should be cut, preferably with a milling machine tool running at a low rate of speed. The samples must not heat in cutting. Sheet samples are first cleaned from oxide on an emery wheel, avoiding heating as much as possible. The sheet should be milled on the edge.

Whenever possible, samples should be cut from bars which are first cleaned by a superficial cut with the milling tool.

Extreme care must be taken in the preparation of the sample.

The entire apparatus must be kept to the top notch of cleanliness, tightness and general good order. Blanks should be run frequently. Analyses should be in duplicate whenever the results are to be used as a basis for specification. The most extreme care should be taken to exclude all oxygen from the sample and apparatus except that which it is the object of the method to determine. When pure iron is worked on, the silver-white iron residues from the boat should be reserved for charging the Kipp hydrogen generator.

In the following table are given a number of oxygen determinations:

TABLE I.

Material.	Sili- con.	Sul- phur.	Phos- phorus.	Car- bon.	Manga- nese.	Nitro- gen.	Oxy- gen.
American Ingot Iron (01107) (Sheet).....	0.003	0.021	0.002	0.01	Trace	0.0050	0.027
American Ingot Iron (02007) (Sheet).....	0.003	0.018	0.004	0.015	0.020	0.0060	0.014
Electrolytic Sheet Iron, by Electrolysis.....	0.000	0.001	0.005	0.006	0.000	0.0030	0.032
American Ingot Iron Chain (Link).....	0.008	0.022	0.008	0.015	0.025	0.0063	0.032
Norway Iron Chain Link, 100 years old.....	0.019	0.007	0.032	0.050	0.000	0.0047	0.058
Puddled Iron 1-1/2" Bar broke in service.....	0.056	0.047	0.140	0.065	0.070	..	0.855
Norway Iron Piano Wire.....	0.007	0.006	0.012	0.025	0.020	..	0.050
Puddled Iron Chain Link.....	0.075	0.009	0.072	0.010	0.010	..	0.145
Puddled Iron Sheet.....	0.077	0.020	0.074	0.015	0.010	..	0.283

TABLE II.

In this table a number of oxygen determinations in steels are given. These results were obtained by Romanoff¹ working with the Ledebur method.

No.	Carbon.	Phos- phorus.	Man- ganese.	Sul- phur.	Oxy- gen.	Specific gravity.
496.....	0.107	0.04	0.57	0.03	0.19	7.79
478.....	0.25	0.01	0.54	0.03	0.15	7.85
572.....	0.25	0.02	0.55	0.04	0.26	7.72
516.....	0.10	0.04	0.50	0.07	0.11	7.92
503.....	0.10	0.08	0.55	0.06	0.25	7.84
526.....	0.095	0.02	0.37	0.06	0.22	7.78
540.....	0.10	0.04	0.48	0.07	0.16	7.82
547.....	0.095	0.04	0.49	0.05	0.11	..
550.....	0.105	0.05	0.49	0.03	0.14	..
551.....	0.09	0.06	0.32	0.04	0.16	7.87
553.....	0.095	0.08	0.39	0.04	0.13	7.80
555.....	0.10	0.05	0.44	0.03	0.13	7.87
570.....	0.095	0.02	0.03	8.08
581.....	0.105	0.06	0.46	..	0.09	7.97
583.....	0.10	0.04	0.42	0.03	0.02	8.08

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.²

By W. F. HILLEBRAND AND WILLIAM BLUM.

In a recent paper on this subject by Brinton,³ the author concludes that an empirical factor is necessary in the bismuthate method if the permanganate solution

¹ Stahl und Eisen, March 15, 1899.

² Published by permission of the Director of the Bureau of Standards.

³ THIS JOURNAL, 3, 237-8.

is standardized by means of sodium oxalate or an iron ore. As all the experience at the Bureau of Standards indicates that no such empirical factor is necessary, the data given by Brinton were examined, leading to the following observations: The theoretical factor for the ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ is 0.16397 and not 0.16024 as stated by Brinton, while the ratio $5\text{Fe} : \text{Mn}$ is correctly stated, *viz.*, 0.1967. If the incorrect factor was used by him, the results given by him in the last two lines of Table I are too low, while if the correct factor was used, the empirical factor necessary to increase these results to the values found with MnSO_4 as a standard should be 0.1694, instead of 0.1656 as stated.

Recalculation of his results upon the former assumption led to the following values for manganese:

TABLE I.

Bureau of Standards sample No. and name.	18—Acid open-hearth. 0.1 C.	10a—Bessemer. 0.4 C. Renewal.	19—Acid open-hearth. 0.2 C.	15—Basic open-hearth. 0.6 C.	24—Vanadium steel.
Bureau of Standards averages...	0.412	0.916	0.760	0.568	0.669
Found with MnSO_4 as primary standard.....	0.410	0.912 ¹	0.757	0.557	0.663
	0.411	0.910 ¹	0.758	0.562	0.665
Found with $\text{Na}_2\text{C}_2\text{O}_4$ as primary standard, using factor 0.16024..	0.397	0.892	0.732	0.539	0.642
	0.398	0.890	0.733	0.544	0.644
Found with $\text{Na}_2\text{C}_2\text{O}_4$ as primary standard, using factor 0.16397..	0.406	0.903	0.749	0.552	0.657
	0.407	0.901	0.748	0.557	0.659

Consideration of the corrected values in the last two lines shows that they are uniformly about one per cent. lower than those found with MnSO_4 as a standard, which in turn are slightly below the Bureau of Standards averages. The question then arises whether these figures are sufficient to justify the recommendation of the empirical factor 0.1656; *i. e.*, addition of 1.0 per cent. to the value derived from sodium oxalate. This factor would depend upon (a) the purity and accurate standardization of the MnSO_4 solution; and (b) the assumption that the general averages given by the Bureau of Standards are accurate to 1 per cent. of their value. It is to be noted that impurities such as iron, calcium or magnesium in the manganous sulphate used would be included in the standardization both as sulphate and pyrophosphate, and would lead to too high results in the Mn values of the permanganate and of the steels.

The following test was applied at this Bureau to determine whether the bismuthate method required the theoretical factor. A measured quantity of a filtered 0.03 N permanganate solution, standardized with sodium oxalate, was reduced with sulphurous acid, of which the excess was expelled. It was then treated by the bismuthate method under exactly the same conditions as were used in the regular determinations. If the reactions proceed according to the theory, the amount of ferrous sulphate oxidized should be equivalent to the original volume of permanganate taken. The results were as follows:

TABLE II.

	Cc. KMnO_4 reduced and oxidized.	Cc. FeSO_4 added.	KMnO_4 equivalent to FeSO_4 .	KMnO_4 required for excess.	KMnO_4 equivalent to FeSO_4 oxidized.	Error, cc.
1.....	20	25	23.78	3.75	20.03	+0.03
2.....	18	25	23.78	5.80	17.98	-0.02
3.....	16	25	23.78	7.80	15.98	-0.02

It was therefore concluded that, within the limits of titration, this method is quantitative, and requires the theoretical factor. Additional evidence as to the correctness of this factor is found in the results on B. S. Standard Sample No. 25, a manganese ore, for which the sixteen values by eight chemists, using in all eight distinct methods, gave a mean of 56.36 per cent. Mn, with an extreme variation of less than one per cent. of the amount present. Of these results, the two by the bismuthate method were 56.33 and 56.50, one chemist using the theoretical factor and the other an empirically determined factor.

From the following table of summaries of manganese determinations on 16 Bureau of Standards steel samples, it may be seen that the mean of the colorimetric determinations in 14 samples is from 1 to 7 per cent. higher, and is in no case lower, than the general mean. The bismuthate results, on the contrary, approach much more closely to the general means, and especially to the averages of all results except the colorimetric. It may be noted that in every case the corrected values of Brinton agree very closely with the averages excluding colorimetric values.

Until an exhaustive comparative study of these methods, as applied to such materials, is made, it is impossible to fix the true manganese value of these samples more accurately than is expressed in the general averages. Since, however, the colorimetric methods as usually employed, involve the use of similar standards in which the manganese can be no more accurately determined, the colorimetric values are probably less independent than those obtained by other methods. In general, these samples are of use as manganese standards only in analyses of similar materials, of approximately equal manganese content; and in using them, due regard should be given to the probable accuracy of the general averages, as indicated by the order of agreement of the values from which they have been derived. On some of the more recent samples, *e. g.*, 9a, 11a, 22 and 23, the agreement between the various methods is quite satisfactory, and the means are probably correct to 1 per cent. of their value.

In conclusion, it may be stated that further work is necessary to establish the value of the various methods for manganese, for both high- and low-grade materials, this being one of the problems which this Bureau hopes to undertake as opportunity offers. Until such work is accomplished, it is doubtful whether the manganese content of low-grade materials can be ascertained with a greater accuracy than one per cent. of the amount present.

¹Typographical error in original.

TABLE III.

Bureau of Standards sample.	8a—Bessemer, 0.1 C. Renewal.	9a—Bessemer, 0.2 C. Renewal.	10a—Bessemer, 0.4 C. Renewal.	11—Basic open-hearth, 0.2 C.	11a—Basic open-hearth, 0.2 C. Renewal.	12a—Basic open-hearth, 0.4 C. Renewal.	13—Basic open-hearth, 0.6 C.	14—Basic open-hearth, 0.8 C.	15—Basic open-hearth, 0.1 C.	16—Basic open-hearth, 1.0 C.	18—Acid open-hearth, 0.1 C.	19—Acid open-hearth, 0.2 C.	20—Acid open-hearth, 0.4 C.	21—Acid open-hearth, 0.6 C.	22—Bessemer 0.6 C.	23—Bessemer 0.8 C.
Bismuthate.....	0.531	0.915	0.897	0.451	0.615	0.407	0.548	0.636	0.512	0.396	0.392	0.735	0.478	0.547	0.712	0.785
Persulphate colorimetric...	0.548	0.928	0.937	0.476	0.620	0.437	0.589	0.678	0.547	0.435	0.423	0.780	0.510	0.573	0.715	0.782
Lead peroxide colorimetric	0.950	0.520	0.620	0.670	0.530	0.460	0.425	0.770	0.500	0.560
Ford Williams.....	0.525	0.920	0.908	0.470	0.615	0.407	0.580	0.670	0.522	0.412	0.411	0.753	0.469	0.557	0.702	0.765
Gravimetric (Ford, etc.)...	0.535	0.915	0.905	0.452	0.627	0.420	0.555	0.636	...	0.399	0.562	0.700	0.765
Noyes.....	0.894	0.436	0.533	0.631	...	0.385	0.539
Volhard.....	0.530	0.890	0.430	0.706	0.775
General average.....	0.536	0.918	0.916	0.464	0.620	0.419	0.568	0.654	0.528	0.414	0.412	0.760	0.486	0.559	0.708	0.775
Colorimetric average.....	0.548	0.928	0.940	0.487	0.620	0.437	0.597	0.676	0.543	0.443	0.424	0.778	0.508	0.570	0.715	0.782
Per cent. above general average.....	2.2	1.1	2.6	5.0	0.0	4.3	5.1	3.4	2.8	7.0	2.9	2.4	4.5	2.0	1.0	0.9
Average excluding colorimetric.....	0.531	0.914	0.901	0.449	0.619	0.414	0.549	0.638	0.519	0.396	0.403	0.746	0.472	0.551	0.704	0.771
Per cent. below general average.....	0.9	0.4	1.6	3.2	0.1	1.2	3.3	2.4	1.7	4.3	2.2	1.8	2.9	1.4	0.6	0.5

NOTE.—The number of determinations involved is indicated in each case by a small superior numeral.

A. One discordant determination omitted.

BUREAU OF STANDARDS, WASHINGTON, D. C.

CORRECTION.

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.

By PAUL H. M.-P. BRINTON.

Dr. W. F. Hillebrand has kindly called my attention to an arithmetical error in my article on this subject, which appeared in the April number of THIS JOURNAL. My error in taking the factor 0.16024 instead of 0.16397 for the ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ is easily explained, though by no means excused, by a glance at a five-place table of logarithms. 2 Mn are equal to 109.86, and for this number I carelessly took 0.03084 as the mantissa, instead of 0.04084. This error in no way influences the correctness of my empirical factor 0.1656, though it may diminish the necessity for the use of an empirical factor. It should also be understood that this error in logarithm does not call into question the iron content of the Sibley ore, as might at first appear. The Sibley ore was first compared with sodium oxalate by a series of standardizations, both standards being correctly calculated to terms of iron. These were perfectly concordant, and then the work with the Sibley ore was discontinued. The comparison of the titer obtained by sodium oxalate and that by manganese sulphate was then taken up, and it was here that the error in computation was made.

April 24, 1911.

A CONTRIBUTION TO THE KNOWLEDGE REGARDING LOEW'S LIME-MAGNESIUM RATIO.

By ROBERT STEWART.

Received Feb. 3, 1911.

A knowledge of the beneficial action of lime on agricultural soils is almost as old as the practice of agriculture itself. Its benefits were known to the old Romans and to the early Japanese and Chinese. The results obtained, however, were not always uniform and seemed to vary with, among other things, the nature of the lime used. Lime which was made from magnesian limestone seemed to have detrimental effects. The presence of the magnesium in the limestone was regarded as exerting a detrimental influence. Why this should be so has been attributed to several different causes. Davy and others have attributed it to the relative slowness with which the caustic magnesia is converted into the carbonate by the absorption of the carbon dioxide of the air. Thus it is generally assumed by agricultural writers that the presence of magnesia, in excess, in the soil is detrimental to plant growth.

In 1901, Löew¹ advanced the hypothesis that when the lime and magnesia were present in the soil in a certain ratio the toxic action of magnesia is not manifested. May,² working under the direction of Löew, furnished experimental evidence of the truth of Löew's contention and advocated the optimum ratio of lime to magnesia of 5 : 4 on the basis of molecular weights, or 7 : 4 on the basis of actual weight.

¹ Bureau of Plant Industry, U. S. D. A., *Bull.* 1.

² *Ibid.*, 1, 52 (1901).

According to these investigators the toxic action of magnesia is due to an excess of magnesia over lime; and therefore the only remedy is such an addition of lime as will re-establish a favorable, or better optimum, ratio.

J. W. Konovalow,¹ in 1909, reported some investigation on the relationship between lime and magnesia, which he obtained by a study of nutrient solutions with various crops as grown by water and sand culture. He found that the best ratios of lime to magnesia were 6.7 : 1 and 3.3 : 1.

About the same time, Löew,² in a plea for including the determination of magnesium in soil analysis, claimed, among other things, that in field soils the lime content should be about one to three times greater than that of magnesium.

Hopkins,³ in 1910, reported the results of experiments carried on at Illinois by himself and associates wherein it was demonstrated by means of pot cultures that magnesium carbonate exerted a beneficial action upon the growth of cereals until the addition of the magnesium carbonate reached 0.8 of one per cent., after which a detrimental effect was produced until the addition reached two per cent., when the addition of magnesium carbonate was fatal to the growth of cereals. The addition of lime in the form of gypsum in the ratio as advocated by Löew (7 : 4) exerted no effect on the toxic action of the magnesium carbonate. Hopkins, therefore, concluded that Löew's ratio received no support from his investigations. He found, however, that the double decom-

position reaction between the gypsum and the magnesium carbonate was effective when the soil was leached so as to remove the soluble magnesium sulphate.

In 1910, Löew¹ discussed some recent work regarding his advocated ratio of lime to magnesia of 1 : 1 and maintained that the work discussed did not refute the theory.

Hilgard,² with respect to magnesia in soils in excess, says: "Soils containing large proportions of magnesia generally are found to be unthrifty, the lands so constituted being frequently designated as 'barrens.'"

In view of this conflicting evidence regarding the validity of the lime-magnesia ratio, it is very interesting to study the results obtained from a natural soil formed from the disintegration of limestone, quartzite and dolomite with the formation of a soil containing over 40 per cent. of calcium-magnesium carbonate, of which nearly one-third is magnesium carbonate.

The Greenville Farm, one of the experimental farms belonging to the Utah Experiment Station, is in the Great Basin district. The soil of this farm was formed by the weathering of the near-by mountain range which consists largely of limestone, quartzite and dolomite. At the time of Old Lake Bonneville, the streams loaded with the decomposed rock particles of limestone, quartzite and dolomite met the quiet waters of the lake and deposited their load. It is of the finer particles thus deposited that the soil of this farm is composed.

In Table I are recorded the results obtained by the mechanical analysis of the soil. The degree of fineness of the particles may have some bearing on the results obtained on this farm.

TABLE I.—PHYSICAL ANALYSIS OF THE SOIL OF THE GREENVILLE FARM.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Coarse sand (above 0.5 mm.).....	0.21	0.17	0.68	1.02	0.09	0.34	0.47	0.09
Medium sand (0.1 to 0.32 mm.).....	9.63	8.29	6.63	9.63	9.53	9.48	8.91	7.08
Fine sand (0.032 to 0.1 mm.).....	30.04	32.54	9.49	33.06	36.92	33.79	35.34	34.25
Coarse silt (0.01 to 0.032 mm.).....	32.25	32.81	32.62	28.51	28.65	30.49	31.65	32.65
Medium silt (0.0032 to 0.01 mm.).....	12.30	10.46	10.89	10.95	10.46	10.85	9.92	9.89
Fine silt (0.001 to 0.0032 mm.).....	6.25	4.81	7.27	6.94	4.85	5.86	5.56	5.84
Clay (below 0.001 mm.).....	7.62	7.12	10.13	7.52	7.82	6.78	6.12	7.57
Moisture.....	1.60	1.47	1.13	1.49	0.95	1.01	1.01	0.84
Soluble and lost.....	0.10	2.33	1.16	0.83	0.73	1.40	1.42	1.99
Specific gravity.....	2.67	2.72	2.80	2.69	2.76	2.79	2.71	2.76
Apparent specific gravity.....	1.23	1.27	1.30	1.29	1.33	1.34	1.39	1.35
Water-soluble salts.....	0.06	0.11	0.14	0.16	0.08	0.09	0.15	0.09

The soil would be classified as a loam.

TABLE II.—CHEMICAL COMPOSITION OF THE SOIL OF THE GREENVILLE FARM.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Insoluble residue.....	42.18	36.51	32.16	41.65	28.72	29.64	31.14	30.75
Potash, K ₂ O.....	0.67	0.89	0.59	0.82	0.61	0.74	0.79	0.75
Soda, Na ₂ O.....	0.35	0.47	0.47	0.62	0.37	0.42	0.45	0.74
Lime, CaO.....	16.88	17.80	21.34	15.60	22.62	23.15	22.24	21.78
Magnesia, MgO.....	6.10	9.46	7.57	7.48	9.36	5.89	6.06	5.63
Oxide of iron, Fe ₂ O ₃	3.03	2.69	3.46	2.95	2.17	2.42	2.47	2.54
Alumina, Al ₂ O ₃	5.64	4.69	3.40	6.09	5.33	8.07	7.90	9.03
Phosphoric acid, P ₂ O ₅	0.41	0.29	0.34	0.19	0.12	0.06	0.07	0.11
Carbon dioxide, CO ₂	19.83	23.11	26.67	20.88	29.31	29.57	28.80	28.13
Volatile matter.....	5.60	3.38	3.93	4.23	0.91	0.95	...	0.24
Total.....	100.69	99.29	99.93	100.51	99.52	100.91	99.92	99.68
Humus.....	0.53	1.00	0.61	0.47	1.13	0.60	0.44	0.57
Nitrogen.....	0.139	0.117	0.080	0.175	0.072	0.070	0.062	0.066
Water at 95 degrees.....	1.60	1.47	1.13	1.49	0.95	1.01	1.01	0.84

The results obtained from a chemical analysis of the soil of this farm are recorded in Table II.

The soil is fairly well supplied with phosphoric

¹ *Chemical Abstracts*, 3, 2991.

² *Ibid.*, 3, 1565.

³ Hopkins, "Soil Fertility and Permanent Agriculture" (1910), p. 171.

¹ *Chemical Abstracts*, 4, 3269.

² Hilgard, "Soils," 382.

³ *Bull.* 106, Utah Experiment Station.

acid, but is low in nitrogen and humus. But from the point of view of this discussion the high content of lime and magnesia is noteworthy.

The results obtained for magnesium carbonate and calcium carbonate calculated from the magnesium oxide and calcium oxide, together with the ratio of lime (CaO) to magnesia (MgO), are recorded in Table III:

TABLE III.—PERCENTAGE OF MAGNESIUM CARBONATE AND CALCIUM CARBONATE AND RATIO OF LIME TO MAGNESIA. RESULTS EXPRESSED AS PER CENT. OF DRY SOIL.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Calcium carbonate.....	30.22	31.86	38.20	27.93	40.49	41.44	39.84	38.99
Magnesium carbonate.....	12.75	19.76	15.82	15.63	19.56	12.31	12.66	11.77
Ratio of lime to magnesia.....	1 : 2.8	1 : 1.9	1 : 2.8	1 : 2.0	1 : 2.4	1 : 4.0	1 : 3.6	1 : 3.8

The results indicate that nearly 43 per cent. of the surface foot of soil is calcium and magnesium carbonate and that the amount increases with depth to the fifth foot, after which the magnesium carbonate content is practically the same as in the first foot, while the calcium carbonate also increases with depth to a maximum in the fifth foot and then remains practically constant.

In Table IV are recorded the results obtained by calculating the amount of calcium-magnesium carbonate (CaMg(CO₃)₂) from the carbon dioxide as determined and also the combined carbonate as determined from the calcium and magnesium oxides.

TABLE IV.—PERCENTAGE OF CALCIUM-MAGNESIUM CARBONATE AS CALCULATED FROM CARBON DIOXIDE AND FROM LIME AND MAGNESIA. RESULTS ARE EXPRESSED AS PER CENT. OF DRY SOIL.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
By calculation from CO ₂	41.54	48.42	55.86	43.74	61.40	61.92	60.34	58.94
By addition of MgCO ₃ and CaCO ₃	42.97	51.62	54.02	43.66	60.05	50.75	52.50	40.76

The results indicate quite fully that to a depth of five feet the calcium and magnesium are nearly in the proportion that they occur in dolomite.

From the work as reviewed above one would almost conclude that such a soil would be sterile, but just the contrary is true; the soil is remarkably fertile and produces excellent crops even without the addition of barnyard manure.

In Table V are recorded the eight-year average results obtained by the application of an ordinary amount of irrigation water. The sugar beets were grown on the Frankhauser farm, which is separated from the Greenville farm by a road four rods in width. The soil of the former is similar to the latter, but the farms differ in that the former has received heavy applications of barnyard manure, while the Greenville farm has not. Sugar beets on this soil will not produce a profitable crop without the addition of barnyard manure.

TABLE V.—EIGHT-YEAR AVERAGE YIELD OF OATS, WHEAT, POTATOES AND SUGAR BEETS ON THE GREENVILLE FARM.

Crop.	Amount of water applied.	Treatment.	Average yield.
Oats.....	15"	Unmanured	82.0 bushels
Wheat.....	15"	Unmanured	50.4 bushels
Potatoes.....	20"	Unmanured	262.3 bushels
Sugar beets.....	15"	Manured	21.8 tons

This land has been cropped for nearly forty years and the Greenville farm, so far as we know, has never had any manure applied. The results obtained from

this soil show quite clearly that the high percentage of magnesia has no toxic action on the growth of the plants. It is evident that the magnesia does not have any toxic action on plant growth for one of two reasons: first, the ratio of magnesia to lime, which falls within the ratio (1 : 3), as recently suggested by Löew,¹ is favorable to plant growth, or, secondly, the calcium and magnesium are present in the form

of a double salt such as CaMg(CO₃)₂, and therefore magnesium carbonate, as such, exists in this soil only in small amounts. It seems possible that such a double salt would have a different action on plant growth than would either the magnesium carbonate or calcium carbonate alone.

Whatever may be the true explanation, the results reported here may have great practical value since they indicate that finely ground magnesian limestone may possibly be used on acid soils to correct the acidity in those sections of the country where such is necessary. The addition of limestone by artificial means for this purpose certainly would never reach

the amount actually present in this soil. Of course, the reaction which would take place between the added limestone and the many acids of the soil may give rise to the formation of new magnesium compounds which would prove to be toxic. This is a phase of the question which would have to be considered in the use of such limestone.

CHEMICAL LABORATORY,
UTAH EXPERIMENT STATION,
January 16, 1911.

THE CHEMISTRY OF ANAESTHETICS, I.: ETHYL ETHER.²

(Concluded from May issue.)

By CHARLES BASKERVILLE AND W. A. HAMOR.

IV. THE CHANGES WHICH OCCUR IN ETHYL ETHER DURING STORAGE.

Schönbein³ studied the action of oxygen and air on ether in the light, and found that it becomes oxidized, responding to the tests for ozone. This investigation was the first conducted with the view of ascertaining the nature of the oxidation of ether, and led to the later assumption that ozone is produced by the action of air and light on ether, and that it may exist in ether in solution.⁴ That such a view is untenable and is not

¹ Löew, *Chemical Abstracts*, 3, 1565 (1909).

² Read before the New York Section, American Chemical Society.

³ *J. prakt. Chem.*, 52, 132, 183; *J. Pharm.*, [3] 20, 258; *Arch. phys. nat.*, 17, 61; see also, *Arch. Pharm.*, [2] 67, 257. Gay-Lussac (*Ann. chim. phys.*, 11, 2, 98) had observed in 1816 the formation of an explosive, strongly oxidizing "oil" in ethyl ether.

⁴ For example, see Büchner, *Ber.*, 1885, 376.

supported by facts now known, we shall endeavor to demonstrate by a consideration of the oxidation of ether under all conditions.

I. THE ACTION OF OZONE ON ETHER.

According to Houzeau,¹ ether exposed to the action of ozone is more rapidly oxidized than alcohol under the same conditions; hydrogen dioxide is produced. Wright,² however, found that dry ozonized oxygen acts with some violence on ether, forming acetic acid, oxalic acid, hydrogen dioxide, and a little formic acid. It is important to note that both found hydrogen dioxide among the products of oxidation; that is, a substance occurred in the ozonized ether which responded to the tests for this substance, which fact is in harmony with the later observations of Berthelot,³ who found that sirupy ethyl peroxide is formed when ethyl ether is ozonized.

Nef⁴ has shown that ethyl peroxide consists mainly of acetic peroxide ($C_4H_6O_4$), which was first obtained by Brodie.⁵ This peroxide owes its oxidizing and explosive character to its ready dissociability into ozone and acetic anhydride; in fact, if kept in loosely closed vessels, it is completely converted into acetic anhydride and acetic acid at the end of four months.

Clover and Richmond⁶ found that the aqueous solution of acetic peroxide gradually suffers hydrolysis with the formation of molecular proportions of acetic and peracetic acids, and that the latter slowly changes into acetic acid and hydrogen dioxide. Later, Clover and Houghton⁷ showed that acetic peroxide is produced by the action of peracetic acid on acetic anhydride, and that when acetic peroxide is dissolved in an aqueous solution of hydrogen dioxide, peracetic acid is produced. These facts would seem to demonstrate what while Wright did not conduct the process of ozonization to the limit, Berthelot obtained a more or less pure acetic peroxide by the direct action of ozone.

The substance prepared by Harries⁸ by passing ozone and carbon dioxide into "dry ether," contained 15.28 to 25.65 per cent. of carbon as against the 58.54 per cent. required for ethyl peroxide,⁹ and was undoubtedly an impure acetic peroxide, which contains 40.67 per cent. of carbon.

A consideration of the action of ozone on various carbon compounds will throw light upon the problem.

Schönbein¹⁰ found that turpentine became oxidized quite readily and than an active substance was thus formed; and Soret¹¹ found reasons to believe that ozone is completely absorbed by turpentine and oil of cinnamon. Kingzett¹² supplied data to confirm this, for he learned that ozonized turpentine contains peroxidized compounds which react with water.

It would appear to be demonstrated that in general ozone acts on carbon compounds in two ways: (1) to form an ozonide, when the ozone attaches itself to an unsaturated carbon linking; and (2) when the ozone molecule is decomposed, labile peroxides of the carbonyl group being formed. These facts are mainly due to the elaborate series of investigations conducted by Harries, who has shown that mesityl oxide yields a peroxide when ozone is passed into it;¹ that aliphatic aldehydes in general are not attacked by ozonized oxygen;² and that methyl alcohol is oxidized by ozone to formaldehyde.³ According to Harries⁴ the nature of the reaction between ozone and unsaturated compounds depends on the presence or absence of water. In the absence of a solvent or in non-dissociating solvents, ozone is added at the double linking, forming ozonides. In the presence of water, these ozonides are decomposed forming ketones or aldehydes and hydrogen dioxide. It is possible that a small quantity of water may be sufficient to cause this decomposition, probably through catalytic action. The ozonides are mostly highly explosive, and in addition to the ones mentioned above, the following have been prepared: ozonides of allyl alcohol, secondary methylheptenol, tertiary dimethylheptenol, allylacetone, citronellal, citral, isocrotonic acid, oleic acid and elaidic acid, and mesitylenetriozone.

In conclusion, it would seem to be established that "dry ether" is acted upon by ozone with the production of an active, explosive substance, consisting mainly of acetic peroxide, and that this is produced by the decomposition of the ozone molecule. In the case of moist ether, the changes which result would be analogous to those which occur during the slow combustion of ether when exposed to the action of atmospheric oxygen in the presence of water, and these will now be referred to.

II. THE ACTION OF OXYGEN ON ETHER.

Evidence indicates that a peroxide may be formed in ether by the union of molecular oxygen with ethyl oxide in the slow process of "autoxidation." The employment of ether which had been carelessly stored has often resulted in unexpected phenomena, which have been found to be due to a substance resembling hydrogen dioxide, but one of much greater activity and of an explosive character.

Cleve⁵ concluded that the explosive nature of a substance formed from ether was due to ethyl peroxide; König⁶ found that explosive results in ether residues were due to the presence of a substance responding to the tests for hydrogen dioxide; Schär reported that ether which contained an extremely high percentage of "hydrogen peroxide" (over 5 per cent.) violently decomposed during an evaporation in a fat estimation, the explosion being favored by the presence of acetic

¹ *Ber.*, **36**, 1933; cf. Vanino and Thiele, *Ber.*, **29**, 1724.

² *Ibid.*, **36**, 2996. It will be shown later, however, that acetaldehyde gives a peroxide on slow oxidation, according to several investigators.

³ *Ibid.*, **36**, 3658; cf. Renard, *Ann. chim. phys.*, [5] **16**, 289.

⁴ *Ibid.*, **37**, 839; see also *Ann.*, **343**, 311.

⁵ *Chem. News*, **63**, 101.

⁶ *Mon. Sci.*, [4] **4**, 2; *Landwirthsch. Versuchsstat.*, **37**, 1.

¹ *Compt. rend.*, **75**, 142.

² *Am. J. Sci.*, [3] **7**, 184.

³ *Bull. soc. chim.*, [2] **36**, 72.

⁴ *Ann.*, **298**, 202.

⁵ *Proc. Roy. Soc.*, **9**, 363.

⁶ *Am. Chem. J.*, **29**, 179.

⁷ *Ibid.*, **32**, 43.

⁸ *Ann.*, **343**, 311.

⁹ Assuming the formula to be $(C_2H_5)_2O_2$.

¹⁰ *Loc. cit.*

¹¹ *Ann. chim. phys.*, [4] **7**, 113.

¹² *J. Chem. Soc.*, **37**, 800.

and formic acids;¹ von Neander² drew attention to certain instances in which the residues left after the evaporation of ethereal extracts exploded, concluding that these explosions were apparently due to the active oxygen; and Kleemann³ and Hertkorn⁴ reported similar experiences. In view of all these communications it is only to be concluded that ether may contain a peroxide, formed, no doubt, when it is carelessly stored.⁵

Rossolimo⁶ found that a perfectly pure ether showed a strong oxidizing power after it had remained in a wash-bottle exposed to the action of the air for about three months, during which time evaporation had been proceeding slowly; and he learned that the oxidizing action of the peroxide contained in ether thus oxidized is a much greater one than that of hydrogen dioxide.⁷ Ditz⁸ has also found that peroxides, when present in ether, are more active than aqueous hydrogen dioxide; and we have observed this on several different occasions. This "activity" is undoubtedly due to the presence of a peroxide other than hydrogen dioxide, since an "inactive" ether can be rendered "active" by conducting through it a current of ozonized oxygen and then leaving it at rest some months;⁹ and although such a peroxide responds to all tests for the detection of hydrogen dioxide, and the latter is also a likely impurity as well, especially when the ether has been oxidized in the presence of moisture, it would appear to be well demonstrated that ether is capable of peroxidation.¹⁰

That a peroxide or peroxides exist in "active" ether may be inductively demonstrated by a consideration of the methods to which it is necessary to resort in order to eliminate the "activity." It has been shown by Dunstan and Dymond¹¹ that ether may be purified from peroxides by the use of an ample quantity of lime, and then twice washing with alkaline water;¹² but the following methods lend particular support to the matter under consideration:

1. Garbarini¹³ made experiments with a view of removing the oxidation product contained in ether that has been exposed to air, and found that a dry

¹ *Arch. Pharm.*, **25**, 632.

² *Chem.-Ztg.*, **26**, 336.

³ *Ibid.*, **26**, 385.

⁴ *Ibid.*, **26**, 407.

⁵ In this connection, see Thoms, *Pharm.-Ztg.*, **1894**, 777; *Ber. Pharm. Ges.*, **1894**, 10, 11. See also, Kappers, *Dissertation Groningen*, **1871**; and Walton, *Am. Druggist*, Aug. 8 (1910), p. 69.

⁶ *Ber.*, **38**, 774.

⁷ An analogous case is found in the case of oleic acid. Harries and Thieme (*Ber.*, **39**, 2844) have found that "oleic acid ozonide peroxide" gives a much more intense hydrogen dioxide reaction than the normal ozonide, when boiled with water.

⁸ *Chem.-Ztg.*, **25**, 109; *Ber.*, **38**, 1409.

⁹ Matignon, *Compt. rend.*, **138**, 82.

¹⁰ Brühl (*Ber.*, **28**, 2847) found that on one occasion when hydrogen dioxide was isolated by the help of ether, the specimen smelled strongly of ozone and an oily substance remained which possessed explosive properties. He did not consider that this substance could be acetic peroxide, however (*Ber.*, **33**, 1709); cf. Stähler, *Ber.*, **38**, 2619.

¹¹ *J. Chem. Soc.*, **57**, 584.

¹² An ether so treated 10 years old showed no trace of peroxides. This, along with facts to be mentioned hereafter, shows the fallacy of the statement that ozone, formed by the decomposition which occurs under the influence of light and heat at the time the test for peroxides is applied, is the cause of the peroxide response.

¹³ *Bull. Assn. Chim. Sucri. et Dist.*, **26**, 1165. Ferrous sulphate solution is also suitable (Stokes and Cain, *J. Am. Chem. Soc.*, **29**, 410).

preparation of ferrous hydroxide is a suitable reagent for the purpose.

2. Ramsay¹ stated that the effects due to the presence of peroxides may be obviated by putting some clean mercury in the ether container, whereby the peroxides are decomposed.²

3. Ditz³ found that ether purified by Brunner's method by agitating with powdered potassium permanganate still contained a substance or substances which are similar to peroxides; but that ether treated with solid caustic potash according to Börrigter's method was freed from peroxides.

Ether may also be freed from peroxides by treatment with manganese dioxide,⁴ with chromic acid, or by treatment with sodium, potassium-sodium alloy, phosphoric anhydride, or a solution of sulphurous acid and hydriodic acid.

Considering that sufficient data have been given to justify the statement that we may assume the existence of peroxidized substances in "active" ether on *a priori* grounds, we shall now refer to the changes *in toto* which occur in ether during its autoxidation.

Regnault found that ether, after standing, no longer has a constant boiling point; and Ramsay and Young¹ found that such ether acts on mercury, but that after agitation with mercury and distilling it does so no longer. However, up to 1876, ordinary ethyl ether had been credited with the power of producing ozone, and, beyond this, the subject was in a similar state to that which occurred in the case of the so-called formation of ozone by the oxidation of the essential oils. That is to say, nothing was known about it, beyond that under these conditions there had been recognized a substance which was mistaken for ozone, and of whose production there was no logical explanation. In 1876, Kingzett² found that ethyl ether gives, apparently by atmospheric oxidation, "acetic ether" and hydrogen dioxide. He concluded that the changes which occur may be explained as follows: First, the ether is oxidized into "acetic ether" and water; second, the ester is oxidized into the anhydride, and that into acetic peroxide; and finally, the latter is decomposed with water, simultaneously with its formation. From Kingzett's experiments, it appeared that ordinary atmospheric oxygen plays the same part as the oxygen of the barium peroxide in Brodie's method of preparing acetic peroxide; that is, he considered that the reaction which occurs is similar to that which we know takes place when ether is ozonized.

Shortly afterwards, Legler³ found that when ether is oxidized by a red-hot platinum spiral, it gives formic

¹ *Nineteenth Century*, April, 1898.

² We have found that finely divided mercury is very suitable for removing peroxides occurring in ether.

³ *Chem.-Ztg.*, **25**, 109.

⁴ *Rep. Chem.-Ztg.*, **1889**, 46.

⁵ *Chem. News*, **61**, 237. Linebarger (*Ibid.*, **70**, 53) observed that mercury on being brought into contact with certain ether of German manufacture, such as he employed in the determination of the boiling point, tarnished, and that the impurity thus removed exercised a considerable influence on the boiling point. In one case the boiling point was diminished 0.9° C.

⁶ *Ibid.*, **34**, 136.

⁷ *Ann.*, **217**, 381.

acid, acetic acid, aldehyde, acetal,¹ formaldehyde, and trimetric prisms of $C_{11}H_{33}O_{21}$. These prisms were found to be soluble in water, alcohol, and ether, and were decomposed by alkalis into formaldehyde and formic acid. The compound liberated iodine from potassium iodide solution and reduced lead dioxide, therefore appearing to be a derivative of hydrogen dioxide.

The investigation of the production of hydrogen dioxide in ether under such conditions as might obtain during storage was initiated by the investigations of Richardson. He found² that hydrogen dioxide is formed when water containing pure ether is exposed to light in an atmosphere of oxygen; and from an extended series of experiments, he observed the following: (1) the amount of hydrogen dioxide formed depends on the proportion of ether to water present; (2) no hydrogen dioxide is formed when a mixture of water-vapor ether-vapor, and oxygen is exposed to sunlight; (3) no hydrogen dioxide is formed when water and ether are exposed in an atmosphere of carbon dioxide; (4) no iodine is liberated from potassium iodide by a mixture of water, ether, and oxygen, from which light has been excluded.

From these and other experiments, he was led to believe that the oxidation under the influence of light involves initially an oxidation of water to hydrogen dioxide, and that oxidation of ether is a result of a secondary interaction between it and the hydrogen dioxide produced.

In partial contradiction to the findings of Richardson, Dunstan and Dymond³ found that pure ether, either wet or dry, does not form hydrogen dioxide when exposed to light, that ether prepared from methylated spirit yields hydrogen dioxide when kept for some time, but not if it has been previously purified by means of dilute chromic acid; that hydrogen dioxide is formed when ozone acts on ether in the presence of water; and that hydrogen dioxide is produced when certain conditions are maintained during the slow combustion of ether in contact with water, *i. e.*, pure ether may yield hydrogen dioxide when imperfectly oxidized, that is to say, hydrogen dioxide is formed as an intermediate product in the process of oxidation of ethyl ether.

Richardson⁴ then repeated the work of Dunstan and Dymond, and found that hydrogen dioxide is formed in ether in every case after exposure to light in contact with moist air or oxygen, but not in the dark at the ordinary temperature. He learned that ether and moist oxygen, exposed to a temperature of 75° to 88° C. in the dark, contained, after four days, considerable quantities of hydrogen dioxide; and similar results were obtained when ether and oxygen were kept at 60° C. for forty hours. Hence, it appeared that when special precautions are taken to ensure the presence of oxygen over ether, hydrogen dioxide is formed at the ordinary temperature, and even at 0° in the light, but not in the dark; it was found, however, that it is formed in the dark at about 60° C.

In his first paper, Richardson attempted to prove that when hydrogen dioxide is formed from moist ether, the water and not the ether is oxidized. Dunstan and Dymond opposed this view, as they considered that they were in possession of evidence that the ether itself is oxidized; and in his later contribution, Richardson appeared to abandon his former view, although he still contended that hydrogen dioxide could be formed from water and oxygen alone in the presence of light.

In the experiments made by Dunstan and Dymond, it was always observed that when hydrogen dioxide is produced in ether, the latter afterwards contains aldehyde, acetic acid, and other substances. Richardson also found that other products of decomposition are formed when ether is exposed to light. In fact, he and Fortey¹ later found that "dry ether" gives a well marked peroxide reaction after three days' exposure to "dry oxygen;" and that when ether is exposed for many weeks in the presence of oxygen and water it becomes rich in hydrogen dioxide and gives an acid reaction. They also proved that aldehyde is formed, and regarded it as the intermediate product. Similar results were obtained by Berthelot,² who found that ether, when mixed with water and exposed to air and sunlight for five months, yields aldehyde, alcohol, acetic acid, and methane; and with hydrogen dioxide, air and water, much larger yields of the same substances resulted. In direct accord with these results is the recognition of the fact that when ether is stored in badly stoppered bottles in the light, it forms considerable amounts of peroxides and other oxidation products, especially acetaldehyde.³

Since aldehydes can hold ozone in solution for a comparatively long time without becoming oxidized, it is exceedingly likely that they form peroxides with it, possibly analogous to the compounds they form with sodium hydrogen sulphite; and as acetaldehyde is only oxidized slowly by air to acetic acid, it is probable that it is peroxidized during the slow oxidation of ether. Ludwig⁴ has found that all the known aldehydes possess the power of absorbing and retaining oxygen in an active or ozonized condition, in which state they are able to liberate iodine, even from very dilute solutions of potassium iodide (1 : 600,000). Since ozonized acetaldehyde may be prepared by exposing acetaldehyde merely to the air, it could be formed under the conditions which obtain in badly stored ether, and its high "activity," and from the fact that it gradually becomes inert in the presence of water, would serve to explain phenomena observed in the case of oxidized ether.

Since Lieben and Berthelot have shown that alcohol is formed during the alteration of ether, and owing to the common occurrence of alcohol in ether, it is appropriate in this connection to consider what changes it undergoes during the oxidation of ether in which it

¹ *Proc. Chem. Soc.*, 1896, 165.

² *Compt. rend.*, 129, 627.

³ In this connection, see Thoms, *Pharm.-Ztg.*, 1894, 777; also Poleck and Thümmel, *Arch. Pharm.*, [3] 27, 961.

⁴ *Ber.*, 29, 1454. According to Bach (*Compt. rend.*, 124 951), acetaldehyde gives a peroxide on slow oxidation in the air, either in the light or dark. "On the Oxidation of Aldehyde," see Slaboszewicz, *Z. physik. Chem.*, 42, 343.

¹ The probable occurrence of acetal in ether will be referred to later.

² *Chem. News.*, 60, 255.

³ *Ibid.*, 61, 237; *J. Chem. Soc.*, 57, 584.

⁴ *Chem. News.*, 62, 256.

is contained. Mathieu¹ has found that alcohol in wine-strength is converted into aldehyde by simple contact with the air at the ordinary temperature, and that the action is markedly accelerated by the presence of oxidizable bodies in the solution and by exposure to sunlight. In direct confirmation of this, assuming, of course, that aldehyde is the intermediate product of such oxidation, we have the results of Duchemin and Dourlen,² who have determined that alcohol is gradually oxidized in contact with air with the production of acetic acid.

It is therefore entirely reasonable to suppose that alcohol occurring in ether or that formed during its oxidation is also subject to oxidation of the following order: alcohol, aldehyde (aldehyde peroxide), acetic acid. In such a conversion, the degree of acidity is liable to vary more or less in both directions in short intervals during storage in glass vessels, just as in the case of the oxidation of ether itself. The variations in acidity—theoretical, but not sensible in general—may be due to differences between the rapidity of the oxidation and the saturation of the acids by the bases of the glass. In fact, it should be mentioned here that the nature of the ether container is of vast importance in the light of the oxidation changes which are possible. The extent of the oxidation—or, for that matter, any oxidation at all—is dependent upon the quality of the glass used in bottles for storing ether; and in the case of metallic containers, in view of some recent researches, it is probable that all metals which show anomalous anodic conductivity are likely to develop free hydrogen dioxide in contact with water and oxygen.³ The presence of such metals should, therefore, be guarded against.

III. THE COMBUSTION OF ETHER.

When a mixture of ether vapor and air comes in contact with platinum black, heated platinum-sponge, or other bodies heated not quite to redness, it undergoes slow and imperfect combustion, forming aldehyde, acetic and formic acids, carbon dioxide, water, etc.; and when ether vapor is passed through a red-hot tube, ethylene, water, carbon monoxide, and aldehyde are produced. Of especial interest, however, is the fact that just as burning hydrogen produces hydrogen dioxide, so does the flame of ether.⁴

IV. SUMMARY.

The conclusion from the preceding is that the oxidation of commercial ether in the presence of moisture would appear to be productive of a series of complex conversions, initiated, however, by the formation of hydrogen dioxide. The slow combustion of pure ether in the presence of water, and under such conditions as exist when it is improperly stored, would appear to occur in the following stages:

¹ *Bull. Assn. Chim. Sucri. Dist.*, **22**, 1283.

² *Compt. rend.*, **140**, 1466.

³ Barnes and Shearer, *J. Phys. Chem.*, **12**, 155, 468. Ordinary distilled water sometimes shows distinct properties of an indirect oxidase, and Tixier (*Bull. Sci. Pharm.*, **1910**, 17; *Pharm. J.*, **84**, 645) attributes such oxidizing properties to extremely minute traces of copper derived from the distilling plant. It is likely, however, that these properties are due to the presence of small amounts of hydrogen dioxide developed by copper in contact with water and atmospheric oxygen.

⁴ Engler, *Ber.*, **33**, 1109.

1. The formation of hydrogen dioxide from water and oxygen of the air. This is particularly likely in cases where there is direct exposure to light, and it is more or less activated by contact action.

2. Dissociation of hydrogen dioxide into water and oxygen, which latter then exerts a direct oxidizing action, resulting in the formation of the following: acetic peroxide, acetaldehyde and acetaldehyde peroxide, and eventually acetic acid. The formation of acetic peroxide facilitates a series of oxidations, and by its hydrolysis alone, acetic and peracetic acids are formed. The peracetic acid would then become converted into acetic acid and hydrogen dioxide. Therefore, it is reasonable to conclude that a continuous cycle of changes occurs in ether during its oxidation, and that such changes result in the simultaneous formation and occurrence of peroxidized compounds, intermediate (aldehyde) and ultimate (acetic acid) resultants.

When anhydrous ether is exposed to the action of atmospheric oxygen during improper storage, there is every reason for the conclusion that peroxidation occurs. Such action is similar to that which takes place when anhydrous ether is ozonized, but the process is much less active, being indirect. During storage under conditions which would be conducive to oxidation, the absolute exclusion of moisture is not attained. It is, therefore, to be concluded that changes occur similar to those which ensue in the presence of water, but of a much slower and much less intense nature.¹

In confirmation of the views expressed above on the formation of peroxides in ether during careless and improper storage, the authors are able to furnish experimental proofs which would seem to establish beyond any doubt the fact that ether of anaesthetic grade contains peroxidized compounds after exposure to varying temperature conditions and sunlight, in the presence of atmospheric oxygen, for considerable periods of time, especially when it is stored in colorless glass vessels or in badly stoppered tin containers.

"Ether was allowed to stand for 200 days in 150 cc. tin containers, partly filled, stoppered as well as the mouth of the containers would permit, and exposed to varying temperature conditions inside of a window with southern exposure. The conditions of storage were similar to those which obtain in many laboratories and hospitals. It should be mentioned that none of the samples so exposed exhibited a peroxide reaction originally, but all contained small amounts of water and alcohol. The following results were obtained, using the vanadic acid and cadmium potassium iodide tests:

"No. 1A (container one-fifth full): strong peroxide reaction; strongly acid.

"No. 1B (container one-half full): marked peroxide reaction, but less pronounced than in No. 1A; strongly acid.

¹ Although it may appear from evidence that ether is subject to direct peroxidation, hydrogen dioxide being formed from the acetic peroxide by a secondary process—by the action of water, yet the precautions taken to exclude water have not been such as to assume that direct peroxidation occurs and it is likely that the presence of water is necessary (cf. Armstrong, *J. Soc. Chem. Ind.*, **24**, 479).

"No. 1C (container four-fifths full): very faint peroxide reaction.

"No. 2A (container two-thirds full): no peroxides present. This container was provided with a tightly fitting stopper. The neck of the can was cylindrical, whereas those holding the preceding were provided with a conical neck, and it was thus possible to cork the can more securely.

"No. 2B (one-half full): no peroxides present. This sample was stoppered similarly to No. 2A.

"No. 3A (one-tenth full): strong peroxide reaction.

"No. 3B (one-third full): no peroxides present. This container was properly stoppered.

"No. 3C (three-fourths full): no peroxides present. Container was well stoppered.

"No. 3D (four-fifths full): no peroxides present. Container was properly stoppered.

"The various fractions from three samples of ether were exposed to varying temperature conditions for 193 days. These fractions were contained in 20 cc. tube vials (colorless glass) and in every case were well stoppered. None had contained peroxides originally. The following results were obtained:"

Fractions.	A.	B.	C.
34—36°	Container half full. Pronounced peroxide reaction. Acid reaction.	Four-fifths full. Faint, yet decided reaction.	One-third full. Traces of peroxides.
36—39°	One-fifth full. Marked reaction; acid reaction strong.	Two-thirds full. Traces of peroxides.	One-half full. Traces of peroxides.
39—42°	One-fifth full. Marked reaction.	One-third full. Traces of peroxides.	Two-thirds full. Traces of peroxides.

In order to determine whether peroxides are formed in anhydrous ether¹ when it is exposed to light and varying temperatures, ether distilled over sodium was subjected to extreme conditions for two weeks in various containers. The results obtained may be tabulated as follows:

Description of container.	Results after 2 weeks' exposure to light and extreme temperature conditions.
500 cc. glass stoppered ether bottle, containing 250 cc. of anhydrous ether (only impurity originally, traces of acetaldehyde). During the exposure, the ether had slowly evaporated, and at the time of the test the bottle contained but 50 cc.	Strong peroxide reaction.
150 cc. tin container, well stoppered with a cork. This container was originally one-half full and no evaporation had occurred at the end of two weeks, apparently.	No peroxides present.
50 cc. glass tube vial, poorly stoppered. The vial originally contained 25 cc. but considerable evaporation occurred during the exposure.	Strong peroxide reaction.
Glass-stoppered Erlenmeyer flask of 50 cc. capacity. This flask had contained 25cc. of ether, but considerable evaporation had occurred.	Decided peroxide reaction.

From these experiments, it is concluded that peroxides, or peroxidized compounds, may form in ether of all grades which is improperly stored, and that such impurities are most likely to be generated by exposing partially filled containers to varying atmospheric conditions, for continued periods of time. The extent of the oxidation of both pure and anaesthetic ether is dependent upon the nature of the container, the purity of the sample, the amount of air present, and, in glass vessels, the intensity of the light, which accelerates the oxidation. Ether should not be stored in glass vessels for any length of time without being tested for oxidation products before use;

¹ One sample of "concentrated" ether which we obtained from a well known firm was found to be rich in peroxidized compounds. This sample, which had been imported from Germany in a can, was contained in a brown glass bottle, into which it had been emptied after the can became corroded. The bottle was entirely filled and well-stoppered; the oxidation must, therefore, have occurred while the ether was in the defective tin container.

and the tin containers should be of such capacity that they need not be opened before being emptied when the ether is employed for anaesthetic purposes. In laboratories, ether should always be kept in completely filled, well-stoppered dry glass bottles, preferably those made of non-soluble blue, green or brown glass, excluded from the light, in cool, dry places, and over mercury, or preferably sodium. If the container is cork-stoppered, the bottom of the cork should be completely covered with tin-foil to prevent penetration of the stopper, with consequent shrinkage and leakage, and to prevent the extraction of organic matter.

V. ON THE EXISTENCE OF ETHENOL IN ETHYL ETHER.

A few compounds of the type of vinyl alcohol are known. In many cases in which their formation might be expected, their isomers are obtained; for example, when water is abstracted from glycol, $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$, vinyl alcohol, CHOH , does not result, but an isomer,



acetaldehyde, CH_3 ; and vinyl alcohol has never



been prepared in a pure condition. However, Poleck and Thümmel² suppose that vinyl alcohol, or ethenol ($\text{CH}_2 : \text{CH.OH}$), is present in ether that has been exposed to air and sunlight, and that its presence is indicated by the formation of a precipitate ($\text{C}_2\text{H}_3\text{O}$, $\text{HgO.Hg}_2\text{Cl}_2$) when a solution of mercury oxychloride

in sodium carbonate is added to common ether.² This precipitate, according to them, is white and is converted by boiling potash into explosive greenish black "acetylene mercury" ($\text{C}_2\text{H}_2\text{O}_4\text{Hg}_4$), and by adding nitric acid to its alkaline solution into $\text{C}_2\text{HHg}_2\text{OCl}_2$, which is not explosive.

With regard to the formation of ethenol which they found in commercial ethers, Poleck and Thümmel consider that it is formed partially during the preparation of ether and partly by the action of atmospheric oxygen with the simultaneous formation of hydrogen dioxide, which reacts on ether with the production of

¹ Ber., 22, 2863; see Arch. Pharm., [3] 27, 961.

² This is founded on an observation by Thümmel (vide Am. J. Pharm., 62, 15). In an examination of the oxychlorides of mercury, he attempted to remove an excess of mercuric chloride from a solution of monochloride of mercury in sodium dicarbonate, by agitation with ether; but this was found to be impossible, as the ethereal solution after some minutes became turbid and deposited a white precipitate, which was found to be due to the presence of "vinyl alcohol."

a further quantity of vinyl alcohol. They found that it may be removed by repeatedly shaking ether with water or by treatment with bromine, phenylhydrazine, or potassium hydroxide.

Since the publication of the above results, it has been quite generally assumed that ether forms vinyl compounds during storage,¹ and in several instances, attempts have been made to explain unusual reactions by attributing these to the presence of ethenol in the ether used. For example, Rimini² found that after shaking cheese with concentrated hydrochloric acid to dissolve the casein, gentle heating and shaking with ether in some cases produced an azure-violet coloration, the intensity of which varied with the sample of ether used. Pure ether, recently distilled over lime and sodium, gave no color, and Rimini stated that the formation of the color was due to the presence of vinyl alcohol in the ether used. Matignon also found reasons to definitely assert that vinyl alcohol occurs in some commercial ethers. He reported³ that commercial ethers which contain vinyl alcohol afford a sensitive reagent for vanadic acid, since they give a rose coloration with solutions of ammonium vanadate or vanadic acid containing 0.1 mg. of vanadium pentoxide per liter. He stated that when the ether is allowed to evaporate spontaneously, the residue becomes richer in vinyl alcohol and gives the characteristic rose color with solutions containing 0.02 mg. per liter; and that the blue color afforded by using "active ether" and pyrogallol is more delicate than with the latter alone. That vinyl alcohol is the active principle in the ethers capable of giving the color reaction was "proved" by the following facts: (1) The active ethers gave a white precipitate with a solution of mercuric chloride and potassium hydrogen carbonate; (2) they lost their activity after treatment with potassium hydroxide, which "resinifies the vinyl alcohol;" (3) they became inactive after being shaken with water, which "dissolves the vinyl alcohol." Matignon found that an "inactive" ether can be rendered "active" by passing a current of ozonized oxygen through it, and then leaving it at rest some months; and stated that ferric salts and chromates also give colorations with "active" ether, and must be removed before testing for vanadates.

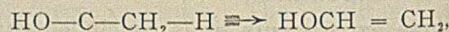
It would seem that reactions attributable to known oxidation products of ether (peroxides, acetaldehyde) have been incorrectly ascribed to the presence of ethenol in every case in which the occurrence of the latter has been reported. Vinyl alcohol may be formed in the oxidation of ether, but we shall endeavor to show that its existence in commercial ethers has never been conclusively demonstrated, and this with due regard to the painstaking work of Poleck and Thümmel.

The assumption of the presence of vinyl alcohol in commercial ethers is entirely based upon the deportment of such ethers with mercury oxychloride. In such cases, white amorphous vinyl mercury oxychloride is precipitated, and this, on treatment with potas-

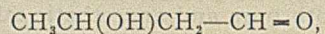
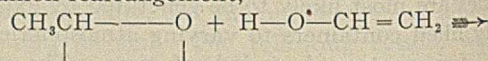
sium hydroxide, is converted into a black explosive powder, and on treatment with a haloid acid yields vinyl compounds; but, as a matter of fact, no definite proof is thus given of the existence of vinyl alcohol or vinyl compounds in an ether which positively responds to the test with mercury oxychloride, and the reaction is undoubtedly due to the presence of a known and long-recognized impurity of commercial ethers, namely, acetaldehyde, vinyl alcohol molecules forming from it during the progress of the reaction.

The compounds which acetaldehyde yields with various mercuric salts have received no little attention. Deniges⁴ found that acetaldehyde forms the compound $\text{SO}_4 : (\text{HgO})_2 : \text{Hg} \cdot \text{C}_2\text{H}_4\text{O}$ with mercuric sulphate; Lasserre⁵ obtained a compound, $\text{CH}_3\text{COH} \cdot \text{HgO}$, by the addition of sodium hydroxide to a solution of mercuric acetate and acetaldehyde; and Auld and Hantzsch⁶ found that the action of mercuric oxide on acetaldehyde in slightly alkaline solution leads to the formation of a colorless solution which probably contains trimercuri-di-aldehyde hydroxide, since it is quite indifferent towards phenylhydrazine, hydroxylamine, or rosaniline decolorized by sulphurous acid. They found that the substance could not be isolated, since it changes more easily than the acetone compound into the polymeride, $(\text{C}_4\text{H}_8\text{O}_5\text{Hg}_3)_x$, which is formed immediately as a white powder by warming a dilute solution of acetaldehyde with a solution of mercuric chloride made alkaline with potassium hydroxide. The formation of this polymeride is one of great significance in this connection, for it results on treating a dilute solution of acetaldehyde in ether with alkaline mercuric chloride. It is necessary, however, to show that vinyl alcohol molecules form under similar conditions; and, as will appear from what follows, this would seem to be established beyond question.

Michael and Kopp⁷ found that an aqueous solution of potassium carbonate gives aldol when allowed to act on aldehyde; and Nel⁸ and McLeod⁷ have proved that an aqueous solution of acetaldehyde contains vinyl alcohol molecules as soon as potassium or sodium hydroxide is present in amounts above 0.1 per cent. The vinyl alcohol, which is formed by intramolecular addition from the hydroxyethylidene,



is then at once absorbed by unchanged acetaldehyde, with anion rearrangement,



giving acetaldol, etc.

Denis⁷ showed that the correctness of the conclu-

¹ *Compt. rend.*, **128**, 429.

² This compound always contains a little mercurous sulphate, which fact is important, in view of the composition of the compound obtained by Poleck and Thümmel.

³ *J. Pharm. Chim.*, [6] **22**, 246.

⁴ *Ber.*, **38**, 2677.

⁵ *Am. Chem. J.*, **5**, 190.

⁶ *Ann.*, **298**, 316.

⁷ *Am. Chem. J.*, **38**, 565.

¹ For instance, see Thoms, *Pharm.-Ztg.*, **1894**, 777; *Ber. Pharm. Ges.*, **1894**, Parts 10 and 11; and Bertsch, *Apoth. und Drogist*, **1893**, No. 12.

² *Gazz. chim. ital.*, **29**, I, 390.

³ *Compt. rend.*, **138**, 82.

sions of Nef and McLeod is thus established: When an aqueous solution of acetaldehyde is allowed to stand for a long time with freshly precipitated oxide of mercury, no action occurs in the cold; if, however, sodium hydroxide or carbonate is added, the aldehyde present is very rapidly and completely converted into white, insoluble, basic mercuric vinylate, $\text{Hg}(\text{OCH}=\text{CH}_2)_2 \cdot \text{HgO}$, from which, by the addition of dilute acids, acetaldehyde can again be regenerated quantitatively. This fully demonstrates that no vinyl alcohol molecules are present in an aqueous solution of acetaldehyde and that these appear only when sufficient alkali has been added. It also proves that vinyl compounds result from an acetaldehyde solution when reagents similar to those employed by Poleck and Thümmel are used.

Hofmann¹ found that when acetylene is passed through a solution of mercuric nitrate acidified with nitric acid, a fine colorless, crystalline precipitate results, which, after washing with 2 per cent. nitric acid solution and drying under reduced pressure, has the composition $\text{C}_2\text{Hg}_2\text{NO}_3\text{H}$. It is practically insoluble in water or 3 per cent. nitric acid, but is decomposed by concentrated acid. With warm, dilute hydrochloric acid, it yields acetaldehyde, and mercuric chloride goes into solution. When treated with alkalis, the nitrogen is obtained in the form of nitrates, and when warmed with sodium hydroxide and potassium cyanide solution, aldehyde resin is formed. Hofmann found that the compound may be obtained in the form of large crystals by using an alcoholic solution of aldehyde in place of acetylene; after remaining for fourteen days, large, colorless, doubly-refractive prisms were deposited. The constitution suggested was $\text{NO}_3 \cdot \text{Hg} \cdot \text{C}(\text{:Hg}) \cdot \text{CH} \cdot \text{O}$. Hofmann considered that the substance obtained by Poleck and Thümmel, by shaking commercial ether with an aqueous solution of mercuric chloride and potassium hydrogen carbonate, was probably a somewhat similar compound, only contaminated by a little mercurous chloride. This seems to be supported by experimental data, since the salts of the compound $\text{C}_2\text{Hg}_2\text{NO}_3\text{H}$ leave a gray residue consisting of mercury and the explosive oxymercureide when treated with alkali.

Köthner,² commenting on the substance obtained by Hofmann by the action of acetylene on a solution of mercuric nitrate, mentioned that he had previously³ obtained results similar to those of Hofmann, and had drawn attention to the relationship of the substance to vinyl alcohol and acetaldehyde. Erdman and Köthner⁴ found that mercurio-carbide nitrate resembles Poleck and Thümmel's mercury derivative of vinyl alcohol, and that it yields acetaldehyde on treatment with dilute acids.

As has been intimated, our object is not to show definitely that vinyl alcohol does not exist in commercial ethers; but sufficient evidence has been given to show that acetaldehyde, an impurity of all commercial ethers, may be converted into a compound pos-

sessing the properties of the substance obtained by Poleck and Thümmel when an ether containing the substance in considerable amounts is agitated with mercury oxychloride.

We have found that the test usually specified for the detection of vinyl alcohol in ether is indicative of the presence of acetaldehyde, and therefore no reliance can be placed upon it as a test for vinyl alcohol:

The test given in the *Pharmacopée Française*¹ for vinyl alcohol was tried with samples of pure ether containing acetaldehyde. This is as follows:

50 cc. of the ether are shaken up with 4.5 cc. of a saturated solution of potassium hydrogen carbonate and 1 cc. of a saturated solution of mercuric chloride, after which no turbidity or white amorphous precipitate should result.²

This test is similar to the one proposed by Bertsch,³ who found that the presence of vinyl alcohol can be detected by shaking the ether under examination with mercury oxychloride. If, after ten or twenty minutes, a turbidity or a white amorphous precipitate results, which, on treatment with potassium hydroxide, is converted into a black explosive powder, the presence of vinyl alcohol may be assumed.

In the first test, the mixture of reagents possesses a pale yellow or reddish color from suspension of the oxychloride formed. At the beginning, the mixture is alkaline and the action results in the formation of a yellow oxychloride, but the alkalinity is overcome by the acid liberated, and a red oxychloride—probably tri-mercur-di-oxychloride—is formed. Carbon dioxide escapes and finally the liquid is alkaline, owing to the equilibrium condition of potassium chloride and mercuric oxide.⁴ It will therefore be observed that an alkaline solution is employed; and, as has been shown, when an acetaldehyde solution is thus treated, vinyl alcohol molecules will make their appearance under such conditions.

On adding 4.5 cc. of a saturated solution of potassium hydrogen carbonate and 1.0 cc. of a saturated solution of mercuric chloride to 50 cc. of an ether rich in acetaldehyde, but containing no other impurities, and shaking thoroughly, the reddish brown oxychloride changed to a white color on standing ten minutes, becoming pure white after fifteen minutes. A saturated solution of potassium hydrogen carbonate was then added to a saturated solution of mercuric chloride until the precipitate of oxychloride which first formed was dissolved to form a clear, reddish yellow solution. 5 cc. of this solution, on being well shaken with an ether containing about 1 per cent. of acetaldehyde, resulted in the formation of a white precipitate after five minutes' standing. Thus, the test specified by the *Pharmacopée Française* for the detection of vinyl alcohol is not indicative of the presence of that substance originally, and the vinyl compound which results, if

¹ 1908, 245.

² This test was proposed by Poleck and Thümmel (*Arch. Pharm.*, **227**, 964; *Z. anal. Chem.*, **29**, 717). They also placed the time limit of ten to twenty minutes.

³ *Loc. cit.*

⁴ Concerning the formation of mercury oxychloride in this reaction, see Millon, *Ann. chim. phys.*, [3] **18**, 372; Roucher, *Ibid.*, [3] **27**, 353; Thümmel, *Arch. Pharm.*, **227**, 589; and Schoch, *Am. Chem. J.*, **29**, 319.

¹ *Ber.*, **31**, 2212.

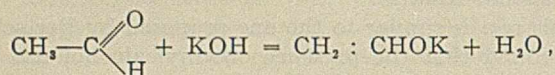
² *Ibid.*, **31**, 2475.

³ *Halle. a-S. Frühjahr*, 1806.

⁴ *Z. anorg. Chem.*, **18**, 48.

there be any, is unquestionably produced by the action of the reagents on acetaldehyde.

According to Poleck and Thümmel, the yellow or brown color imparted to commercial ether on the addition of potassium hydroxide is due to the presence of vinyl alcohol. We do not think so, since acetaldehyde is the cause of such coloration. In this case, too, a vinyl compound is probably formed, and as an intermediate product, by the action of potassium hydroxide on acetaldehyde. At all events vinyl alcohol molecules are present in the acetaldehyde solution so treated and, as in the reaction between sodium and acetaldehyde,¹ it is undoubtedly true that a vinyl alcohol compound, capable of only a brief existence, is formed, according to the following,



and that this soon decomposes, forming high molecular condensation products, as aldehyde-resin. It cannot be said, however, that the test with potassium hydroxide is indicative of the presence of vinyl alcohol.

With regard to the other communications dealing with the reported occurrence of vinyl alcohol in ether, it would seem that no efforts were made to establish the absence of acetaldehyde or peroxides in the samples of ether employed. The azure-violet color observed by Rimini may be explained in three ways: (1) that the hydrochloric acid used alone produced the color observed;² (2) that the peroxides occurring in the ether gave the coloration in the presence of aldehyde;³ (3) that the peroxides occurring in the ether gave the coloration in the presence of aldehydes from the cheese.

It is obvious that since the coloration may be satisfactorily accounted for by known reactions, it is unnecessary to attribute it to the presence of vinyl alcohol in the ether used.

With regard to the observations of Matignon, an ether containing peroxides and acetaldehyde, that is, an ether rendered "active" by ozonization, would deport itself similarly to the samples used by him. Treatment with potassium hydroxide would serve to remove both of these impurities; agitation with water would eliminate such "active" substances; and ether containing peroxides gives a rose color with vanadic acid.⁵

In conclusion, the occurrence of acetaldehyde in ether, especially in commercial ether, is well known, and this impurity fully accounts for the department of the ethers examined by Poleck and Thümmel. It would, therefore, seem, that any attempts to explain or establish the existence of ethenol in ether are un-

necessary with the data now at hand. Moreover, it has been shown that ethenol may be formed from the acetaldehyde produced from the oxidation of ether, or that present as a primal impurity, and that the reactions attributed to it may be accounted for in this manner.¹

VI. (a) ON THE DETECTION OF PEROXIDES IN ETHYL ETHER.

It has been shown that peroxidized compounds are produced through contact with air in the presence of light, as well as in the dark. The occurrence of these substances in anaesthetic ethers² is rare; this is due to the fact that the latter are generally supplied to the consumer in sealed tins containing a minimum amount of air. Since it is highly important that ether intended for anaesthetic purposes should be carefully manufactured and properly stored, as prolonged exposure to light and air greatly affect the results of etherization, causing coughing, suffocation, and even dangerous after-effects,³ such ether should always be tested for peroxides and aldehyde, and the presence of the latter should be rigorously guarded against. The same precautions should be taken when the ether is intended for analytical purposes.⁴

The following tests have been proposed for the detection of peroxides (ethyl peroxide and hydrogen dioxide, as well as all other peroxidized compounds) in ethyl ether:

I. TESTS DEPENDENT UPON OXIDATION.

(a) Tests Dependent upon the Liberation of Iodine.

1. *The Test with 10 Per cent. Potassium Iodide Solution.*—Saladin⁵ stated that potassium iodide imparted a yellow coloration to ether if the latter contained sulphuric acid; but Cloez⁶ suggested the employment of the salt as a reagent for ozone. DeVry⁷ found that pure ether has no action upon iodides, and Borriger found that ether containing hydrogen dioxide liberates iodine from potassium iodide. Poleck and Thümmel⁹ found that the liberation of iodine from iodides,

¹ Others have also found reasons to doubt the existence of vinyl alcohol in ether. Abraham (*J. Soc. Chem. Ind.*, **11**, 836) considered its existence as improbable; and Nef (*Ann.*, **298**, 202) mentioned that its identity is not fully established.

² None of the fresh samples of ether of anaesthetic grade examined by the authors contained peroxides. Even two samples in sealed tins which had been exposed to varying temperature conditions for about one year were free from peroxides, and a tin containing 100 g. of ether which had been stored for one year and a half, sealed and unopened, gave no peroxide reaction; and it would appear from our experiences that these substances are only likely to occur in ether which has been stored in badly stoppered containers. In general, then, the fault is that of the consumer and not of the manufacturer, since ether is supplied, as a rule, in vessels which preclude the possibility of considerable amounts of peroxides forming.

³ Buxton's *Anaesthetics*, 1907, 117.

⁴ As an illustration of the importance of guarding against the presence of peroxidized compounds in ether for analytical purposes, this case may be cited: It has been stated that solutions of quadrivalent titanium give a yellow color with ether in the presence of alcohol. This, however, is only the case when the ether contains peroxidized compounds (cf. Stähler *Ber.*, **38**, 2619). See also the experiences of Lunge and von Keler (*Z. angew. Chem.*, 1894, 670; 1896, 3; Lunge's *Chem. techn. Untersuchungs-methoden*, 5 Aufl., **1**, 385) and of Stokes and Cain (*J. Am. Chem. Soc.*, **29**, 410) in the colorimetric determination of iron.

⁵ *J. chim. med.*, **1831**, 51.

⁶ *Compt. rend.*, **43**, 38.

⁷ *J. Pharm. Chim.*, December, 1872.

⁸ *Chem. News*, **53**, 69. See also, Houzeau, *Compt. rend.*, **67**, 714, 1138, who has found that "oxygenated water" decomposes KI (1868).

⁹ *Arch. Pharm.*, **1889**, 961.

¹ See Freer, *Am. Chem. J.*, **18**, 558.

² Fuming hydrochloric acid is well known as a test for proteins; and Reichard (*Pharm.-Ztg.*, **55**, 158, 167) has found that 25 per cent. hydrochloric acid also gives a blue color.

³ Feder (*Z. Nahr. Genussm.*, **15**, 234) has found that hydrogen dioxide gives a violet coloration when heated with milk and hydrochloric acid in the presence of formaldehyde. A violet color is also produced when formaldehyde is treated with a protein in the presence of hydrochloric acid (see Voisenet, *Compt. rend.*, **150**, 40).

⁴ The production of aldehydes in cheeses may be attributed to the fermentation of lactose (Trillat and Sauton, *Compt. rend.*, **144**, 495).

⁵ See tests under "Peroxides."

especially in the presence of acetic acid, is due to the presence of hydrogen dioxide; and it is generally recognized, especially since the work of Dunstan and Dymond,² that the impurity in ether which liberates iodine is hydrogen dioxide, although several have maintained that ozone is the cause of the reaction.² Ethyl peroxide also causes the separation of iodine from potassium iodide solution,³ and the latter serves for the detection of peroxidized compounds in general in ether. It lacks the reliability required for a specific test, however, and is open to the following objections:

(i) Potassium iodide solutions are decomposed by light.

(ii) Dissolved oxygen may often cause the separation of iodine.

(iii) The presence of sulphurous and sulphuric acids can cause the liberation of iodine; and the test is also interfered with by the presence of chlorine, bromine, and nitrous acid.⁴

It has been stated that perfectly pure ether may liberate iodine from potassium iodide,⁵ but this is incorrect when the proper precautions are observed; and the facts which establish its unreliability⁶ are limited to those enumerated above.⁷

The potassium iodide test is given in the pharmacopoeias of Germany,⁸ Switzerland,⁹ Japan,¹⁰ France and Holland.

¹ *Pharm. J. and Trans.*, [3], 17, 841. Warden (*Pharm. J.*, [3] 15, 521) concluded that the liberation of iodine from potassium iodide indicated the presence of aldehyde, and Dunstan and Dymond demonstrated that the impurity which liberates iodine is hydrogen dioxide. Aldehyde is without action on potassium iodide.

² Werner (*Pharm. J.*, [3], 16, 660) regarded the liberation of iodine from potassium iodide as an indication not of an actual impurity in ether, but of its decomposition under the influence of light and air, whereby ozone is formed; and Buchner (*Chem.-Ztg.*, 9, 69) stated that ozone is rapidly formed when ether is exposed to light, and that this body is the cause of the liberation of iodine. We have already shown that ozone cannot exist in a free state in moist or "dry" ether.

³ "On the Action of Ozone on Potassium Iodide Solutions," see Brunck, *Z. anorg. Chem.*, 10, 222; and Garzarolli-Thurnlackh, *Monatsh.*, 22, 955.

⁴ "On the Action of Hydrogen Dioxide on These Solutions," see Kingzett, *J. Chem. Soc.*, 37, 805; and Schöne, *Ann.*, 195, 228.

⁵ Von Neander, *Chem.-Ztg.*, 26, 336.

⁶ Allen [*Commercial Organic Analysis*, 1, 181 (1908)] states that "some specimens of commercial ether liberate iodine from potassium iodide, a reaction which is not improbably due to the presence of traces of ethyl nitrite." This suggestion is not supported by known facts, since, although, as shown by Berthelot, perfectly dry ether can form, on long standing under the influence of air, traces of nitric acid, as well as ethyl peroxide, ethyl nitrite has never been observed in commercial ethers and its formation is, in our opinion, improbable.

⁷ Dunstan and Dymond, *loc. cit.*

⁸ "On the Reliability of the Potassium Iodide Test," see also Schobig, *Apoth.-Ztg.*, 9, 210; and Leeds, *J. Am. Chem. Soc.*, 1, 65.

⁹ The potassium iodide test is usually specified as follows: 10 cc. of ether and 1 cc. of aqueous 1:10 potassium iodide solution, when frequently shaken in a well-stoppered bottle, must show no coloration during one hour's exposure to diffused daylight. Krauch and Merck (*Chemical Reagents, Their Purity and Tests*, 1907, 101) direct that the mixture be shaken vigorously in a completely filled glass-stoppered bottle, and state that neither the ether nor the potassium iodide solutions should acquire a color after standing one hour in the dark.

¹⁰ The German Pharmacopoeia employs potassium iodide solution, 1 cc. to 10 cc. of ether, and protects the mixture from the light; it is stated that no coloration should result within 3 hours. In this connection, see Hirsch's *Universal Pharmakopöe*, 1, 29, (1902); *Deutsches Arzneibuch*, 5th revision, 1910, 34.

¹¹ The *Pharmacopoea Helvetica*, 1907, 25, gives the test with potassium iodide for "vinyl alcohol."

¹² The *Pharmacopoeia of Japan*, 1907, 25, specifies that if 10 volumes of ether and 1 volume of potassium iodide solution be put in a well-stoppered glass bottle, so as to make it quite full, and then set aside, protected from the light, and with frequent shaking, it should acquire no coloration within an hour. According to this Pharmacopoeia (p. 26) narcotic ether should acquire no coloration under the same conditions within three hours. This test is more complete than those usually specified.

We found that pure ether containing 0.01 per cent. of hydrogen dioxide produced a faint coloration with a 10 per cent. potassium iodide solution, when the hydrogen dioxide was added to the ether and thoroughly mixed just before applying the test; but when the ether was allowed to stand in the dark for several days, the coloration was very pronounced. We cannot recommend the test, however, on account of its unreliability.

2. *The Test with Potassium Iodide and Starch Solution.*—Heldt¹ suggested the employment of potassium iodide-starch solution as a reagent for ozone, and this reagent may be used for the detection of peroxides in ether, a blue coloration resulting from the liberation of iodine. In fact, 0.05 mg. of hydrogen dioxide per liter may be detected in an acid solution, and the blue color is visible in solutions containing the iodine yielded by one part of potassium iodide in 600,000 parts of water at 0° C. The test is, however, subject to the same limitations as the potassium iodide test, and even to a greater degree.

3. *The Test with Potassium Iodide and Phenolphthalein Solution.*—This test, which is identical with the one proposed by Houzeau for the detection of ozone, except that phenolphthalein is substituted for litmus, is given by Wobbe² as follows: If 20 cc. of ether are shaken with 5 cc. of a potassium iodide-phenolphthalein solution (a mixture of equal parts of a 50 per cent. solution of potassium iodide and a 1 per cent. solution of phenolphthalein), the latter should not be reddened. Rosolic acid may be employed instead of phenolphthalein.

The action of light and alkali from the glass render this test open to serious objections. It is also disturbed by the presence of acids. The test is, however, an exceedingly delicate one, a pronounced reaction resulting in the presence of the merest traces of peroxidized compounds.

(b) Tests Dependent upon Color Reactions.

1. *The Vanadic Acid Test.*—Jorissen³ proposed the following test for the detection of peroxides in ether: 0.1 gram of powdered vanadic acid and 2 cc. of sulphuric acid are placed in a small porcelain capsule, and the whole is heated for 10 to 15 minutes on the water-bath, and then allowed to cool. The red-brown mass is then dissolved in water and made up to 50 cc.; one or two cc. of this pale yellow reagent are placed in a test-tube, 5 or 10 cc. of the suspected ether are added, and the whole is well shaken. Should peroxides be present, the mixture assumes a color varying from rose- to blood-red. Jorissen found this test more delicate than the perchromic acid test and more rapid than the potassium iodide test. It is specified by the *Pharmacopoea Belgica*⁴ as follows: 10 cc. of ether when shaken with 1 cc. of vanadic acid solution, should acquire no red color.

We have found that the vanadic acid test is a re-

¹ *Chem. Centr.*, 1862, 886; see also Ferriere, *Compt. rend.*, 74, 17. Potassium periodate may be used in place of potassium iodide in this reagent. In the *Pharmacopoea Nederlandica* (1905 27) the water extract is tested with potassium iodide and starch solutions.

² *Apoth.-Z g.*, 18, 458

³ *Ann. chem. anal.*, 8, 201; *Chem.-Ztg.*, 27, R. 128 *Képeri. d. Pharm.*, 15, 167

⁴ 1906, 15.

liable and ready one, being of great delicacy and of easy application. When peroxides are present in the ether under examination, a permanent color is afforded which is readily distinguishable, even when the ether contains but 0.003 per cent. hydrogen dioxide. The reagent may be more conveniently prepared by using ammonium metavanadate and sulphuric acid.

2. *The Ferrous Hydroxide Test.*—This test was given by Thoms¹ as follows: In a watch glass dish, let one cc. of freshly prepared ferrous sulphate solution, 1 : 10, be superposed by 10 cc. of ether and let a few drops of "soda solution" be added. The resulting greenish white ferrous hydroxide should not turn brown within one minute. This test was stated to be preferable to the one with potassium iodide.

We have found that an ether containing 0.01 per cent. of hydrogen dioxide gives a slight but decided reaction in a half a minute in this test; but it is less delicate and more liable to errors than the vanadic acid test of Jorissen. Care must be taken that perfect superimposition occurs when the ether is added, else ferric hydroxide may form almost immediately (less than half the time limit of the test).

3. *The Ferrous Sulphocyanate Test.*—Stokes and Cain² found that hydrogen dioxide may be readily detected in ether by shaking it with freshly reduced acidified ferrous sulphate solution to which a sulphocyanate has been added, when ferric sulphocyanate is generated and is taken up by the ether. Since, however, "even the best grades of ether show this behavior unless especially purified," and on account of the many possible sources of error, this test, although of decided theoretical merit, cannot be recommended.

(c) Tests Dependent upon the Formation of Periodides.

1. *The Caffeine Alkyl iodide Test.*—Rossolimo³ found that ether containing hydrogen dioxide possesses the property of oxidizing caffeine alkyl iodide to a slight extent, but that the oxidizing power of ethyl peroxide would appear to be a much greater one, as caffeine alkyl iodide is decomposed by it with copious formation of periodides.

II. TESTS DEPENDENT UPON REDUCTION.

1. *The Chromic Acid Test.*—This test, which originated with Schönbein,⁴ may be given as follows: Some potassium chromate, with a few drops of dilute sulphuric acid, is added to the ether and the mixture is well shaken; a blue color shows the presence of hydrogen dioxide. It is specified in the Pharmacopoeias of Great Britain,⁵ Hungary, Switzerland and France.

Deniges⁶ stated that 0.5 mg. of hydrogen peroxide is the smallest quantity which can be detected by the

¹ *Ber. Pharm. Ges.*, 1894, 240; *Merck's Annual Report for the Year 1900*, 8, 27.

² *J. Am. Chem. Soc.*, 29, 409; *Bull. Bur. Standards*, 3, 115.

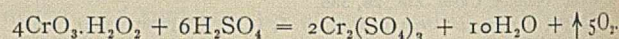
³ *Ber.*, 38, 774.

⁴ *Ann.*, 109, 134.

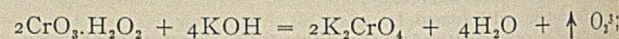
⁵ The British Pharmacopoeia employs potassium dichromate acidified with sulphuric acid, requiring that the ethereal solution shall not develop a blue color. This test is mentioned in the *National Standard Dispensatory*, 1905, 111. White (*Pharm. J.*, [4], 25, 780) directs that this test be made thus: Dissolve about 0.1 gm. of potassium dichromate in 9 mils. of water, add 1 mil. of dilute sulphuric acid, and then shake with 2 mils. of ether. After separation, the ether should be colorless.

⁶ *Bull. soc. chim.*, 1890, 797.

chromic acid test, but Fairley¹ has detected 0.1 mg. by this method. He employed chromic acid solution directly. Dunstan and Dymond² found that it will show the presence of 0.02 per cent. hydrogen dioxide in ether; and we have found that when 10 cc. of an ether containing 0.01 per cent. of hydrogen dioxide are added to 10 cc. of potassium dichromate solution and 2 cc. of sulphuric acid, the ether becomes faintly colored, but no blue color results. With an ether containing 0.02 per cent. of hydrogen dioxide, however, a blue color results at once. This disappears on shaking, and, even when 0.05 per cent. of hydrogen dioxide is present, the ether layer assumes a pale green tint after such treatment. Therefore, since the blue color is not permanent even in an ether containing 5 per cent. of hydrogen dioxide, the test should be specified as follows: A blue color should not result on addition of the ether under examination to the chromic acid solution, and the ether layer, after separation following agitation, should not have acquired a coloration. The blue coloration is due to some such an additive compound as $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$, which is very unstable and has but a brief existence. It is at once destroyed in weak hydrogen dioxide solutions by shaking the mixture. In an acid solution—for example, in the official test of the British Pharmacopoeia for peroxides in ether—the chromic acid is reduced immediately upon the spontaneous decomposition of the additive compound, and green $\text{Cr}_2(\text{SO}_4)_3$ results. The blue color is not necessarily prolonged by larger amounts and disappears when small amounts of peroxides are present, by simple agitation. When an ether containing peroxides—for simplicity, one containing hydrogen dioxide—is mixed with a potassium dichromate solution acidified with sulphuric acid, the ethereal layer is colored blue from the temporary solution of the compound formed, if the amount of hydrogen dioxide present amounts to or exceeds 0.2 per cent. On mixing by agitation, this reaction occurs:



This is confirmed by the fact that ferrous salts are oxidized by the ethereal liquid containing the blue substance in solution and that alkalis decompose it to alkali chromates and oxygen,



and by the fact that the ethereal solution evolves oxygen when evaporated, and CrO_3 remains.⁴

Owing to its comparative lack of delicacy and the instability of the blue coloration indicative of the presence of peroxides, this test is less preferable than the vanadic acid test and should only be employed for confirmatory reasons.

2. *The Potassium Ferricyanide-Ferric Chloride Test.*—Potassium ferricyanide-ferric chloride solu-

¹ *Chem. News*, 62, 227.

² *Pharm. J.*, 17, 849.

³ See Moissan, *Compt. rend.*, 97, 96; Martinon, *Bull. soc. chim.*, [2] 45, 862.

⁴ Aschoff (*J. prakt. Chem.*, 81, 401, 487), Barreswill (*Ann. chim. Phys.*, [3] 20, 364), Schönbein (*Pogg. Ann.*, 108, 471; *J. prakt. Chem.*, 70, 257), Lensen (*Ibid.*, 81, 278), and particularly Bach (*Ber.*, 35, 872) have investigated the action of chromic acid on hydrogen dioxide solutions also.

tion has been recognized as an efficient test for the detection of hydrogen dioxide.¹ Wobbe² has suggested it for determining the presence of peroxides in ether as follows:

If 20 cc. of ether are shaken with 5 cc. of a freshly prepared potassium ferricyanide-ferric chloride solution (two drops of a ferric chloride solution free from acid and of a specific gravity of 1.280 to 1.282, diluted to about 90 cc., a freshly prepared potassium ferricyanide solution added drop by drop until the liquid acquires a "wine-yellow" color, and the whole made up to 100 cc.), the aqueous liquid, in the dark, should acquire neither a green nor a blue color.

Since other substances (SO₂, etc.) will reduce ferricyanide to ferrocyanide, this reaction cannot always be relied upon. Some of the higher aldehydes will also give the same reaction as hydrogen dioxide with potassium ferricyanide-ferric chloride solution.³

Jorissen's vanadic acid test is the most satisfactory test of those which have been proposed for the detection of peroxides in ether. When the other tests are applied, the presence of such substances as interfere with the reaction must be carefully guarded against, and this is not always possible. The limitations of these tests and the need of more reliable reagents for the detection of peroxides in ether induced the authors' endeavor to devise more appropriate tests, and the results of this inquiry follow.

VI. (b) SOME SUPPLEMENTARY TESTS FOR THE DETECTION OF PEROXIDES IN ETHER.

Quite a number of tests have been proposed for the recognition of hydrogen dioxide. We have, for example, the well known guaiacum-malt test;⁴ and sulphuric acid solutions of ammonium molybdate and titanate,⁵ various aniline bases,⁷ lead and copper hydroxides,⁸ dimethyl-paraphenylenediamine, phosphorus tribromide-copper nitrate,⁹ and the benzene solution of the cobalt salt of naphthenic acid,¹⁰ have also been employed for the detection of hydrogen dioxide. None of these tests has been proposed for the detection of peroxides in ether, and this would appear to be due to the following reasons: (1) some are not applicable in ethereal solutions; (2) others lack the delicacy necessary for the detection of hydrogen dioxide in very dilute solutions; (3) some of the reagents are uncommon, and this would result in inconvenience to the worker.

It is well known that *cobaltous hydroxide* changes to a brown color through oxidation, going over into *cobaltic hydroxide*; and it would seem, therefore, that either

a cobalt or manganese¹ salt could be employed in the -ous form in place of ferrous sulphate in the test proposed by Thoms for the detection of peroxides in ether.

Schmatolla² found that when 200 cc. of the solution to be tested are acidified with a few drops of dilute sulphuric acid, and about the same quantity of a 1 per cent. cobalt nitrate solution is added, a sharp brown coloration results on adding potassium hydroxide solution if hydrogen dioxide is present. This test was found capable of detecting hydrogen dioxide in a dilution of 1 : 1,000,000. Ditz³ suggested employing a solution of cobaltous oxide in concentrated potassium hydroxide as a test for peroxides in ether, finding that the blue color disappears if peroxides are present in even minute amounts.

We have found that the presence of 0.003 per cent. hydrogen dioxide may be quickly and easily detected in ether by adding three drops of dilute sulphuric acid and the same amount of a 1 per cent. solution of cobalt nitrate to 25 cc. of the ether, then adding potassium hydroxide solution and shaking. A brown precipitate is produced under these conditions, whereas if pure ether is used, a white precipitate results. Acetaldehyde is without action on the precipitate.

A *cerous salt* may be similarly used for the detection of peroxides in ether. On shaking 5 cc. of a 10 per cent. cerous nitrate or cerous chloride solution, rendered barely alkaline with ammonium hydroxide, with 25 cc. of the ether, the white cerous hydroxide should not assume a darker tint. The cerous hydroxide must be prepared just prior to performing the test and must not be allowed to stand in the air. The test is most satisfactorily conducted in an almost completely filled bottle, and the observation as to color should be made by comparison with a blank test on pure ether immediately after shaking one minute. Ether containing 0.003 per cent. of hydrogen dioxide will cause the cerous hydroxide to assume a yellow color, while larger amounts cause varying shades of color from yellow to dark orange; the precipitate resembles ferric hydroxide. Ammonium carbonate solution may be advantageously employed in the place of ammonium hydroxide in this test, since it may be added to the acidified cerous salt solution upon which the ether to be examined is superimposed, and thus the carbon dioxide liberated will expel all air in the bottle in which the test is being conducted.

Fairley⁴ showed that in very dilute solutions 0.5 to 0.25 mg. of uranium may be detected by means of the reaction between *uranium nitrate* and hydrogen dioxide. However, he only observed the time required for precipitation, and made no experiments with a view of devising an easily applied colorimetric test.

Aloy⁵ found that on adding to the solution of any uranium compound a little hydrogen dioxide and then potassium carbonate, either solid or in a very concentrated solution, a fine red coloration is developed.

¹ In fact, manganous chloride and manganous acetate papers are well known as being suitable for detecting nascent oxygen and ozone, respectively.

² *Pharm.-Ztg.*, 50, 641.

³ *Chem.-Ztg.*, 25, 109.

⁴ *Chem. News*, 62, 227.

⁵ *Bull. soc. chim.*, [3] 27, 734.

¹ Weltzien (*Ann.*, 138, 129) observed that K₄Fe(CN)₆ becomes K₃Fe(CN)₆ in the presence of hydrogen dioxide, and Schönbein (*J. prakt. Chem.*, 78, 67) found that 0.02 mg. of hydrogen dioxide may be detected by this method. Barralet (*Chem. News*, 79, 136) stated that one cc. of a 1/165000 solution of hydrogen dioxide is sufficient to intensify the pale blue color of ferrous ferrocyanide in 20 cc. of the fresh compound.

² *Loc. cit.*

³ Cf. Molinari and Fenaroli, *Ber.*, 41, 2789.

⁴ Schönbein, *J. prakt. Chem.*, 105, 219; Houzeau, *Compt. rend.*, 66, 44.

⁵ Denigès, *Compt. rend.*, 110, 1007; Crismer, *Bull. soc. chim.*, [3] 6, 22.

⁶ Richarz, *Pogg. Ann.*, 31, 912.

⁷ Ilosvay, *Ber.*, 28, 2029; Denigès, *J. Pharm.*, [5] 25, 591.

⁸ *Analyst*, 15, 120.

⁹ Christomanos, *Verh. Ges. Deut. Naturf. Aerzte*, 1905, II, 76.

¹⁰ Kharichkov, *Chem.-Ztg.*, 34, 50.

The addition of alcohol, he found, resulted in the precipitation of the unstable red compound.

We have ascertained that this test may be suitably elaborated and employed for the detection of peroxides in ether. On adding 5 cc. of a 5 per cent. solution of uranium nitrate, previously saturated with either sodium carbonate or potassium carbonate, to 25 cc. of ether and thoroughly shaking, the greenish yellow color of the uranium solution should not be changed. If the ether under examination contains 0.01 per cent. of hydrogen dioxide, a yellowish brown color is assumed by the uranium solution, and this may be readily distinguished by comparison with a blank test made on an ether of known freedom from peroxides. Even the presence of 0.003 per cent. of hydrogen dioxide causes the production of a sharp orange color, while the presence of considerable amounts produces a red coloration. In fact, the color grades from a golden color to red, according to the amount of impurity present. Acetaldehyde in no way interferes with this test.

Arnold and Mentzel¹ found that hydrogen dioxide can be recognized in the presence of ozone by means of a solution of *benzidine* and *copper sulphate*, which gives a blue precipitate with hydrogen dioxide, but only a reddish yellow precipitate with ozone; and, according to Molinari and Fenaroli,² the benzidine reaction is the best test for hydrogen dioxide in the presence of aldehydes.

In order to ascertain whether this test is applicable in the case of ether, a saturated solution of benzidine (Merck's H. P.; m. p. = 122°) in pure ethyl alcohol and a 10 per cent. solution of pure copper sulphate were employed. When several drops of each of these solutions are added to pure ether, a brick-red separate results upon agitation; but in the presence of hydrogen dioxide, this changes to a blue or greenish color, varying generally from grayish green to greenish black, depending on the amount of peroxide present, and in the presence of considerable amounts of hydrogen dioxide the separate possesses a brownish black color. Benzidine is usually slightly oxidized and the pure substance should be used. Acetaldehyde is without apparent action when present and causes no alteration in color.

This test, besides being easily applied, is productive of a marked color change in the presence of minute amounts of hydrogen dioxide, and is to be recommended for the detection of peroxides in ether.³

The Reactions of Hydrogen Dioxide with Various Iodides.

The unreliability of the potassium iodide test for the presence of hydrogen dioxide and ethyl peroxide in ether caused us to investigate the deportment of various metallic iodides with "ozonized" ethers of various strengths, in order to ascertain whether any of them would serve as delicate and reliable reagents for the detection of these impurities of badly-stored

ether. The iodides were considered the most promising, in the case of stable compounds, on account of their ready oxidation and the fact that the separation of free iodine imparts a coloration which is readily determinable even in very minute amounts, Kastle⁴ having found that 0.000066045 g. of iodine is sufficient to impart a distinct yellow color to 20 cc. of water.

Schönbein² found that the addition of a few drops of lead acetate solution, followed by potassium iodide and starch, and a little acetic acid produces a blue color in the presence of hydrogen dioxide. He also found that when hydrogen dioxide is added to a solution of zinc or potassium iodide and ferrous sulphate, iodine is set free, indicated by the formation of blue iodide of starch. Although it has a delicacy of 1 in 25,000,000 parts, this test is only suitable for neutral solutions. Traube³ adds a small quantity of copper sulphate in acid solutions.

Caffeine alkyl iodide and the double iodides of lead and ammonium, lead and potassium, and potassium and mercury, cannot be used as reagents for peroxides, as they decompose in the presence of moisture.

Directly bearing upon the subject under consideration is the test proposed by Buchner² for the detection of ozone in ether. Buchner found that cadmium iodide forms cadmium oxyiodide and free iodine in the presence of ether containing ozone (sensitive to 0.05 per cent.), but he failed to consider the action of hydrogen dioxide and of ethyl peroxide on this salt, although he stated that hydrogen dioxide is formed in ether in the presence of water and that oxidation occurs after some time.

In view of the possibilities presented by the iodides as reagents for the detection of peroxides in ether and the fact that these have received little consideration so far in this connection, it seemed desirable to examine the action of ether containing known amounts of hydrogen dioxide with the following iodides: cadmium potassium iodide, the iodides of arsenic, lead iodide, stannous iodide, zinc iodide, and calcium iodide.

From the results obtained in the preliminary tests, it was concluded that only cadmium potassium iodide, lead iodide, stannous iodide, and zinc iodide might be suitable as reagents for the detection of peroxidized compounds in ether.

A 10 per cent. solution of cadmium potassium iodide was prepared. This solution acquired a yellow color in the presence of hydrogen dioxide, but was unaffected by sulphuric or acetic acids and by acetaldehyde. On adding several cc. to a 0.01 per cent. solution of hydrogen dioxide in pure ether, a decided reaction occurred at once on shaking and the ethereal layer assumed a yellow color. With a 0.0025 per cent. solution of hydrogen dioxide in pure ether, a faint, yet distinguishable, coloration resulted on shaking. 10 cc. of ether and 2 cc. of the reagent were used.

Since a 10 per cent. potassium iodide solution assumes a pronounced yellow color in one hour on exposure to sunlight, and a decided coloration in even 30 minutes,

¹ *Ber.*, **35**, 1902.

² *Ibid.*, **41**, 2789.

³ Wilkinson and Peters (*Z. Nahr. Genussm.*, **16**, 172) have devised a test for the detection of hydrogen dioxide in milk, using benzidine.

⁴ *Am. Chem. J.*, **21**, 398.

² *J. prakt. Chem.*, **86**, 129; see also, Struve, *Z. Chem.*, **1869**, 274.

³ *Ber.*, **17**, 1062.

⁴ *Chem.-Ztg.*, **9**, 69; *Ber.*, **1885**, 376.

whereas, a 10 per cent. cadmium potassium iodide solution remains perfectly colorless and is not decomposed on like exposure, and since the latter is unaffected by any likely amounts of acids in ether, yet possesses great delicacy and is easy to apply, its use is preferable to potassium iodide as a reagent for peroxides in ether, and we can recommend it for the purpose.

Lead iodide is by no means so suitable. On account of its insolubility, this salt is not advantageous to use alone, yet its deportment with ether containing hydrogen dioxide was determined.

Hydrogen dioxide in considerable amounts was found to decompose lead iodide, the ether assuming a brown color.¹ When a small amount of the salt was added to a 0.01 per cent. solution of hydrogen dioxide in pure ether (0.5 g. PbI_2 to 10 cc. of ether), and the mixture was thoroughly shaken, the ether layer assumed a yellow color; however, no reaction occurred when a 0.0025 per cent. dioxide solution was used. Since all the double iodides of lead, except those with the quaternary ammonium bases, are decomposed by water, none of these possess signal advantages over lead iodide.

Stannous iodide was found to dissolve in ether, forming a red solution. When water was added to this and the mixture was well shaken, the ethereal layer assumed a yellow color and the aqueous layer became turbid. The addition of hydrogen dioxide produced a dark brown color in the ethereal layer. A test for peroxides in ether may be applied with this salt as follows: Dissolve 0.5 g. of the iodide in 20 cc. of pure ether, and then dilute the red solution with an equal amount of water, when an almost gelatinous pale yellow mixture should result. An equal quantity of the ether to be examined is added to this mixture, and, upon thorough agitation, the ethereal layer, after separation, should be pure white in color. This test will detect minute traces of peroxides, the coloration resulting from an ether containing 0.0025 per cent. hydrogen dioxide being very marked. It is not to be preferred to the cadmium potassium iodide test, however.

Arnold and Mentzel² pointed out that the zinc iodide and starch test for ozone is not sufficiently characteristic and is interfered with by chlorine, bromine, nitrous acid, and hydrogen dioxide. Zinc iodide, in an anhydrous state, absorbs water and deliquesces, and takes up oxygen from the air, with the liberation of iodine. It is rather a delicate test for the presence of peroxides in ether, but is neither so characteristic nor so delicate as the cadmium potassium iodide test.

VI. (c) ON THE OCCURRENCE OF ACETAL IN ETHYL ETHER.

It is possible that acetal (di-ethyl-acetal) occurs in many, if not all, commercial ethers, especially those which have been carelessly manufactured or stored. The occurrence of acetal in commercial ether may be accounted for in two ways:

¹ The reaction is similar to that which occurs when moist lead iodide is exposed to direct sunlight in contact with air. This would seem to suggest that the formation of hydrogen dioxide induces the decomposition of the salt under such conditions.

² *Ber.*, 35, 1324.

1. As a primary impurity. Acetal is well known as an impurity of raw spirit, and is formed in this case, as indicated by Döbereiner,¹ Liebig,² Stas,³ and Wurtz,⁴ by the imperfect oxidation of alcohol. It is likely, however, that any acetal existing in alcohol used for the manufacture of ether would be destroyed during etherification, although small amounts, at least, could be again formed by the action of sulphuric acid on alcohol containing aldehyde,⁵ or as a product of the probably limited amount of oxidation which occurs during etherification.⁶

2. As a product of the slow oxidation of alcohol present in ether, such oxidation occurring during imperfect storage. We are unprepared at present to give direct proofs from which the existence of acetal in ether may be adduced.

"It may be mentioned here that samples of acetal (Kahlbaum's pure) examined by us readily liberated iodine from potassium iodide and cadmium potassium iodide solutions, and oxidized cerous hydroxide. They also gave a coloration with vanadic acid solution; but gave no reaction with Aloy's uranium test-solution or benzidine-copper sulphate solution thus differing from a hydrogen dioxide solution. They possessed a slightly acid reaction, but the presence of acetic acid did not give rise to the reactions in the case of the iodide solutions, since cadmium potassium iodide is very stable towards acids. Therefore, since acetaldehyde is without action on this solution, the reaction could only have been caused by the presence of a peroxidized compound (peracetic acid or aldehyde peroxide) or by the acetal itself. For the present, we are inclined to attribute the deportment to the presence of the former."

VII. (a) TESTS FOR THE DETECTION OF ACETALDEHYDE IN ETHER.

As has been mentioned, acetaldehyde may form in ether during storage, and several⁷ have found occasion to emphasize the objectionable presence of aldehyde in many ethers on the market. It is, therefore, very important that anaesthetic ether be examined for acetaldehyde, an impurity which, when present in "excessive amount," would seem to give rise to respiratory irritation during anaesthesia.⁸

The Potassium Hydroxide Test.—Weidenbusch⁹ in-

¹ *Ann.*, 1, 185; *Gmelin's Handb.*, 4, 805.

² *Ann.*, 5, 25; 14, 156.

³ *Ann. chim. phys.*, [3] 19, 146.

⁴ *Ibid.*, [3] 48, 370; *Ann.*, 108, 84.

⁵ Delépine (*Compt. rend.*, 132, 331) has found that the laws regulating the production of acetals are similar to those observed in the analogous cases of esterification and hydrolysis. Acids are peculiarly efficacious in facilitating the reaction, and the nature of the acid and its concentration, if the latter is not too great, are without influence on the result.

⁶ We are of the opinion that during initial action in etherification various oxidation products of alcohol result; that is, that strong sulphuric acid plays the same, or a similar, rôle as when it acts on metals. Many facts lend support to this view.

⁷ Thoms, *Pharm.-Ztg.*, 1894, 777; Warden, *Pharm. J. and Trans.*, 1885, 521; *Am. J. Pharm.*, 57, 148; and Graham, *Proc. Penn. Pharm. Assn.*, 1906, 153.

⁸ Acetaldehyde vapor, when inhaled, produces asphyxia. Prolonged exposure to light and air gives rise to aldehyde in ether, and such treatment greatly affects the results of etherization. In one case of which we have record, a sample of ether which induced irritation of the respiratory tract during etherization was examined and the only impurity found was acetaldehyde.

⁹ *Ann.*, 66, 153.

icated that aldehyde forms a resin with aqueous potassium hydroxide, and this observation was later utilized for the detection of an impurity of ether, which, until quite recently, was found to commonly occur, sometimes in considerable amounts, in all ethers on the market. Traub¹ stated that ether suitable for anaesthesia should undergo no change when placed in contact with caustic potash for twelve hours; and it has been specified that 30 cc. of ether and about 5 g. of solid potassium hydroxide, after standing for one day in a dark place and being occasionally shaken, must show no appearance of a brownish substance having separated out. Some, however, consider that a much shorter time limit should be placed. White² recommends that 5 g. of potassium hydroxide in stick form be added to 20 cc. of ether in a stoppered bottle, and that the mixture be then shaken and set aside for two hours; and Krauch and Merck³ direct that on covering pieces of potassium hydroxide the size of a pea with the ether, and setting aside in the dark for one-half hour, the liquid must not acquire a yellow color.

The potassium hydroxide test is specified by the Pharmacopoeias of Great Britain, Germany, United States, France, Holland, Hungary, Spain, Switzerland, Japan, and Belgium. It has, therefore, attained wide recognition.

The British Pharmacopoeia⁴ and the German Pharmacopoeia use the solid form of potassium hydroxide, and the Pharmacopoeia of the United States the solution. The British Pharmacopoeia gives neither a time limit nor the quantities to use; the Pharmacopoeia of the United States uses 10 cc. of ether and 1 cc. of potassium hydroxide (T.S.) and a time limit of one hour, while the German Pharmacopoeia requires that 20 cc. of "narkoseäther," when allowed to stand over solid potassium hydroxide in the dark, shall afford no yellow color within six hours; in the case of ether not intended for anaesthetic purposes, the time limit is placed at one hour. *The National Standard Dispensatory*⁵ specifies the test according to the Pharmacopoeia of the United States.

The Pharmacopoeias of Germany, Holland and Switzerland⁶ state that the test with potassium hydroxide is for the presence of "vinyl alcohol" as well as of aldehyde. The Pharmacopoeia of Japan⁷ states that if ether "be sprinkled upon newly ground potassium hydroxide, and set aside tightly closed and protected from the light, the latter should not assume a yellowish color within half an hour;" and that if narcotic ether "be sprinkled upon newly ground potassium hydroxide, and allowed to stand tightly closed and protected from light, the latter should not acquire a yellowish color within six hours."⁸ The latter test is almost identical with the German requirement, and is more reliable than the test given in the United States Pharma-

copoeia. The *Pharmacopoea Belgica*¹ specifies that "20 cc. of ether and about 4 g. of fragments of sodium hydroxide should assume no yellow color when allowed to stand one-half hour in the dark." This test is less rigorous in requirements than the German and Japanese.

Traub,² Vulpius³ and Schobig⁴ have investigated the deportment of potassium hydroxide with ether, but it would appear that others have found reasons to state that impurities other than aldehyde will impart a yellow or brown color to commercial ether on the addition of potassium hydroxide. Poleck and Thümmel⁵ state that "vinyl alcohol" will cause such a coloration, and Borrigter⁶ found that ether containing hydrogen dioxide colors a portion of potassium hydroxide yellowish brown, an observation which had previously been made by Schönbein.⁷ Solid potassium hydroxide is colored an intense orange-brown by ozone,⁸ but peroxides produce no coloration, hence, we are of the opinion that acetaldehyde is the only substance likely to respond to the test with potassium hydroxide when it is applied to ether, except certain organic substances that are referred to later.

"In order to determine this experimentally, 5 g. of potassium hydroxide were added to the following samples of ether, 30 cc. of each being used in the tests:

"1. Ether distilled over sodium, and containing mere traces of acetaldehyde.

"2. An ether containing 0.5 per cent. of hydrogen dioxide but otherwise pure.

"3. An ether intended for analytical purposes; this ether contained small amounts of moisture.

"4. No. 3 after the addition of 3 per cent. of absolute alcohol.

"5. No. 3 after the addition of 0.05 per cent. of hydrogen dioxide.

"6. No. 1 after the addition of 0.05 per cent. of acetaldehyde.

"7. No. 3 after the addition of 0.05 per cent. of acetaldehyde.

"8. No. 3 after the addition of 0.10 per cent. of acetaldehyde.

"9. No. 8 after the addition of 3 per cent. of absolute alcohol.

"After standing 30 minutes, Nos. 6, 7, and 8 possessed a brown color, and No. 9 had assumed a yellow color. At the end of 24 hours, the following results were observed:

"1. *Nil*.

"2. Clear, uncolored, separate; potassium hydroxide and ether colorless.

"3. Very small amount of a brownish substance.

"4. Brown solution; no colored substance on the potassium hydroxide as in No. 3.

¹ 1906, 15.

² *Schw. Wschr. f. Chem. u. Pharm.*, 1892, No. 3.

³ *Apoth.-Ztg.*, 1894, No. 1.

⁴ *Ibid.*, 1894, 22.

⁵ *Z. anal. Chem.*, 29, 6.

⁶ *Chem. News*, 53, 69.

⁷ *Ann.*, 109, 134.

⁸ Wurtz, *Dictionnaire de Chimie pure et applique*, 721; Von Baeyer and Villager, *Ber.*, 35, 3038; and Bach, *Ibid.*, 35, 3424.

¹ *Pharm. Z. Russland*, 31, 504.

² *Pharm. J.*, [4] 25, 780.

³ *Chemical Reagents, their Purity and Tests*, 1907, 101.

⁴ See Squire's *Companion to the latest Edition of the British Pharmacopoeia*, 1908, 103.

⁵ 1905, 111.

⁶ *Pharmacopoea Helvetica*, 1907, 25.

⁷ 1907, 25.

A similar test is prescribed in the *Pharmacopoea Hungarica*, 1909, 18.

- "5. Clear, uncolored separate; no brownish substance.
- "6. Yellow solution and considerable "aldehyde resin."
- "7. As in No. 6.
- "8. Much more considerable in amount than in No. 6.
- "9. Red-brown solution.

"From these experiments, it was concluded that the yellow or brownish separate is only caused by the presence of acetaldehyde, and in cases where the ether is tinted yellow or brown, this is often due to the presence of alcohol as well as aldehyde, the former dissolving the resin formed by the latter. Peroxides may produce a turbidity, but no coloration or colored separate."

There is a source of error in the potassium hydroxide test, however. Just as spirits stored in casks made of wood containing tannin show a coloration with potassium hydroxide, so do samples of ether containing pieces of cork, the latter being introduced from the stoppers. The coloration in this case is probably due to the presence of quercitannic acid and resinous matter extracted from the cork through contact with ether. An ether containing mere traces of acetaldehyde—that is, aldehyde not detectable by the potassium hydroxide test—may thus become colored when the test is applied, providing it has remained in contact with cork or contains pieces of broken cork, the latter being by no means unusual owing to the form of the neck of the tin containers in use. We have proved these facts experimentally.

Pure or anhydrous ether, carefully stored, gives a negative result with potassium hydroxide, but few anaesthetic ethers on the American market give an absolute non-response when 30 cc. are tested with 5 g. of solid potassium hydroxide. We obtained the following results:

Sample.	Results.
L.....	After 2 hours, a yellowish brown separate; after 24 hours, a marked brown separate. At the end of four days, ether became turbid.
M.....	After 2 hours, ether was turbid and there was a yellowish brown separate; after 24 hours, a marked brown separate. Ether was clear at the end of four days.
N.....	At the end of 2 hours the ether was turbid, but the separate had a darker color than that in M, and was in clots; at the end of 24 hours, the brownish separate appeared larger in amount and darker than in the preceding.
O..... (A known anhydrous ether.)	No colored substance was formed even after the mixture had stood for five days. Ether remained clear.
P.....	After standing 30 minutes, the mixture had a pale yellowish separate, but the ether was clear; at the end of one day, a yellow-brown separate was found. The latter was more pronounced and the ether was turbid at the end of 48 hours.
X.....	After standing 30 minutes, a pale yellowish brown substance was found; ether was clear. Even after 48 hours, ether was clear, but separate became darker in color.
Y.....	After standing 30 minutes, the ether became turbid (white), but no colored substance separated. Ether was still turbid at the end of one day; and at the end of 48 hours ether possessed a yellowish color, but even then no colored substance had formed.

Sample.	Results.
Z.....	At the end of 30 minutes, ether became slightly turbid and a yellowish substance separated. This was considerably increased at the end of one day.
W.....	After standing 30 minutes, ether became slightly turbid, but no colored substance was formed; no separate even after 48 hours but ether was still turbid.

From our experience, we consider that the potassium hydroxide test for the presence of acetaldehyde in anaesthetic ether is sufficiently rigorous and exacting when specified as follows: On covering 5 g. of solid potassium hydroxide, in freshly broken pieces about 5 mm. in diameter, with 30 cc. of the ether, and allowing the mixture to stand for six hours, tightly closed and protected from the light, and occasionally shaking, the potassium hydroxide should not acquire a yellowish or brown color, no colored substance should separate, and the ether should not become turbid or assume any color.

Those ethers which have been carefully purified and which have been properly stored will give a negative reaction in this test; and ether containing more than mere traces of acetaldehyde may be readily recognized. This test is considerably superior to the U. S. P. test for aldehyde. Anhydrous ether should give no response after standing over potassium hydroxide for twenty-four hours.

The Test with Fuchsine Sulphite.—Schiff¹ found that when a dilute sulphurous acid solution of the sulphate, or any other salt, of rosaniline is shaken with a few drops of aldehyde, sulphurous acid is given off; the solution turns red, then violet, and a precipitate is gradually formed. Cazeneuve² learned that rosaniline salts decolorized by sulphurous acid give a violet coloration with an alcoholic solution of form- or acetaldehyde;³ and Müller,⁴ Urbain,⁵ Lefevre,⁶ and von Bitto⁷ have also studied the deportment of aldehyde with Schiff's reagent.

Mohler⁸ found that aldehyde produced a reddish violet coloration in the presence of "rosaniline bisulphite;" but Francois⁹ ascertained that Mohler's reagent will not mix with ether and that it precipitates sodium salts in the presence of the latter. Therefore, he made attempts to find a reagent of similar delicacy which could be used for the detection and estimation of aldehyde in ether, and found that an aqueous solution of sulphurous acid could be employed in place of sodium bisulphite. He also added to the ether, at the moment of making the test, its own volume of 95 per cent. alcohol free from aldehyde. He learned that 5 cc. of pure ether, 5 cc. of pure 95 per cent. alcohol, and 4 cc. of the reagent remained uncolored for fifteen minutes, but when the pure ether was replaced by an ether containing more than $\frac{1}{10,000}$ part of aldehyde, the mixture assumed a red-violet color, the intensity

¹ *Compt. rend.*, 1865, 45.

² *J. Pharm. Chim.*, 3, 595.

³ "On the Detection of Traces of Formaldehyde in the Presence of Acetaldehyde by Means of Fuchsine Bisulphite," see Denigès, Paris Academy of Sciences, Feb. 28, 1910.

⁴ *Z. angew. Chem.*, 1897, 634.

⁵ *Bull. soc. chim.*, 15, 455.

⁶ *Bull. soc. Ind. Mulhouse*, 1897, 84.

⁷ *Z. anal. Chem.*, 36, 369.

⁸ *Mon. Sci.*, 1890, 893; 1891, 582.

⁹ *Chem. News*, 76, 7; *J. Pharm. Chim.*, 5, 521.

increasing with the content of aldehyde. Based upon this reaction, Francois elaborated a method which may be used for the estimation of aldehyde in ether.

Klar¹ reported that ether distilled over sodium gives an aldehyde reaction with fuchsine sulphite, and Thoms² stated that it was impossible for him to obtain ether which would not restore the color to fuchsine decolorized by sulphurous acid.

All of the ethers examined by us gave a more or less red-violet color with Francois' reagent (220 cc. sulphurous acid, 30 cc. 1 : 1000 fuchsine solution, and 3 cc. sulphuric acid), and even ether which had been distilled over sodium and then purified by means of potassium permanganate in alkaline solution responded, the coloration being exceedingly faint, however. By adding less sulphuric acid to Francois' reagent, its sensitiveness may be exaggerated, even to the extent of becoming colored with pure ether, and this may account for the observations of Thoms. Increasing quantities of sulphuric acid cause this fault to disappear, and care should always be taken to ensure a sufficient amount being present. Anhydrous ether should give only a slight reaction with fuchsine sulphite, immediately upon adding the latter, and the coloration should not be considerably intensified after the mixture is allowed to stand fifteen minutes.

A test similar to the above, but inferior in delicacy, is the one proposed by Blaser,³ who found that a very weak solution of magenta (1 : 100,000) is bleached completely by exposure to sunlight, and that this solution gives very sharp reactions with aldehyde. It would appear that pure acetone will not affect the recoloration of magenta decolorized by sulphurous acid.⁴

The Aldehyde-Ammonia Test.—The test of Liebig⁵ was applied by Adrian⁶ to ether. The latter found that aldehyde-ammonia may be precipitated by passing a current of dry ammonia gas through the ether and may be filtered off. This test will serve for the detection and approximate estimation of quantities of aldehyde varying from 0.5 to 3.0 per cent., and upwards, but lacks the delicacy of the potassium hydroxide and fuchsine-sulphurous acid tests.

The Test with Alkaline Silver Nitrate Solution.—It is well known that aldehyde forms a mirror when heated with ammoniacal silver nitrate solution, and that this reaction affords a delicate test for the presence of aldehyde.⁷ Wobbe⁸ has suggested that aldehyde be tested for in ether as follows: 20 cc. of the ether are shaken with 5 cc. of alkaline silver nitrate solution (8 g. of silver nitrate dissolved in 20 g. of water, plus 30 g. of ammonia solution of specific gravity 0.923 and 10 g. of 30 per cent. sodium hydroxide solution), after which no mirror should form. When ether which had readily responded to the potassium hydroxide test was tested with Wobbe's reagent, a very slight and indefinite mir-

ror resulted on shaking; this was rendered distinct on immersing in boiling water.

The Test with Nessler's Reagent.—Although it has been stated that ether should be completely indifferent to Nessler's reagent, and notwithstanding the fact that this reagent is one of the best tests for the presence of aldehyde (and alcohol), it is impossible to obtain an ether which gives a totally negative reaction when this test is applied.¹ Modified, however, the test is convenient and suitable for the purpose; such a test is specified in the pharmacopoeias of Belgium and Holland. The former² directs that *aether pro narcosi* should not deposit "a red or black precipitate, although it may assume an opalescent yellow color, when 10 cc. are shaken with 2 cc. of Nessler's reagent," and the latter³ states that 5 cc. of ether should produce no reaction with 5 cc. of water and 3 drops of Nessler's reagent within fifteen minutes.

The German Pharmacopoeia now requires that when 10 cc. of anaesthetic ether ("narkoseäther") are agitated with 1 cc. of Nessler's reagent, there should result no coloring or darkening of the mixture, but at the most a faint white opalescence. A response is stated to be indicative of the presence of aldehyde or "vinyl alcohol."

We found that ether distilled over sodium and containing very slight traces (1 : 10,000) of acetaldehyde imparted an opalescent yellow color to Nessler's reagent after shaking, but no precipitate resulted at once; after the mixture had stood for fifteen minutes, however, it became darker and a small amount of a red precipitate settled out. In ethers containing larger amounts of acetaldehyde, a grayish black precipitate was produced immediately on shaking. We therefore think that the tests of the German, Belgian and Dutch Pharmacopoeias are unnecessarily rigid, and consider that it is sufficient to require that no black precipitate is produced, unless pure ether is wanted.

The Test with Meta-phenylenediamine Hydrochloride.—Schiff⁴ found that meta-phenylenediamine hydrochloride may be used as a reagent for aldehyde; Girard and Rocques⁵ devised a method for estimating the quantity of aldehyde in commercial alcohols by means of the salt; and Windisch⁶ studied its deportment with aldehyde in the presence of alkalis and acids.

Meta-phenylenediamine hydrochloride is very easily decomposed. A 1 : 20 water solution of this compound should be colorless and should not be exposed to the air. In preparing this reagent, only nitrite-free water must be used, although aldehyde-free alcohol may be employed instead of water. When such a solution of meta-phenylenediamine hydrochloride is shaken with ether containing 0.05 per cent. of acetaldehyde, a yellowish brown color is imparted to the solution. It serves, however, to detect even smaller

¹ *Chem. Ind.*, **19**, 141.

² *Ber. Pharm. Ges.*, **4**, 239. In this connection, see also Schönheimer, *Pharm. Centralh.*, **1894**, No. 26.

³ *Pharm. Centralh.*, **40**, 607.

⁴ Villiers and Payolle, *Bull. soc. chim.*, **12**, 691.

⁵ *Pharm. Centr.*, **6**, 639.

⁶ *Mon. Sci.*, **44**, 835.

⁷ Many other substances also give this reaction, so it is not reliable.

⁸ *Loc. cit.*

¹ Cf. Lassar-Cohn, *Ann.*, **284**, 266; *Rept. Chem.-Ztg.*, **1895**, 58. In this connection, see Crismer, *Deutsch Chem.-Ztg.*, **4**, 81; *Rept. Chem.-Ztg.*, **13**, 198.

² *Pharmacopoea Belgica*, **1906**, 15.

³ Concerning the requirements of the Ph. Ndl. IV. for *aether pro narcosi* see Weigl, *Pharm. Centralh.*, **47**, 397. Feist (*Apoth.-Ztg.*, **25**, 104) recommends agitating 5 cc. of ether with 1 cc. of Nessler's solution.

⁴ *Ann.*, **263**, 328.

⁵ *Compt. rend.*, **107**, 1158.

⁶ *Z. Spiritus-Industrie*, **9**, 619.

amounts, but is decisive only in the absence of peroxides.¹

Since meta-phenylenediamine hydrochloride appeared to be a delicate reagent for the detection of acetaldehyde, it seemed desirable to ascertain the deportment of its ortho- and para-isomers with ether containing acetaldehyde.

When ortho-phenylenediamine hydrochloride is shaken with ether containing considerable amounts of acetaldehyde, the compound becomes converted into a reddish brown oily separate and the ether becomes turbid. It was found, however, that the test may be most conveniently conducted by employing a water solution of the compound. When ether is shaken with a 1 : 20 water solution, the latter should not assume any color on agitating in an almost totally filled bottle. In the presence of acetaldehyde, a yellow to red-brown color is assumed by the solution, depending on the amount of acetaldehyde present. The presence of 0.06 per cent. acetaldehyde in ether may be thus easily detected, the solution of the compound assuming a marked yellow color. Peroxides, however, give a similar coloration, so their absence must be assured. We recommend, therefore, that this test be used only as a confirmatory one. To apply it, 25 cc. of the ether under examination are superimposed on 10 cc. of water and then 0.05 to 0.10 g. of ortho-phenylenediamine hydrochloride is added; the mixture is then shaken. No coloration should result within one or two minutes. The solution should not be exposed to the air or light.

Para-phenylenediamine hydrochloride is by no means so sensitive and reliable a reagent as the preceding. It is readily oxidized by the air, oxygen, and peroxides, and is not so delicate a reagent for acetaldehyde.

No attempt was made to determine the applicability of the other various tests for the detection of aldehydes in general² to the detection of acetaldehyde in ether, as those tried were of ample sensitiveness and sufficiently easy to apply.

VII. (b) THE PURIFICATION OF ETHER FROM ALDEHYDE.

A variety of methods have been devised for the removal of aldehyde from ether, but, as has been mentioned, it is exceedingly difficult to eliminate this impurity completely.

Treatment with potassium hydroxide or metallic sodium serves to remove not only water but also aldehyde, and an ether so treated contains mere traces of the latter impurity: Lassar-Cohn³ has found that ether may be most satisfactorily freed from alcohol and aldehyde, however, by boiling it with a reflux condenser for twenty-four hours with an alloy of potassium and sodium. This alloy is fluid at low temperatures, and is superior to metallic sodium in that it is

¹ In this connection, see Cazeneuve, *Bull. soc. chim.*, [3] 5, 855.

² These include the sodium nitroprusside test of von Bitto (*Ann.*, 267, 372), the phenol-sulphuric acid test of Barbet and Jaudier (*Ann. chim. anal. appl.*, 1896, 325), the various reagents proposed by Istrati (*Bull. soc. sciinte din Bucuresci*, 7, 163), the phenylhydrazine hydrochloride-sodium acetate test of Fischer (*Ber.*, 17, 572), and the phenylhydrazine oxalate test of Riegler (*Z. anal. Chem.*, 42, 168). For the most part, these were considered to be deficient in necessary delicacy and applicability.

³ *Ann.*, 284, 226.

not liable to become encrusted with a protective layer of hydroxide and resin.

Ekenberg¹ found that ether, pure enough for most analytical purposes, may be readily obtained from ordinary ether containing water, alcohol, and oxidation products by adding 5 to 10 per cent. by volume of liquid paraffin and then distilling between 40° and 50° C. The paraffin, the boiling point of which lies above 300° C., remains behind in the retort and retains the impurities. The method probably suffices to free ether from acids, peroxides, and badly-smelling substances, but it does not eliminate, by any means, aldehyde.

Adrian² found that distillation removes any acetic acid present in ether, and recommended that the aldehyde be precipitated by passing a current of dry ammonia gas through the ether, when aldehyde-ammonia separates out and may be filtered off. The ether is subsequently purified by treatment with sulphuric acid, which separates ammonium sulphate, and, after filtering off, the ether is distilled over potassium carbonate.

A well-known method of purification of ether from aldehyde is that based upon the action of potassium permanganate in alkaline solution on ether at 18.3° C. The ether is placed in a stoppered liter flask with 200 cc. of a saturated solution of potassium permanganate and 20 g. of sodium hydroxide. After twenty-four hours and frequent agitation, the ether is decanted off and again submitted to the same treatment. The filtered ether is then left for twenty-four hours in contact with a mixture of 50 g. of quicklime and 50 g. of fused calcium chloride, then filtered and distilled. Francois states that this method serves to completely eliminate aldehyde from ether, but we have found that ether so treated gives a faint coloration with the fuchsine-sulphurous acid reagent; there is also considerable loss of ether, no matter how much care is exercised.

Other methods for the removal of aldehyde from ether are the following:

(a) Precipitation with an alkaline mercuric chloride solution; (b) distillation over hydriodic acid; and (c) by means of phenylhydrazine.

The last method serves also to remove acetic acid and acetone.

VIII. (a) SCHEME FOR THE EXAMINATION OF ETHYL ETHER FOR ANALYTICAL AND ANAESTHETIC PURPOSES, WITH PARTICULAR REFERENCE TO THE DETECTION OF AVOIDABLE IMPURITIES.

1. *Specific Gravity*.—Determine the specific gravity by means of a pycnometer at 15° C. (See discussion under *specific gravity*.)

2. *Boiling Point*.—In the case of anaesthetic ether, at least 97 per cent. of the sample should distil over between 34° and 36° C. (at 760 mm.), and none of it should come over above 37°; after the fractionation to this temperature, no residue should remain in the fractionating vessel.

In the case of anhydrous ether, at least 99.50 per cent. should distil off between 34° and 36°, and none should come over above 36°.

3. *Organic Impurities*.—When 20 cc. of the sample are added

¹ *Chem.-Zig.*, 18, 1240.

² *Mon. Sci.*, 8, 835.

drop by drop to 20 cc. of pure concentrated sulphuric acid, which is kept cooled during the test, and which is contained in a glass-stoppered bottle previously rinsed with concentrated sulphuric acid, the resulting solution should be colorless. The sulphuric acid should be gently shaken after the addition of each drop of ether in order to ensure perfect solution.

4. *Odor*.—When 50 cc. of the sample are allowed to evaporate spontaneously on filter paper, 10 cm. in diameter, contained in a flat porcelain dish, the paper should be odorless after the evaporation of the ether. The latter should be added to the paper in portions in such a manner as to completely moisten it. In the case of a decided odor being imparted to the filter paper, the ether should be rejected, but for further information may be tested for such impurities as "heavy oil of wine," fusel oil, etc.

5. *Residue (Extractive Matter, Odor and Acidity)*.—(1) When 25 cc. of the sample are allowed to evaporate spontaneously in a clean, dry glass dish, the moist residue must possess no odor, and must neither redden nor bleach blue litmus paper; this residue must evaporate completely on a water-bath—that is, there should be no *fixed* residue.

(2) 100 cc. of the ether under examination are allowed to spontaneously evaporate in a flask until about 15 cc. remain in the vessel. This residue should be free from color and foreign odor, and should comply in full with the following tests: (a) When 5 cc. are allowed to evaporate at room temperature after the addition of 2 cc. of water, the residue should neither redden nor bleach sensitive light-blue litmus paper. (b) When another portion of 5 cc. is allowed to evaporate on a 9 cm. filter paper contained in a porcelain dish, there should be perceptible no foreign odor (amyl compounds, empyreumata, pungent matters, etc.) as the last portions disappear from the paper, and the latter should be left odorless. (c) On the addition of the remaining 5 cc. to 5 cc. of concentrated sulphuric acid, kept cool during the test and contained in a glass-stoppered tube previously rinsed with concentrated sulphuric acid, there should result no perceptible coloration. Anaesthetic ether should comply in full with these tests.

6. *Acidity*.—(1) When 25 cc. of the sample are allowed to evaporate at room temperature after the addition of 5 cc. of pure water the residue should neither redden nor bleach sensitive light blue litmus paper.

(2) When 20 cc. of pure ether are shaken with 10 cc. of pure water and 2 drops of phenolphthalein, the same depth of color should result on adding an equal amount of *N*/100 potassium hydroxide solution as in a test using pure water alone. In the case of ether intended for special analytical purposes, the addition of 0.3-0.5 cc. of *N*/100 potassium hydroxide should produce an alkaline reaction. When more than 1 cc. is required, the ether should be rejected for anaesthetic purposes.

7. *Water and Alcohol (Exclusion Tests for Pure and Anhydrous Ethers)*.—(1) (This test is superfluous, if the ether possesses a correct specific gravity.) A minute quantity of powdered fuchsin (rosaniline acetate), previously dried at 100° C., is placed in a dry test tube, 10 cc. of the ether are added, and the tube is corked and shaken well. In the case of pure and anhydrous ethers, no amethystine color—even faint—should result. If the coloration imparted to the ether is considerable, the approximate percentage of impurity is determined by Allen's method.¹

(2) When several milligrams of anthraquinone and the same amount of sodium amalgam are added to 10 cc. of the ether there should result no formation of red or green substances. The presence of both water and alcohol may be detected by this test.

8. *Water (Exclusion Tests for Pure and Anhydrous Ethers)*.—

¹ All colorimetric tests should be performed preferably with a colorimeter, having tubes with an internal diameter of 1.5 cm. But other forms of vessels may be used; for example, a ground glass stoppered Erlenmeyer flask, of suitable size for the amounts of liquid prescribed in the test, has been found to answer.

(1) On shaking 1 g. of anhydrous copper sulphate with 20 cc. of ether, the salt should not assume a green or blue color.

(2) In important or doubtful cases, the test with amalgamated aluminum may be used. If the ether contains no moisture and it responds to the tests under "Water and Alcohol," the presence of the latter may be really assumed, especially if the colors are marked.

9. *Water and Aldehyde (Exclusion Test for Pure and Anhydrous Ethers)*.—When 15 cc. of the sample are placed in a perfectly dry test tube and a piece of metallic sodium about 5 mm. in diameter is added, there should result only a slight evolution of gas and the sodium should not possess, after standing six hours, a white or yellow coating and the ether should not be colored or turbid. Only when the ether has been previously treated with sodium will the latter retain a distinct metallic luster at the expiration of the test; otherwise the metal becomes coated with sodium hydroxide. In the presence of aldehyde the sodium hydroxide is more or less colored.

10. *Acetaldehyde*.—(1) Apply the fuchsine-sulphurous acid test of François. Pure ether should not restore the color to fuchsine decolorized by sulphurous acid. The red-violet color should be *faint* in the case of anhydrous ether.

(2) On covering 5 g. of solid potassium hydroxide, in freshly broken pieces about 5 cm. in diameter, with 30 cc. of the sample, and allowing the mixture to stand for *six hours*, tightly closed and protected from the light, and occasionally shaking, the potassium hydroxide should not acquire a yellowish color, no yellowish or brown colored substance should separate, and the ether should not become turbid or assume any color. This is recommended as the exclusion test for anaesthetic ether. Pure or anhydrous ether should give no response after standing 24 hours.

(3) In the absence of alcohol, as indicated by the tests for water and alcohol, and confirmed by those given below, the following test may be applied for the detection of aldehyde: When 10 cc. of the sample are agitated with 2 cc. of Nessler's solution, a yellow color or black precipitate is indicative of the presence of aldehyde. Pure ether is indifferent towards this reagent, but it is impossible to purchase ether which does not show a yellow color within 15 minutes. For anhydrous or anaesthetic ether, it is sufficient to require, therefore, that no black precipitate settles out, although the mixture may assume an opalescent yellow color.

11. *Alcohol*.—The occurrence of alcohol may be ascertained as follows:

(1) In the presence of water, a portion of the sample is dried over anhydrous potassium carbonate and then tested, in 10 cc. portions, with (a) rosaniline acetate, and (b) anthraquinone-sodium amalgam.

(2) In the absence of other than mere traces of acetaldehyde, by Lieben's iodoform test.

(3) In the presence of acetaldehyde, by this method: The amount of aldehyde in 25 cc. is approximately determined colorimetrically by François' method. A portion of 25 cc. is then agitated with 25 cc. pure water in a ground glass-stoppered bottle, and the aqueous layer, which will show an increase in volume greater than 10 per cent. of the ether taken depending on the amount of alcohol present, is removed and freed from dissolved ether by careful warming at 40° C., until ether is expelled. The alcohol in the water is then oxidized by potassium dichromate and sulphuric acid, the aldehyde produced is distilled off, and the amount contained in the distillate is determined approximately colorimetrically. By comparison with the percentage of aldehyde found as originally existing in the ether, the amount of alcohol may be calculated; however, we do not recommend the method as an exact quantitative one, but only as one for arriving at the approximate amount of alcohol contained in ether, and as a confirmatory test.

12. *Peroxides (Exclusion Test for Ether of All Grades).*—When 2 cc. of a 10 per cent. cadmium potassium iodide solution are well shaken with 10 cc. of the sample, there should result no liberation of iodine within one hour. This may be easily determined by adding starch solution, although the yellow color which results in the presence of the merest traces of peroxides is easy to distinguish. The presence of peroxides may then be confirmed by any of the other tests devised by the authors, or by Jorissen's vanadic acid test.

VIII. (b) THE DEGREES OF PURITY OF AMERICAN ETHYL ETHERS USED FOR ANAESTHESIA.

The main impurities contained in American ethers are, beside alcohol and water, acetaldehyde and acids. As previously noted, the presence of small amounts of alcohol is permissible or may even appear necessary; but anaesthetic ethers should contain but mere traces of moisture, and, as has been indicated, it is desirable that they should be absolutely water-free. This would undoubtedly increase the cost of production; however, so long as ether is supplied in small tins of such a size that the contents are used completely at an operation or that not used, being small, may be discarded, and not stored, it is only necessary that the amount of moisture present be reduced to very small percentage.

Acetaldehyde is undoubtedly the commonest contaminant of anaesthetic ether, and its presence may account for some of the observations in practice usually attributed to idiosyncrasy. With regard to the acidity of the various anaesthetic ethers on the American market, it may be said that none of those we have examined contained acid in what may be termed injurious amounts.

The following table will serve to show the comparative purity of three samples of anaesthetic ether, purchased in the open market by an expert anaesthetizer and submitted to us, numbered, and without our knowing the name of the manufacturer:

Test.	D.	E.	F.
Sp. gr. at 25°.....	0.7162	0.7189	0.7161
Odor.....	No foreign odor	<i>Ibid.</i>	<i>Ibid.</i>
Ether distillate.....	98.50%	97.00%	97.50%
Distillate above 36°....	0.5%	2.00%	1.50%
"Organic impurities"....	None	<i>Ibid.</i>	<i>Ibid.</i>
Relative acidity in g. acetic acid in 100 cc.....	0.0006	0.00015	0.00165
U. S. P. litmus test....	Negative	<i>Ibid.</i>	<i>Ibid.</i>
Residue.....	None	<i>Ibid.</i>	<i>Ibid.</i>
Water.....	Present ¹	<i>Ibid.</i>	<i>Ibid.</i>
Alcohol.....	Present in permissible amount	Excessive	As in No. D
Relative total impurity (Allen's approximate method).....	5.00%	6.00%	5.50%
Peroxides.....	None	<i>Ibid.</i>	<i>Ibid.</i>
Aldehyde.....	Present in permissible amount	<i>Ibid.</i>	Excessive as compared to others

Since the authorization of two denaturant formulas for ether by the Commissioner of Internal Revenue,² we need no longer consider contamination from methyl

¹ In all three samples, the amount of water present was not excessive providing the ether would have been properly stored or at once consumed completely by the user. All the samples were properly canned. The samples of "D" examined possessed a relatively higher degree of uniformity than the samples "E" and "F."

² See Regulations No. 30, Supplement No. 1, United States Internal Revenue, and *Bulletin No. 130*, Bureau of Chemistry, 1910, 163.

alcohol oxidation products, and the general use in this country of special denatured spirit has rendered probable the production of high-grade anaesthetic ether. It only remains for the manufacturer to consider more carefully contamination from acetaldehyde.

It is encouraging to note that only a little over 1 per cent. of the ether consumed in the United States is imported¹ and that the American product is universally recognized as of high grade; however, not sufficient attention has been given to the storage of ether by the consumer, and until the latter cooperates with the manufacturer, fully and knowingly, the results obtained may continue to be variable, and rigid requirements on the part of the producer are useless. Ether freed from moisture and all but traces of aldehyde by means of sodium or other methods is not required in this country for anaesthetic purposes, and it is generally considered satisfactory if no "after-effects" are observed.

VIII. (c) VALUE OF CHEMICAL TESTS FOR ANAESTHETIC ETHYL ETHER.

The authors feel that the great lack of uniformity among the pharmacopoeias of the world need not obtain, especially where the analytical methods are involved. True, as Remington maintains, "The Pharmacopoeia is a book of standards for medicines, and not for analytical chemists," yet the methods of standardizing should be comprehensive, accurate, and reliable, as well as rapid and as simple as possible. It is unquestionably impossible for every pharmacist to determine the quality of his chemicals and drugs, but the druggist may easily apply simple tests to determine their purity, especially when these tests are decisive and simple; and he should, like the physician, be familiar with the changes which chemicals undergo when improperly stored, in order that he may not allow impurities to develop and may guard against their formation.

Leffmann has stated that tests may in all cases be improved and supplemented by the knowledge of the worker or by resorting to chemical or pharmaceutical literature. This is, as a rule, no doubt true for him who has the training, time and facilities at his disposal; but desirable and necessary literature is not available to all who at times deem it advisable to test their chemicals and drugs. The legal recognition of the Pharmacopoeia, especially that of our own country, renders it all important that inaccuracies be corrected, and improved and omitted methods be included, where necessary, so that these are available to those required to resort to an official work to assure themselves of the quality of the drugs they may use or dispense. The practical difficulty of putting forth frequent editions at short intervals of the entire Pharmacopoeia may be overcome by the issuance of annual supplements. What a step modern civilization would take if the leading nations decided to issue an international standard pharmacopoeia, revised in full each decennium, with annual supplements in the meantime!

¹ No consideration is taken of the ether consumed in the establishments where manufactured. About three-fourths of the ether produced in the United States is used by the manufacturers themselves.

In the case of ether for anaesthetic purposes, some pharmacopoeial tests are unnecessarily rigid; some are open to improvements; others should be replaced entirely by improved methods of detection; and several should be incorporated for detecting impurities not considered.

Furthermore, the demand for a good ether for anaesthesia involves difficulties inherent in the practical application of chemical methods by hospitals and physicians. As has been stated, anaesthetic ether should be provided in small containers, and it is impracticable, and should be unnecessary, to test the contents of each container before use; hence, reliance, as is the common practice now, must be placed on the experience and integrity of the manufacturer and on the uniformity of his product, for we have found that some ethers of the market vary not only in specific gravity and absolute ether content, but also in impurities, from time to time, yet they may comply with the requirements of the Pharmacopoeia.

Finally, in regard to anaesthetics in general, there is no doubt that, though even the most improved chemical and physical tests may be stated ever so clearly in print, and may properly serve to eliminate low-grade material, yet clinical experience must have the final word.

COLLEGE OF THE CITY OF NEW YORK,
1910.

THE ESTIMATION OF LIME AND POTASH IN THE ASH OF CEREALS.

By FIRMAN THOMPSON AND H. H. MORGAN, JR.
Received January 25, 1911.

In the course of some experimental work with cereals being carried on at this station the analysis of a large number of samples of the ash of corn and wheat grains was found to be necessary. During the prosecution of this work it was found that the A. O. A. C. methods, as given in *Bull. 107* of the Bureau of Chemistry, left much to be desired with respect to accuracy as well as rapidity of execution. Our efforts were then directed to removing these defects by modifications of these or other existing methods with a view to increasing the speed while not sacrificing any of the accuracy of the standard methods. We have met with such success in the estimation of potash and lime that we are prompted to publish them at this time, and while not claiming originality for the basic principle involved, we believe that our modifications are very vital to their rapid and accurate execution and trust that they may receive a thorough testing in laboratories other than our own.

CALCIUM OXIDE.

In the A. O. A. C. method for the determination of CaO in plant ash it is necessary to add sufficient FeCl_3 to combine with all of the P_2O_5 present, and the combined phosphates of iron and aluminum are then removed by precipitation with ammonia or an alkali acetate. The ash of cereal grains consists in great part of potassium phosphate, the P_2O_5 amounting to from 40 to 50 per cent. and the K_2O to about 30 per

cent. while the CaO is comparatively low. It is quite obvious that a sample containing sufficient CaO for accurate determination would require a large amount of FeCl_3 to combine with all of the P_2O_5 . In an ash containing 40 per cent. P_2O_5 and 2 per cent. CaO, which is about the average for wheat grains, the amount of iron required to combine with the P_2O_5 would be about fifteen times the amount of CaO and the resultant precipitate of ferric phosphate would amount to about forty times the amount of CaO present. Granting that none of the CaO would combine with the P_2O_5 , under such conditions the danger of mechanical loss by absorption is quite apparent to say nothing of the inconvenience of handling such a large precipitate and filtrate. That this danger is a very real one has been the experience of every chemist in this laboratory who has used the method, the results being uniformly low even after repeated re-resolution and reprecipitation, as some of the following figures will show.

In devising a method for the determination of CaO which would be free from these objections, advantage was taken of the fact that calcium and magnesium phosphates are very easily soluble in dilute acetic acid while the phosphates of iron and aluminum are quite insoluble.

Method.—50 cc. of the hydrochloric acid solution of the ash, corresponding to 0.500 g., are heated to boiling, made slightly ammoniacal and then acidified again with acetic acid, adding about 10 cc. of 50 per cent. acetic acid in excess, making the total volume not more than 75 cc. The precipitate is boiled for a few minutes, allowed to settle and the combined phosphates of iron and aluminum filtered off and washed thoroughly with hot water. Since this precipitate is usually very small a reprecipitation has not been found necessary. About 10 cc. of saturated ammonium oxalate solution are added to the filtrate while still hot and the CaO determined in the usual way, either by ignition or titration with permanganate.

In order to test the method, known amounts of calcium carbonate and calcium phosphate and potash alum were dissolved and the CaO determined in the solution according to the above method with the following results:

CaO present.	CaO found.
Gram.	Gram.
0.13475	0.1353
0.13517	0.1348
	0.1345

When large amounts of Al_2O_3 are present a reprecipitation of the AlPO_4 will be necessary as is shown by the analysis of a solution containing 0.0273 g. Al_2O_3 and CaO in the form of chloride and phosphate.

CaO present.	CaO found with one precipitation of AlPO_4 .	CaO found with reprecipitation of AlPO_4 .
Gram.	Gram.	Gram.
0.1460	0.1383	0.1462
0.1460	0.1329	0.1462

A comparison of the percentages of CaO found in a number of samples of the ash of wheat grains by the two methods is shown in the following table:

FeCl ₃ method.	Acetic acid method.
1.55	2.27
1.24	2.43
1.34	2.43
1.33	2.56
1.03	2.43
0.93	2.68
0.83	2.76
1.14	2.96
0.72	2.88
0.62	2.43
0.83	2.47
0.72	2.27

It will be noted that while the results are considerably higher by the acetic acid method they also show a greater uniformity, as might be expected with samples of such similar origin.

It should also be stated here that, although aluminum is commonly supposed to be a comparatively rare constituent of plant ash; we have found a quite appreciable amount in every sample of ash of wheat straw and grains examined by this method. A more complete account of its occurrence will be given later.

POTASSIUM OXIDE.

As is well known the standard method for the determination of K₂O, although quite accurate, is a very long and tedious one, involving as it does the removal of all other bases with the exception of sodium and also requiring, where a large number of determinations are to be made, a large stock of platinum chloride. For these reasons a shorter, more inexpensive method is very much to be desired and our attention was directed to the cobaltinitrite method of Adie and Wood¹ as possibly overcoming the faults mentioned. In working with this method it was found that the best results were secured by allowing the precipitate of potassium cobaltinitrite to crystallize out from the cold acetic acid solution by standing for at least twelve hours, decomposing the precipitate with an alkali, filtering off the cobaltic hydroxide thus formed, cooling the solution and titrating with acidified permanganate. A serious difficulty was met with in the fact that in using a fixed alkali for the decomposition it was almost impossible to effect a complete precipitation of the cobalt, which presumably passed the filter as soluble double salts. As the presence of any cobalt would vitiate the titration with permanganate, it seemed necessary that some other means for the decomposition of the cobaltinitrite should be found. Since the alkaline earths do not have the same tendency to form double salts with cobalt, a saturated solution of Ba(OH)₂ was substituted for the NaOH, and it was found that the precipitation was very complete and the barium sulphate formed in the subsequent treatment interfered in no way with a sharp end reaction. It was also found advisable to titrate by allowing the alkaline solution of the nitrite to run into the hot, acidified, standard permanganate. While this procedure has the disadvantage that the end point must be judged by the disappearance of the color, this is more than compensated for by the elimination of danger of loss of nitrous acid. With a little practice it has been found that it is quite easy to determine the end within one or two drops.

Method.—The hydrochloric acid solution of 0.500 g. of ash is neutralized with NaOH and acidified again with acetic acid, adding 10 cc. of 50 per cent. acetic acid in excess. The solution is boiled and the precipitate of iron and aluminum phosphates filtered off and washed thoroughly with hot water. The filtrate is concentrated to about 75 cc. and allowed to cool. 25 cc. of cobaltinitrite solution, made according to the method of Adie and Wood, given below, are now added. Allow to stand over night at the room temperature and filter on an asbestos felt in a Gooch crucible, washing several times with cold, 10 per cent. acetic acid and finally once with cold water. The asbestos and precipitate are transferred with water to a small beaker, 40 cc. of a saturated Ba(OH)₂ solution added and heated to boiling when a copious precipitate of cobaltic hydroxide will be formed. Allow the precipitate to settle and while still hot filter into a 200 cc. graduated flask, washing thoroughly with hot water. Cool and make up to 200 cc.

Measure off 25 cc. of standard permanganate solution into a casserole, add 5 cc. of 1 : 1 H₂SO₄ and 150 cc. of hot water and run in the alkaline nitrite solution slowly from a burette until the color disappears.

On the basis of the formula K₂NaCo(NO₂)₆·H₂O, 1 cc. of tenth-normal permanganate is equivalent to 0.000785 g. K₂O. It has, however, been found to be more convenient to use a permanganate solution of such strength that 1 cc. is equivalent to 1 milligram of K₂O, which would be 0.1274 normal.

Sodium Cobaltinitrite Solution.—113 grams of cobalt acetate are dissolved in 400 cc. of 20 per cent. acetic acid. 220 grams of sodium nitrite are dissolved in 400 cc. of water. The two solutions are mixed, allowed to stand at the ordinary temperature for 24 hours, removing the nitric oxide formed by evacuation with a filter pump, and then filtered.

In order to test the method a stock solution was made by dissolving chemically pure K₂CO₃, MgSO₄ and Ca₃(PO₄)₂ in HCl and determining the K₂O by the platinum chloride method. 20 cc. of this solution gave the following amounts of K₂O in grams:

Calculated from K ₂ CO ₃ taken.	Found by platinum chloride method.
0.19856	0.1990
0.19856	0.1984

In testing the method 20 cc. of the stock solution were precipitated and the precipitate decomposed with 20 cc. of saturated Ba(OH)₂ solution, the filtrate made up to 250 cc. and 20 cc. taken for analysis. The titration was made by adding the permanganate from a burette after first making a preliminary titration to ascertain the approximate amount of permanganate required. This feature has been improved upon in the final procedure adopted. The following results were obtained:

K ₂ O present. Gram.	Tenth-normal KMnO ₄ , cc.	K ₂ O found. Gram.
0.015896	20.1	0.01578
0.015896	20.2	0.01586
0.015896	20.2	0.01586
0.015896	20.1	0.01578

Another determination was made using exactly the

¹ *Jour. Chem. Soc.*, 77, 1076-80 (1900).

same method but with 30 cc. of Ba(OH)₂ solution to determine the effect of an excess of alkali, with the following results:

K ₂ O present. Gram.	Tenth-normal KMnO ₄ , cc.	K ₂ O found. Gram.
0.015896	20.1	0.01578
0.015896	20.1	0.01578

The effect of different amounts of NaOH used for the decomposition of the cobaltinitrite precipitate is shown by the following results. The method used was exactly the same as before, but 50 cc. of the alkaline nitrite solution were used for the titration.

With 25 cc. of five per cent. NaOH.		
K ₂ O present. Gram.	Tenth-normal KMnO ₄ , cc.	K ₂ O found. Gram.
0.03974	41.6	0.03266
0.03974	41.8	0.03281
0.03974	41.8	0.03281
With 50 cc. of five per cent. NaOH.		
0.03974	48.4	0.03799
0.03974	48.4	0.03799
0.03974	48.4	0.03799
With 75 cc. of five per cent. NaOH.		
0.03974	52.8	0.04145
0.03974	52.9	0.04153
0.03974	52.9	0.04153

With still larger amounts of NaOH the cobalt was taken into solution to such an extent that the blue color was quite perceptible in the filtrate and no determinations were made. It is quite evident from the above results that NaOH is very unsuitable as a precipitant of the cobalt and its use was therefore abandoned.

In order to determine the ratio of N₂O₃ to K₂O in the cobaltinitrite precipitate a solution of 0.500 g. of K₂CO₃ in HCl was precipitated as before and the precipitate decomposed with Ba(OH)₂. The filtrate was made up to 200 cc. and N₂O₃ and K₂O determined in 25 cc. portions by titration with tenth-normal permanganate and precipitation with platonic chloride with the following results:

K ₂ O in original solution.	N ₂ O ₃ found.	Ratio found.	Ratio theor.
0.04189	0.04285	0.1027	0.4173
			0.4130

AGRICULTURAL EXPERIMENT STATION,
DELAWARE COLLEGE.

TREATMENT OF CREAMERY SEWAGE BY THE SEPTIC TANK PROCESS.¹

By JAMES TEN BROECK BOWLES.²

Received January 20, 1911.

In the manufacture of butter and cheese there is a comparatively large amount of waste product, part of which can be returned to the farmer for stock-feeding, but a considerable amount cannot be so disposed of, and it is liable to create a nuisance when discharged into a stream or run upon land. That such a nuisance is created is shown by the following court decisions:

"The deposit of refuse from a creamery into the bed of a stream flowing through plaintiff's land and

¹ This research work was carried on while Chemist of Wisconsin State Hygienic Laboratory, University of Wisconsin.

² Sanitary Chemist, Cristobal, Canal Zone.

near his buildings, polluting the water and giving off noxious gases affecting the use and enjoyment of the plaintiff's property, is a nuisance."

"A creamery company will be enjoined from causing offensive waste matter to flow upon another's pasture to its injury." (Price vs. Oakfield Highland Creamery Co., 87 Wis., 536.)

The question of how creamery waste can be disposed of so as not to create a nuisance is therefore one of considerable importance, and although some work has been done on this subject in Europe and America the best method of treating such waste is a problem that still remains to be solved, and the following investigation was undertaken in the hope of throwing a little more light upon the subject.

Composition of Creamery Wastes.—Creamery waste consists of, pieces of cheese, butter, skim milk, whey, buttermilk, etc., diluted by washing from the floor, churns and pasteurizers. This mixture was found to be full of acid-producing bacteria which give the medium more or less acid reaction at first. After decomposition sets in and fermentation and putrefaction are well started, the medium gradually changes to a neutral rather than an acid one. It is plain to see that one is dealing with an undigested product, putrefaction not having yet started. In municipal sewage we have what is called a predigested product, that is, when the waste leaves the body it is full of putrefying bacteria, putrefaction and fermentation having already started. Thus when municipal sewage enters the septic tank decomposition has already set in and liquefaction goes on rapidly, while with creamery waste a long time elapses before putrefaction has even started.

The flow of creamery waste is not constant and for that reason is difficult to manage. In the mornings a large amount is received soon after churning, towards noon another large amount is received consisting largely of water used in cleaning up the floor where milk and cream are spilt. In the afternoon buttermilk and skim milk and washings are often turned into the tank.

Most of the cooling water has been cut off from the septic tank as the water is clean and there is no need of it going through the tank.

TABLE I.—CHEMICAL COMPOSITION OF CREAMERY SEWAGE FROM UNIVERSITY DAIRY AS COMPARED WITH OTHER CREAMERIES AND WITH MUNICIPAL SEWAGE.

	PARTS PER MILLION.			
	University dairy.	Elkhorn creamery.	Garnet creamery.	Madison City sewage.
Free ammonia.....	26.98	32.2	47.0	39.25
Alb. ammonia.....	38.55	43.8	105.5	6.0
Nitrates.....	0.0	0.0	0.0	0.0
Nitrites.....	0.0	0.0	0.0	0.0
Total solids.....	1702.8	2121.5	7575.0	896.4
Loss on ignition.....	169.3	1200.0	2216.0	201.0
Oxygen cons.....	396.2	311.6	261.0	79.6
Suspended matter.....	134.16	521.0	668.0	130.0
Putrescibility.....	7.9 hrs.	6 hrs.	4 hrs.	1/2 day

The free ammonia figures of the creamery sewage do not vary a great deal from those of the municipal sewage. The University Dairy sewage figures are much lower than those of the other creameries.

In the albuminoid ammonia the University Dairy is still lower than the other creameries, but all of the creamery sewage is much higher in albuminoid ammonia than the municipal sewage.

The total solids and loss on ignition are much lower in the University Dairy sewage than in the other creameries, but are higher than in the municipal sewage.

The oxygen consumed figures, as well as the sus-

As noted in the description of the plant, the tank holds a day's flow and the dosing chambers hold about one-sixth of the amount of the tank. The tank would hold a little more if the dosing chambers were closed; thus, by dosing the tank six times per day, the sewage would remain one day in the tank. In Table III can be seen the results.

In comparing the total solids, nitrogen figures, oxygen consumed and putrescibility, it is found

TABLE II.—THE VARIABILITY OF CREAMERY SEWAGE AT UNIVERSITY DAIRY.

	PARTS PER MILLION.							Average
	17.	20.	22.	24.	26.	27.		
July, 1907.								
Free ammonia.....	34.4	25.0	26.0	29.0	24.3	23.2	26.98	
Alb. ammonia.....	43.6	45.5	41.2	38.0	32.0	31.0	38.55	
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total solids.....	3494.0	1208.0	1106.0	2201.0	1206.0	1202.0	1702.8	
Loss on ignition.....	300.0	121.0	132.0	200.0	141.0	120.0	169.3	
Oxygen consumed.....	227.2	600.0	425.0	465.0	410.0	250.0	396.2	
Suspended matter.....	139.0	140.0	138.0	142.0	125.0	121.0	134.16	
Putrescibility.....	8 hrs.	8.5 hrs.	8 hrs.	7.5 hrs.	6.5 hrs.	8.5 hrs.	7.9 hrs.	

ended matter, are higher than in the municipal sewage.

All of the creamery sewages are more putrescible than the municipal sewage.

From this comparison it can be seen that creamery sewage is much higher in organic matter than municipal waste. The University Dairy sewage does not seem to be as concentrated a sewage as the other creameries' sewage.

In looking over Table II, one cannot find two sets of data that are very near alike. Creamery sewage is very hard to treat because it sometimes comes at

that the tank is not doing more than fifteen, to sixteen per cent. purification. The effluent from the septic tank is much less putrescible than the raw sewage. When this effluent is turned out upon the beds a further purification is obtained in Table IV.

In dosing the septic tank three times per day it gives an improvement over that of dosing six times per day. This improvement is very slight and is noticed more in the putrescibility test than in any other place. The next greatest change is in the total solids and loss on ignition.

There seems to be a greater improvement in the

TABLE III.—COMPOSITION OF RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS EMPTIED SIX TIMES PER DAY.

	Raw sewage.							Effluent from septic tank.						
	17.	20.	22.	24.	26.	27.	Aver.	17.	20.	22.	24.	26.	27.	Aver.
July.														
Free ammonia.....	34.4	25.0	26.0	29.0	24.3	23.2	26.9	10.0	12.0	11.0	13.5	10.0	12.6	11.6
Alb. ammonia.....	43.6	45.5	41.2	38.0	32.0	31.0	38.5	15.6	35.0	20.5	36.0	18.9	33.0	26.5
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	3494.0	1208.0	1106.0	2201.0	1206.0	1002.0	1702.0	1090.0	1850.0	1764.0	1541.0	1691.0	1521.0	1726.1
Loss on ignition.....	300.0	123.0	132.0	200.0	141.0	120.0	169.3	164.0	168.0	171.0	159.0	162.5	161.0	164.2
Oxygen consumed.....	227.2	600.0	425.0	465.0	410.0	250.2	396.2	137.0	140.0	135.0	143.0	130.0	128.0	135.8
Susp. matter.....	139.0	140.0	138.0	142.0	125.0	121.0	134.0	85.0	96.0	100.0	106.0	110.0	108.0	100.1
Putrescibility.....	8 hrs.	8.5 hrs.	8 hrs.	7 hrs.	6.5 hrs.	8.5 hrs.	7.9 hrs.	1/2 day	1/2 day	1 day	13 hrs.	12 hrs.	15 hrs.	13 hrs.

one time very dilute, then again very concentrated. In some instances the total figures are three or four times as great as in others.

The creamery sewage does not contain any nitrites or nitrates. In using the septic tank, the important

effluents from the sand beds than there is in the effluents from the septic tank. In the effluents from the sand bed the albuminoid ammonia has decreased and a trace of nitrites is found, showing that nitrification is going on.

TABLE IV.—COMPOSITION OF RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS BEING EMPTIED THREE TIMES PER DAY.

	Raw sewage.						Effluent from septic tank.					
	1.	8.	10.	12.	14.	Average.	1.	8.	10.	12.	14.	Average.
Free ammonia.....	20.0	27.0	21.0	8.5	13.0	16.9	30.0	28.0	32.0	32.0	27.0	29.8
Alb. ammonia.....	38.2	32.4	35.0	43.0	50.0	39.7	18.5	19.6	40.0	19.5	51.0	29.7
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	1580.0	1468.0	1562.0	1660.0	2500.0	1754.0	1420.0	1310.0	1222.0	1460.0	1211.0	1324.6
Loss on ignition.....	740.0	692.0	685.0	700.0	570.0	677.4	150.0	148.0	152.0	150.0	160.0	150.0
Oxygen consumed.....	306.2	310.5	290.1	227.2	147.2	256.2	138.5	129.2	132.4	138.5	128.5	133.4
Suspended matter.....	128.0	130.0	125.0	180.0	130.2	101.5	128.0	126.0	100.0	120.0
Putrescibility.....	6 hrs.	5.5 hrs.	6 hrs.	7 hrs.	5 hrs.	5.9 hrs.	18 hrs.	17 hrs.	18 hrs.	18 hrs.	17 hrs.	17.6 hrs.

point to be considered is how long a time it is necessary for the sewage to remain in the tank in order to have it sufficiently decomposed.

In Table V, dosing tank twice per day, obtains an improvement over dosing three times per day. First, there is a decrease of albuminoid ammonia and an

increase of free ammonia figures, which shows that the organic compounds are breaking up and passing off as free ammonia and that less organic substances remain to break up and pass off as albuminoid ammonia.

The putrescibility point was higher in the last table than it was in the former, but the effluent is not yet good enough, and further investigation must be made.

In Table VI the septic tank has been dosed once per day and a great improvement is noticed. In this table the ammonia content is lower and the albuminoid ammonia figures are about half as high as formerly.

TABLE V.—RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS BEING EMPTIED TWICE PER DAY.

August.	PARTS PER MILLION.				PARTS PER MILLION.			
	Raw sewage.				Effluent from septic tank.			
	16.	19.	23.	Aver.	16.	19.	23.	Aver.
Free ammonia.....	30.0	17.0	19.7	22.23	46.5	50.6	48.6	46.5
Alb. ammonia.....	47.5	56.0	62.0	55.1	26.25	29.2	30.1	28.85
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	2580.0	3080.0	2890.0	2850.0	1430.0	1260.1	1360.2	...
Loss on ignition.....	570.0	1050.0	986.4	868.8	370.0	180.6	182.9	...
Oxygen consumed.....	147.2	390.0	416.0	317.7	239.2	182.9	179.3	...
Putrescibility.....	5 hrs.	4.5 hrs.	5 hrs.	4.8 hrs.	1 day	1 day	1 day	1 day

There are traces of nitrites and quite a little of nitrates. The total solids are lower and the putrescibility point a great deal higher. There is at least a reduction of sixty per cent. of solid matter. Taking the albuminoid ammonia figures, there is at least a reduction of two-thirds in organic matter; with respect to oxygen consumed figures there is a reduction of two-thirds in organic matter which is able to be oxidized.

effluents, dosing at periods from six times a day to once per week.

There is shown a gradual increase of free ammonia and a decrease of albuminoid ammonia. This is caused by the bacterial action upon the organic matter, the longer the sewage remains, the less albuminoid ammonia there is since it goes off as free ammonia after being decomposed. There is also an increase in the nitrites and nitrates, commencing with none at first. As to the solids, there is not much change until the dosing of the tank once per day is reached, then there is a general decrease. The same is true of the oxygen consumed figures. In the putrescibility test

there is not much difference between dosing once per day and dosing once every two and one-half days. The end point seems to be reached when dosing once per day. There is not enough change after that to pay to let it remain longer.

CONCLUSION.

From the study of creamery sewage disposal the

TABLE VI.—RAW SEWAGE AND EFFLUENT FROM THE SEPTIC TANK, WHEN THE TANK IS BEING EMPTIED ONCE PER DAY.

	PARTS PER MILLION.									
	Raw sewage.									
	Aug. 20.	Aug. 28.	Sept. 2.	Sept. 16.	Oct. 30.	Nov. 25.	Dec. 10.	Jan. 10.	March 10.	
Free ammonia.....	19.7	13.0	10.4	25.0	15.0	20.0	15.0	12.0	10.0	
Alb. ammonia.....	62.0	50.0	53.1	45.5	25.1	30.0	30.0	30.0	28.5	
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total solids.....	2350.0	1666.0	1492.0	1202.0	1356.0	1000.0	1521.0	1421.0	1132.0	
Loss on ignition.....	1002.0	700.0	739.1	223.0	434.0	625.0	721.0	521.0	3334.0	
Oxygen consumed.....	451.2	227.2	245.0	340.0	292.0	248.5	361.0	282.0	195.0	
Suspended matter.....	
Putrescibility.....	5 hrs.	7 hrs.	7 hrs.	7.5 hrs.	6 hrs.	8 hrs.	9 hrs.	8.5 hrs.	6.5 hrs.	

	PARTS PER MILLION.									
	Effluent from septic tank.									
	Av.	Aug. 20.	Aug. 28.	Sept. 2.	Sept. 5.	Oct. 30.	Nov. 25.	Jan. 10.	Feb. 22.	Aver.
Free ammonia.....	15.5	36.2	35.4	43.0	40.3	60.0	50.4	40.2	36.0	42.6
Alb. ammonia.....	39.9	12.9	13.75	12.0	12.8	8.25	12.4	12.5	20.4	13.12
Nitrites.....	0.0	trace	trace	0.2	0.1	trace	0.05	0.09	trace
Nitrates.....	0.0	trace	0.5	0.09	0.10	0.60	0.7	1.0	0.895	0.385
Total solids.....	1482.2	1106.4	1008.5	980.2	890.0	984.0	865.0	721.0	628.0	897.98
Loss on ignition.....	588.78	149.3	152.4	102.0	99.0	105.0	141.0	102.0	110.0	120.08
Oxygen consumed.....	293.5	102.4	108.3	80.0	78.0	80.0	85.3	95.0	79.6	88.57
Suspended matter.....
Putrescibility.....	7.1 hrs.	1 day	1 day	1.5 days	1 day	1.25 day	1.25 day	1.5 day	1.5 day	1.25 days

Then with the nitrites and nitrates appearing, it is safe to say that with respect to the above figures, the tank will average sixty-five per cent. in reduction of organic matter when dosing once per day. The effluent has a putrescibility test of one and a half to two days when incubated at 37.5° C., which signifies a good effluent.

Table VII takes up the comparisons of the septic

following conclusions are obtained:

1. It has been shown that the septic tank, when the sewage remains in it six days, will liquefy and decompose the solid particles in the creamery sewage.
2. By allowing the sewage to remain in the tank six days gives a reduction of sixty to sixty-five per cent. of the organic matter.

3. This sewage must remain in the tank much longer than municipal sewage. There are many lactic acid organisms at work which keep the putrefactive organisms from growing. Just as soon as the lactic acid organisms have acted upon all the sugar these organisms will not be as active as formerly, and putrefactive bacteria will commence to grow.

4. When the sewage is allowed to remain in the tank six days, a stable effluent is obtained with no putrid odor.

5. If a creamery was so situated that it would be impossible to turn the effluent into a stream, then the effluent would have to be run on to a pasture or field near-by, or on to gravel beds. Care must be used in turning the effluent on to gravel beds as there is some

was shipped several hundred miles, some of it having been purchased in the open market, and irregularities in composition, as pointed out by them, may in part be due to differences in degree of ripeness at the time of gathering.

In 1904 Hume and Miller¹ published the results of a study of a number of varieties of pineapples grown in Florida, including several of the same varieties used by Munson and Tolman, and concluded from their studies that the acid content and total sugars in different varieties vary between wide extremes. These authors state that pineapples which ripen during the winter months contain less sugars than when ripening in summer; also, that usually the acidity varies inversely with the total sugars. Recently, Blair and

TABLE VII.—COMPARISON OF SEPTIC EFFLUENTS, DOSING FROM SIX TIMES PER DAY TO ONCE PER WEEK.
PARTS PER MILLION.

Dosing.	6 times per day.	3 times per day.	Twice per day.	Once per day.	Once every 2 1/2 days.	Once per week.
Free ammonia.....	11.6	29.8	48.6	42.6	58.1	75.6
Alb. ammonia.....	26.5	29.7	30.1	13.12	1.5	1.25
Nitrites.....	0.0	0.0	0.0	1.0	2.0
Nitrates.....	0.0	0.0	0.0	0.385	0.0	0.0
Total solids.....	1726.1	1324.6	1360.2	897.98	325.0	195.0
Loss on ignition.....	164.2	150.0	182.9	120.08	115.0	85.0
Oxygen cons.....	135.8	133.4	179.3	88.57	18.0	17.0
Suspended matter.....	100.1
Putrescibility.....	13 hrs.	17.6 hrs.	1 day	1.80 day	2 days	3 days

liability of contaminating the creamery well water with the sewage. This has happened at Elkhorn, Wisconsin.

6. When a creamery has only a small septic tank, then filter beds should be used to further purify the effluent.

7. Cleaning of the septic tank and filter beds will depend upon the amount of flow, and should be attended to whenever the effluent deteriorates.

8. The results of this study answer the purpose of the investigation and show, first, the septic tank will dispose of creamery waste; second, it is a cheap method; third, it is applicable to both large and small creameries.

Wilson² made an extensive investigation of the composition of pineapples as affected by the use of fertilizers.

The pineapple soils of Hawaii³ have been derived from the disintegration of basaltic lava, and as regards both chemical and physical properties, are very unlike soils elsewhere that are devoted to pineapple culture. A study of the composition of pineapples from these soils is, therefore, not without interest. In addition, the chemical changes taking place during the process of development and ripening have also been investigated. The Smooth Cayenne is practically the only pineapple cultivated in these islands and hence the discussion in this paper relates to this variety only. In nearly every instance the pineapples were gathered by the writer, and were selected with special reference to securing representative fruit of uniform ripeness. Generally, except as otherwise noted, the analyses were made on the following day.

The methods employed in this work are essentially those given under the Official Methods for the Analysis of Fruits and Fruit Products.⁴ The solids in the juice were calculated from the specific gravity by use of the tables of H. Ellion, nitrogen was determined by the ordinary Kjeldahl method, reducing sugars by the volumetric Fehling solution method and sucrose by double polarization, the cane sugar being calculated from the formula $S = \frac{100(P - I)}{142.66 - \frac{T}{2}}$. The total sugars

as invert were determined by digesting for two hours at the temperature of boiling water, 20 grams of the fruit in 200 cc. dilute hydrochloric acid, neutralizing, filtering and then determining the reducing power

¹ Florida Sta., *Bull.* 70, 59-61.

² *Ibid.*, 101.

³ THIS JOURNAL, 1, 533-8 (1909).

⁴ U. S. Dept. Agric., *Bur. Chem.*, *Bull.* 107, 77-82 (revised).

[CONTRIBUTION FROM THE LABORATORY OF THE HAWAII EXPERIMENT STATION, PAPER NO. 3.]

A STUDY OF THE COMPOSITION OF HAWAIIAN PINEAPPLES.

By W. P. KELLEY.

Received December 9, 1910.

In 1903 Munson and Tolman¹ concluded, from an extensive investigation of pineapples from Florida, Cuba, Porto Rico, Bahama and Singapore, that neither the variety nor the latitude in which the fruit was grown exercised any influence on its composition. The ratio of reducing sugars to sucrose in a given variety, however, was found to vary greatly. One pineapple of the Smooth Cayenne variety, for instance, was found to contain 3.17 per cent. reducing sugars and 7.51 per cent. sucrose, while another of the same variety contained 9.75 per cent. reducing sugars and only 2.98 per cent. sucrose. Some pineapples were also reported which contained abnormally small percentages of sugars. The fruit used by these authors

¹ *J. Am. Chem. Soc.*, 35, 272-80; U. S. Dept. Agric., *Bur. Chem.*, *Bull.* 87.

of the filtrate by use of Fehling's solution. The acidity was determined by direct titration with $N/10$ KOH with the aid of phenolphthalein, and the results expressed as sulphuric acid. The chief acid of pineapples is citric but is here expressed as sulphuric.

Table I contains the results of the analyses of pineapples that thoroughly ripened in the field. These pineapples were taken from several districts in the

TABLE I.—THE COMPOSITION OF NORMALLY RIPENED PINEAPPLES.

Serial No.	Nitrogen. Per cent.	Acidity as H_2SO_4 . Per cent.	Sugars.			Polarization		
			Reducing. Per cent.	Sucrose. Per cent.	Total. Per cent.	Direct.	Invert.	Temperature °C.
101	..	0.56	3.94	7.97	11.91	6.4	-3.7	32.0
102	..	0.53	3.84	8.36	12.20	6.9	-3.7	31.5
103 ¹	..	0.31	5.14	4.01	9.15	2.3	-2.8	31.0
104 ¹	0.06	0.22	6.20	3.63	9.83	2.0	-2.6	32.3
105	0.09	0.43	5.10	7.54	12.64	5.8	-3.8	30.5
106	0.08	1.05	3.86	9.45	13.31	7.7	-4.3	31.4
107	0.09	1.16	4.18	8.40	12.58	7.1	-3.6	30.8
108	0.08	0.63	2.78	7.36	10.14	5.4	-4.0	30.0
109	0.09	0.75	3.56	8.12	11.68	6.3	-4.0	31.7
110	0.09	1.03	4.72	9.88	14.60	7.4	-5.1	32.3
111	0.07	0.86	5.18	10.05	15.23	8.0	-4.7	32.7
112	..	0.99	4.59	10.12	14.71	8.4	-4.4	32.3
113	..	1.06	3.50	8.47	11.97	6.6	-4.2	30.3
114	0.09	0.71	4.12	6.93	11.05	4.9	-3.9	31.4
115	0.07	0.82	3.14	7.15	10.29	5.3	-3.8	31.0
123	..	0.42	4.54	7.41	11.95	5.0	-4.5	29.2
140	..	0.45	4.35	6.08	10.43	4.2	-3.5	32.0
141	..	0.68	4.00	6.97	10.97	4.9	-4.0	30.0
142	..	0.63	4.87	6.47	11.34	3.9	-4.3	30.2
143	..	0.65	4.85	6.85	11.70	4.6	-4.2	28.6
144	..	0.61	5.55	6.03	11.58	4.0	-3.7	30.0
Av.	0.08	0.74	4.23	7.88	12.11			

islands, from soils of vastly different composition and growing under a wide range of rainfall. While not noted in the table a careful study of the pineapples from different sections has failed to reveal any great variation in the composition due to rainfall or soil. Individual pines from the same field, however, vary considerably, especially in regard to total sugars and acidity. In the main there is a fairly definite ratio between the reducing sugars and sucrose, this being usually about as 1 to 2. In the case of pineapples Nos. 103 and 104 the ratio is somewhat reversed, but this is probably due to the fact that each of these pines was slightly overripe at the time of gathering, and in the opinion of the author had begun to ferment. This would not only account for the partial inversion of the sucrose, but also for the abnormally low sugar content. By further reference to this table it may be seen that there is a considerable variation in the acidity and that the percentage of acidity is somewhat proportional to the total sugar content.

Table II contains the results of the analyses of green pineapples. These pines were fully grown but had not begun to ripen. Pineapples used in fresh fruit shipment to California are generally gathered at this stage of development. Some peculiarities in the composition merit our attention. The acidity is not above that of the ripe fruit. The fiber is low as are the solids in the juice. The total invert sugar which was determined in such a way as to hydrolyze any carbohydrates

that it may be supposed could give rise to sugars in the process of ripening, shows that a green pineapple even though full grown does not contain substances in sufficient quantity to produce a normal sugar content. In other words the pineapple plant does not store up in its green fruit any considerable amount of reserve material which is later converted into sugar. In this connection repeated tests have revealed not more than a mere trace of starch or dextrin in the fruit at any stage of development. The slightly greater percentage of total invert sugar than of the

TABLE II.—THE COMPOSITION OF GREEN PINEAPPLES.

Serial No.	Acidity as H_2SO_4 . Per cent.	Fiber. Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.			
				Reducing. Per cent.	Sucrose. Per cent.	Total by addition. Per cent.	Total by hydrolysis. Per cent.	Direct.	Invert.	Temp. °C.
127	0.48	..	7.32	3.57	1.96	5.53	..	1.0	-1.5	30.5
128	0.44	0.19	5.92	3.17	0.78	3.95	5.00	0.0	-1.0	30.4
131	0.30	0.16	..	3.36	0.87	4.23	5.07	4.0	-0.7	33.7
132	0.33	0.17	..	3.03	1.88	4.91	5.10	1.3	-1.1	30.0
145	0.39	..	7.44	3.33	3.14	6.47	8.02	2.5	-1.5	31.0
Av.	0.39	0.17	6.89	3.29	1.72	5.01	5.80			

combined sucrose and reducing sugars may possibly be due to the fact that it is very difficult by use of the method of cold maceration to rupture each cell in a sample of green pineapple; whereas, under the influence of boiling hydrochloric acid, all the sugars were brought into solution. The proportion of reducing sugars to sucrose is almost the reverse of that in the ripe fruit. The reducing sugars are present in almost as large quantity as in the ripe fruit, while the accumulation of sucrose had only fairly begun.

A number of pineapples gathered when green were held at the laboratory until thoroughly ripe. Table III contains the analyses of such pineapples. The

TABLE III.—THE COMPOSITION OF PINEAPPLES WHICH RIPENED AFTER BEING PICKED GREEN.

Serial No.	Acidity as H_2SO_4 . Per cent.	Fiber. Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.			
				Reducing. Per cent.	Sucrose. Per cent.	Total by addition. Per cent.	Total by hydrolysis. Per cent.	Direct.	Invert.	Temp. °C.
133	0.53	0.20	..	1.48	3.92	5.40	5.32	2.4	-2.6	30.7
134	0.60	0.21	6.78	1.13	2.26	3.39	3.57	1.3	-1.6	28.4
135	0.55	0.21	6.04	1.19	3.17	4.36	4.75	2.0	-2.0	32.8
136	0.63	0.25	6.54	1.06	2.26	3.32	3.75	1.1	-1.8	29.1
146	0.49	..	5.30	1.33	2.06	3.39	..	1.1	-1.5	32.4
147	0.39	..	5.13	1.27	2.03	3.30	..	1.0	-1.6	29.2
148	0.39	..	4.99	1.37	1.10	2.47	..	0.0	-1.4	31.4
Av.	0.51	0.22	5.79	1.26	2.40	4.12 ¹	4.35			

data show that in the ripening of pineapples after having been severed from the plant, the only change of importance that takes place is the conversion of reducing sugars into sucrose. The ratio between these sugars is practically the reverse of that in the green fruit. A general softening of tissue, and liquefaction within the cells had taken place, with a simultaneous development of a more pleasing flavor, but the total sugar content had not been increased.

¹ The fiber was determined according to the usual method for fiber determination in feeds.

² Average of 133, 134, 135 and 136 only.

¹ Not included in averages.

Table IV contains the analyses of pineapples when approximately one-fourth ripe. We note that there is a

TABLE IV.—THE COMPOSITION OF PINEAPPLES ABOUT ONE-FOURTH RIPE.

Serial No.	Acidity as H ₂ SO ₄ . Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.		Temp. °C.
			Reducing. Per cent.	Sucrose. Per cent.	Total. Per cent.	Direct.	Invert.	
126	0.62	7.34	3.03	3.79	6.82	2.8	-2.0	32
129	0.59	7.56	2.53	3.34	5.87	2.2	-2.1	28.4
130	0.59	8.36	2.83	3.83	6.66	2.6	-2.3	29.4
149	0.72	9.20	2.77	5.89	8.66	4.5	-3.0	30.8
150	0.75	10.93	2.56	5.25	7.81	4.0	-2.7	30
Av.	0.65	8.68	2.74	4.42	7.16			

slight increase in acidity and also a considerable increase in sucrose as compared with the green fruit.

Table V shows the composition of pineapples when half ripe. When the fruit has attained this develop-

TABLE V.—THE COMPOSITION OF PINEAPPLES HALF RIPE.

Serial No.	Acidity as H ₂ SO ₄ . Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.		Temp. °C.
			Reducing. Per cent.	Sucrose. Per cent.	Total. Per cent.	Direct.	Invert.	
116	0.78	11.83	2.74	7.33	10.07	5.7	-3.6	31.8
117	0.67	10.36	2.61	6.70	9.31	5.0	-3.5	31.7
124	0.63	...	2.38	6.83	9.21	4.9	-3.8	30.5
125	0.54	...	4.16	6.09	10.25	5.0	-2.7	32.2
Av.	0.65	...	2.97	6.74	9.71			

ment fully three-quarters of its maximum sugar has been stored up.

SUMMARY.

The composition of Hawaiian pineapples varies considerably. The total sugar content on the one hand was found to vary from 9.15 per cent. to 15.23 per cent., while on the other there is a range in acidity of from 0.22 per cent. to 1.16 per cent. Generally, though not always, the acidity increases with an increase in sugars. The average composition of pineapples grown in Hawaii is about equal to that reported from other countries.

Green pineapples contain less acidity than the ripe fruit and also a small percentage of fiber, reducing sugar and sucrose. Dextrin and starch do not occur in important quantities in pineapples at any stage. The reducing sugars and sucrose stand in inverse ratio to that of the ripe fruit. In the ripening of pineapples gathered green, the most important chemical change that takes place is the conversion of reducing sugars into sucrose, but the total sugar content appears not to be increased.

The cells of green pineapples as seen under the high-power microscope contain a thickened layer on the cell walls, which renders it difficult to express the juice from the cells. In the ripening process this layer gradually becomes dissolved away until at maturity the cell walls are extremely thin and easily ruptured. With pineapples that are gathered green and allowed to ripen the thickened coat on the cell walls also becomes dissolved, thus apparently increas-

ing the juice in the fruit but without materially changing its concentration.

During the normal ripening of the pineapple a rapid accumulation of sugars and a slight increase in acidity takes place. When the fruit becomes approximately half ripe, it contains at least three-fourths of its maximum sugars.

THE DETERMINATIONS OF TOTAL SOLIDS IN MILK.¹

By PAUL POETSCHKE.

Received Feb. 24, 1911.

In the routine contamination of milk, the analysis is usually restricted to the determination of total solids, fat and specific gravity. Generally an examination for the more common preservatives is also included.

The object of the present article is to consider particularly the determination of total solids as accomplished by the aid of a special pipette devised for delivering five grams of milk of known specific gravity. Inasmuch as the specific gravity is essential to the proper use of this pipette some essential features relating to specific gravity will be considered.

Specific Gravity.—The New York Board of Health lactometer is the instrument usually employed in routine milk inspection. These instruments, as commonly constructed, require a comparatively large volume of milk, and if used for general laboratory work, would greatly inconvenience the inspector when many samples are taken for examination. Although many lactometers of reduced size are in use, it may be of interest to describe one of these forms,² which require but four ounces of milk. Fig. 1 is an exact representation of the instrument. A cylindrical jar (height 11.0 cm., diameter 4.3 cm.), made of brass tubing with a copper bottom soldered thereto, serves as a container for the milk. A sufficient quantity of the well-mixed sample, cooled to a few degrees below 60° F., is poured into the jar and stirred with a dairy thermometer until the temperature reaches 60° F. The lactometer is then carefully lowered into the jar, and when it becomes stationary, the reading recorded. Too much stress cannot be laid upon a proper standardization of the instrument. I have found lactometers to be incorrectly graduated in some cases to the extent of 4° to 5°. The simplest method of standardization is to compare the instrument in question with a standard lactometer. However, if such a standard is not at hand, a series of salt solutions are prepared and their specific gravity determined at 60° F. with a pycnometer, as in the following case, Table I:

TABLE I.

Specific gravity at 60° F., by pycnometer.	Corresponding lactometer.	Observed reading on instruments (Standard).	
		One.	Two.
1.0245	84.5°	84.0°	84.0°
1.0278	96.0	96.0	96.0
1.0312	107.0	107.0	107.0

¹ Read before N. Y. Section Am. Chem. Soc., Feb. 10, 1911.² Devised some years ago by Dr. Deghué, of this laboratory.

Having thus verified the standard, we can proceed to standardize other instruments by comparison, which is much simpler, since it is not necessary to standardize at 60° F. The comparison can be made at any other temperature, as long as the temperature of the solution remains uniform while the instrument in question is compared with the standard. Table II gives the result of comparison of several instruments with the standard:

TABLE II.

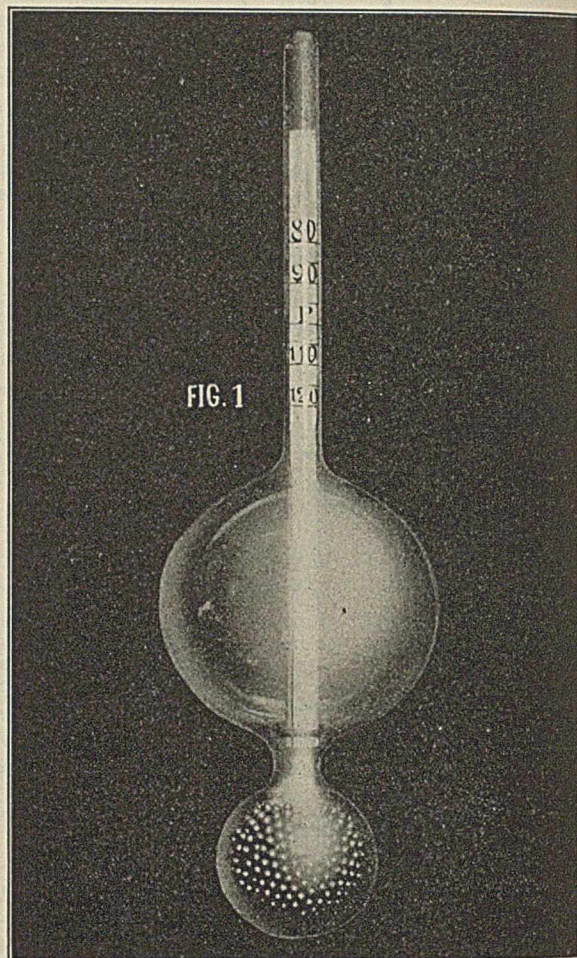
Lactometer number.	Reading on Standard lactometer.	Observed reading on lactometer.	Correction.
3	82	86	-4°
	95	98	-3
	108	110	-2
	117	118	-1
4	82	86	-4
	94	98	-4
	107	108	-1
	116	117	-1
5	81	85	-4
	94	97	-3
	106	108	-2
	116	117	-1
6	87	86	+1
	94	92	+2
	107	104	+3
	118	114	+4
7	83	82	+1
	91	89	+2
	112	100	+2
	114	111	+3

The observed corrections noted in Table II are plotted on cross-section paper to facilitate ready reference and avoid errors in interpretation. If the lactometer reading of a sample of milk is taken at any temperature other than 60° F., a correction of one degree is necessary for a difference of 2° F. Of course, a corresponding amount is added if the temperature is above 60° F., and subtracted if below 60° F.

Total Solids.—The usual method of determining total solids is to introduce five grams of milk into a weighed flat-bottomed dish. After the dish has been weighed, a five-gram weight is added to those already on the balance pan, and five cc. of the thoroughly mixed sample drawn into a dry five cc. pipette. This is emptied into the dish until counterbalanced by the weights, which is readily accomplished. By this means five grams are weighed quicker than if a full five cc. were delivered and weighed, and this procedure has the further advantage of shortening the final calculation. The dish is then placed in the water bath, until nearly all of the water is evaporated, and finally dried to constant weight at 100° C. Provided the temperature is constantly maintained at 100° C., a practically constant weight is obtained in 2½ hours. A thermoregulator,¹ very convenient for controlling the temperature, has been described by the author.

To reduce as much as possible the time required for all routine determinations, is an object worthy of consideration in the laboratory where many similar determinations are carried out. However, any shortening of an accepted or reliable process must not

noticeably affect its accuracy. The author has devised a pipette graduated so as to deliver five grams of milk of known specific gravity, which for convenience is graduated in degrees of the N. Y. Board of



Health lactometer. Although graduated in this manner, the equivalent specific gravity and Quevenne lactometer degrees can be interchanged according to Table III, which also gives the weight of water, corresponding in volume to five grams of milk at 60° F.

Repeated trials of pipettes of varying dimensions were made until one of satisfactory form was secured. The body of the pipette is not of much significance, but the suction tube and calibrated delivery tube must be of such internal diameter as to allow of accurate measurement and fairly uniform time of delivery. The pipette is shown (¼ actual size) in Fig. 3. The internal diameter of the calibrated tube is 1.0 mm. and of the suction tube 2.5 mm. The temperature of the milk is preferably adjusted to 60° F., well mixed and drawn into the pipette until the zero mark coincides with the lower meniscus. It is then allowed to drain into the weighed dish, by touching the side of the dish with the tip of the pipette, until the mark corresponding to the lactometer reading of the milk is reached. Ordinarily the sample for the total solids determination is taken directly after the lactometer reading is recorded so as to obviate

¹ J. Am. Chem. Soc., 31, 1218.

TABLE III.

Specific gravity, 60° F.	N. Y. Board of Health.	Quevenne scale.	Weight of water corresponding in volume to five grams of milk at 60° F.
1.0203	70°	20.3	4.9005
1.0206	71	20.6	4.8991
1.0209	72	20.9	4.8976
1.0212	73	21.2	4.8962
1.0215	74	21.5	4.8948
1.0217	75	21.7	4.8938
1.0220	76	22.0	4.8924
1.0223	77	22.3	4.8909
1.0226	78	22.6	4.8895
1.0229	79	22.9	4.8881
1.0232	80	23.2	4.8866
1.0235	81	23.5	4.8852
1.0238	82	23.8	4.8838
1.0241	83	24.1	4.8823
1.0244	84	24.4	4.8809
1.0246	85	24.6	4.8799
1.0249	86	24.9	4.8785
1.0252	87	25.2	4.8771
1.0255	88	25.5	4.8757
1.0258	89	25.8	4.8742
1.0261	90	26.1	4.8728
1.0264	91	26.4	4.8714
1.0267	92	26.7	4.8700
1.0270	93	27.0	4.8686
1.0273	94	27.3	4.8671
1.0275	95	27.5	4.8661
1.0278	96	27.8	4.8648
1.0281	97	28.1	4.8633
1.0284	98	28.4	4.8619
1.0287	99	28.7	4.8605
1.0290	100	29.0	4.8591
1.0293	101	29.3	4.8577
1.0296	102	29.6	4.8563
1.0299	103	29.9	4.8549
1.0302	104	30.2	4.8534
1.0304	105	30.4	4.8525
1.0307	106	30.7	4.8511
1.0310	107	31.0	4.8497
1.0313	108	31.3	4.8482
1.0316	109	31.6	4.8468
1.0319	110	31.9	4.8454
1.0322	111	32.2	4.8440
1.0325	112	32.5	4.8426
1.0328	113	32.8	4.8412
1.0331	114	33.1	4.8398
1.0333	115	33.3	4.8388
1.0336	116	33.6	4.8374
1.0339	117	33.9	4.8361
1.0342	118	34.2	4.8347
1.0345	119	34.5	4.8333
1.0348	120	34.8	4.8319
1.0351	121	35.1	4.8305
1.0354	122	35.4	4.8290
1.0357	123	35.7	4.8276
1.0360	124	36.0	4.8262
1.0362	125	36.2	4.8253
1.0365	126	36.5	4.8239
1.0368	127	36.8	4.8225
1.0371	128	37.1	4.8211
1.0374	129	37.4	4.8198
1.0377	130	37.7	4.8184

total solids, proteids and fat. First of all, the sample must be uniform and reasonably fresh, since if it is partly churned or sour a reliable result cannot be obtained. Such milk requires preliminary treatment in order to secure a proper sample for any determination whatsoever. With slightly churned milk, the sample is warmed so as to melt the particles of but-

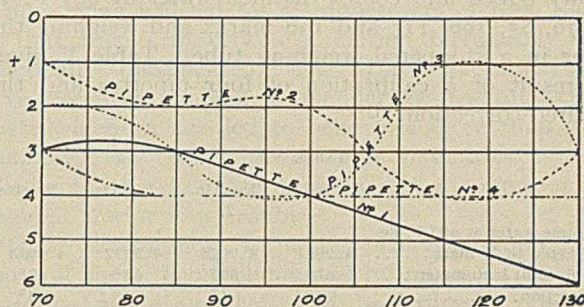


Fig. 2.

ter and shaken until a uniform mixture is obtained. In the case of sour milk it becomes necessary to treat the sample with a small quantity of alkali, preferably ammonium hydroxide, which dissolves the coagulated casein. Any sample which requires such treatment should not be measured by means of the pipette for the total solids determination. The largest source of error is due to the variable retention of different milks, but the time of delivery (average 100 seconds) is sufficiently great to reduce the retention to a min-

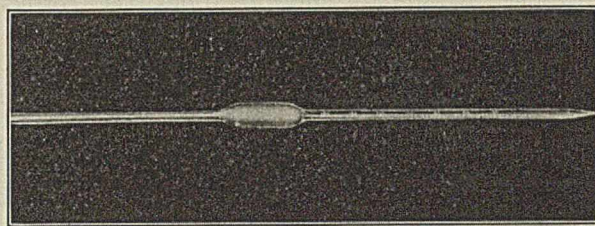


Fig. 3.

imum. Table IV shows the amount of retention for various samples and the influence on the total solids determination. The amount retained was obtained by delivery to the requisite mark on the pipette into a stoppered weighed tube:

TABLE IV.

Sample number.	Lactometer reading at 60° F.	Weight delivered corresponding to lactometer.	Retention in grams.	Total solids corrected for retention.	Total solids assuming five grams to have been delivered.
1	113	4.9985	0.0015	12.06	12.06
2	110	4.9974	0.0026	12.28	12.27
3	115	4.9945	0.0055	12.39	12.38
4	117	4.9957	0.0043	12.73	12.72
5	82	4.9976	0.0024	9.25	9.25
6	90	4.9966	0.0034	9.82	9.81
7	113	4.9911	0.0089	12.34	12.32
8	114	4.9875	0.0125	12.37	12.33
9	114	4.9860	0.0140	12.39	12.35
10	113	4.9906	0.0090	12.34	12.32
11	113	4.9917	0.0083	12.33	12.32

the necessity of again adjusting the milk to the proper temperature. The pipette is of still greater advantage when a complete analysis is required, as in the case of human milk. For instance, in the determination of total proteids by the Kjeldahl method five grams of the milk are delivered directly into the digestion flask without any weighing whatever. The same is true in the case of the fat determination by the Adams' paper coil method.

We now come to a consideration of the various factors which influence a correct delivery of five grams of milk, although it will be shown that these errors have little significance in an actual determination of

From the results obtained the minimum retention was 0.0015 gram, the maximum 0.0140 gram, and

the average 0.0066 gram. Assuming an average total solids of 12.00 per cent., the maximum error from this source is 0.04 per cent., and the average 0.02 per cent., which is well within the ordinary limits of accuracy.

Pipettes delivered by the makers require to be standardized. This is accomplished by delivering freshly boiled and cooled distilled water at 60° F. to the 70, 85, 100, 115 and 130 marks and weighing the water in a stoppered weighing tube. Table V gives the result of a calibration of four pipettes and the required corrections:

TABLE V.

	Pipette 1.	Pipette 2.	Pipette 3.	Pipette 4.
Volume water at 60° F. delivered to 70 mark.....	4.9051	4.9026	4.9032	4.9053
Equivalent lactometer.....	67°	69°	68°	67°
Correction.....	+3°	+1°	+2°	+3°
Volume water at 60° F. delivered to 85 mark.....	4.8836	4.8828	4.8838	4.8851
Equivalent lactometer.....	82°	83°	82°	81°
Correction.....	+3°	+2°	+3°	+4°
Volume water at 60° F. delivered to 100 mark.....	4.8650	4.8615	4.8644	4.8650
Equivalent lactometer.....	96°	98°	96°	96°
Correction.....	+4°	+2°	+4°	+4°
Volume water at 60° F. delivered to 115 mark.....	4.8453	4.8436	4.8403	4.8443
Equivalent lactometer.....	110°	111°	114°	111°
Correction.....	+5°	+4°	+1°	+4°
Volume water at 60° F. delivered to 130 mark.....	4.8260	4.8228	4.8220	4.8236
Equivalent lactometer.....	124°	127°	127°	126°
Correction.....	+6°	+3°	+3°	+4°

In order to simplify interpretations the corrections noted in Table V are plotted as in Fig. 2.

Table VI gives the result of total solids determinations made with the use of the pipette and in the ordinary manner:

TABLE VI.

Sample number.	Lactometer reading at 60° F.	Fat. Per cent.	Total solids.	
			By pipette. Per cent.	By direct weighing. Per cent.
52710	114	3.6	12.35	12.37
52711	113	3.6	12.32	12.31
52712	113	3.6	12.32	12.28
53064	106	3.3	11.42	11.40
53117	111	3.3	11.78	11.83
53124	112	4.5	13.21	13.28
53126	111	3.6	12.19	12.19
53018	110	3.4	11.83	11.89
53396	112	3.7	12.38	12.37
53397	112	3.7	12.24	12.41
53398	110	3.4	11.77	11.84
53399	112	3.4	12.06	12.06
53400	112	3.5	12.16	12.20
53403	113	3.5	12.24	12.20
53259	107	3.4	11.70	11.68
53261	110	3.5	12.12	12.10
53449	113	3.2	11.90	11.89
53450	113	3.5	12.15	12.19
53492	112	4.0	12.55	12.60
52293	110	3.4	11.85	11.91
52294	110	3.4	11.89	11.95
52309	102	5.6	13.94	13.93
52310	111	3.7	12.29	12.38
52335	110	3.7	12.28	12.28

In 31 additional determinations, omitted for lack of space, the average variation by pipette and direct weighing was ± 0.045 per cent.

It is apparent that the results show good agreement, and considering the time and labor saved, I feel justified in describing the instrument. Mr. Gottlieb Greiner, of 81 John Street, New York City, has undertaken to make this pipette at a reasonable cost. I wish to acknowledge my indebtedness to my assistants, Messrs. J. Schroff, J. F. Kahrs, and E. S. Lieb-scher, for their assistance in the analytical work.

LEDERLE LABORATORIES,
39-41 WEST 38TH STREET,
NEW YORK CITY.

PLANTS AND MACHINERY.

FILTRATION OF WATER.

By CHURCHILL HUNGERFORD, Engineer, Hungerford and Terry, Philadelphia.

Received April 12, 1911.

For a great many years the streams flowing through the more densely populated portions of our country have been subjected to a steadily increasing contamination. In spite of the various commissions, boards of health, prohibitive statutes and other attempts to regulate this condition the last ten years has seen a retrogression in the purity of surface waters that is most startling. Occasionally a very active commonwealth may deal with certain individual sources of contamination with a heavy hand, but instead of these attempts being received with acclamation their authors have been excreated as people who are attempting to prevent the normal growth of the country by the repression of its industries.

The occasional sewage disposal plant met with or the perfunctory attempts of the manufacturers to disguise the unpleasant features of their waste liquors have had little result on the general flow. So discouraged are sanitarians and others becoming that they no longer demand that such streams shall retain their original purity, but are willing to compromise the entire matter by simply requiring that the contaminations shall not make a nuisance of the stream itself, that is, that all forms of matter may be emptied into it provided these forms are not of a sufficiently putrefactive nature to make the stream offensive. Of course, certain chemical wastes, if discharged into the stream, would cause manufacturers below to protest and perhaps bring suit to stop their discharge, but this form of litigation is never of a satisfactory nature and is always enormously expensive. As a matter of fact the average manufacturer is placed between the devil and the deep sea. Above him is the in-

considerate manufacturer who persists in defiling the stream, and below him is the obdurate and unreasonable factory owner who objects to his industrial wastes. It is really remarkable the way a man's point of view can change merely by looking up or down stream. Everything that comes from above seems to be of a pernicious nature while everything discharged below seems perfectly harmless.

While the nature and degree of contamination may vary greatly in different streams, due to the population, nature of the industries upon its banks and proportion of pollution to the normal flow, the general contamination consists of sewage, paper mill wastes, waste dye liquors from wool, cotton and silk industries, waste from wool washeries, bleacheries, possibly a chemical factory waste and occasional spent tannery liquors. Nearly always will we also find profuse growths of organisms of a low type, particularly beggiatoa, which will frequently be seen in such enormous quantities as to interfere with the

acid it can be handled in a purifying plant. The strawboard factory waste, if sufficiently diluted, presents no serious problem but as a rule these factories are located on small streams and the strongly alkaline waste makes the general flow of the stream very alkaline indeed. The neutralization of this alkali, if it exists in large quantities, is an expensive and unsatisfactory process. The beet sugar waste is now being utilized by manufacturers of beet sugar so that this form of contamination fortunately has practically disappeared. The starch factories also have recently evolved a manner of treating their waste which we are led to believe is more than self-sustaining, so that both of these industries can be relied upon to eliminate what is now a source of infrequent but serious trouble.

These uncommon forms of contamination are, many of them, being eliminated by reason of the fact that the waste products can be utilized. The remainder are usually located in territories quite remote

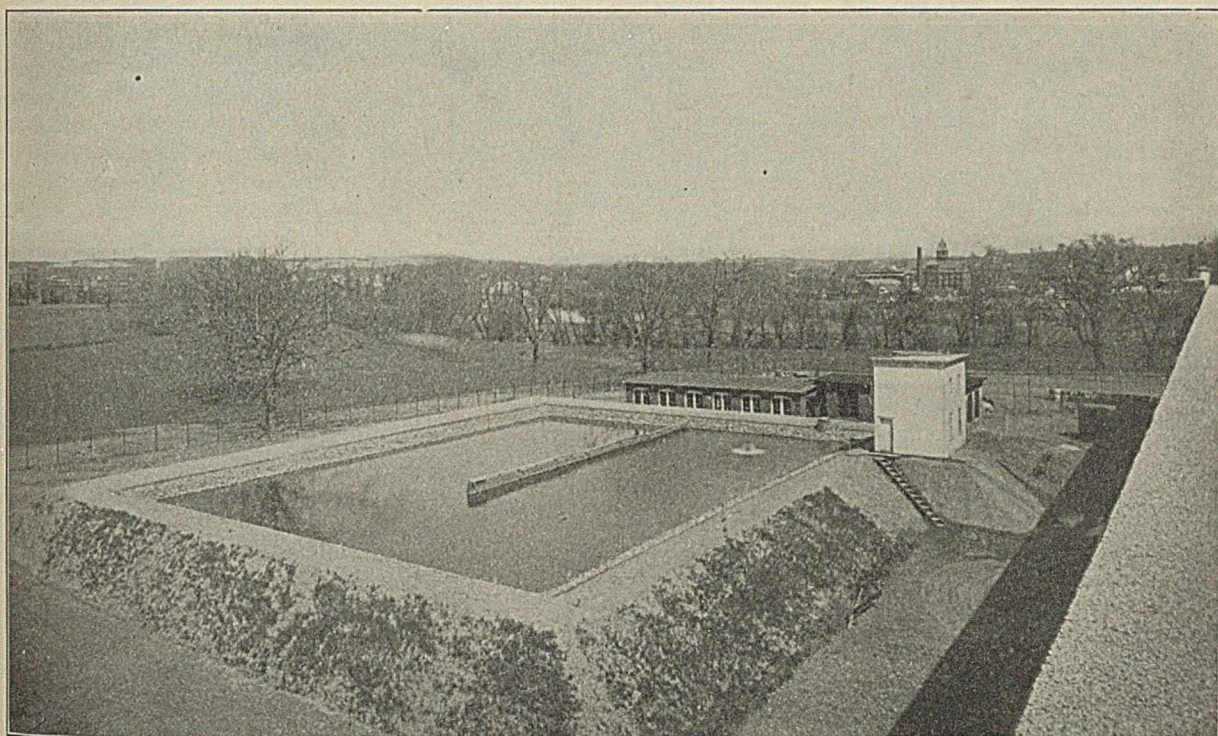


Fig. 1. Settling basin for highly polluted water. Frame chemical feed house at right and brick filter houses at end of basin.

flow of the stream. Then there are uncommon forms of contamination such as the waste liquor from sulphite pulp mills, strawboard factories, beet sugar waste, starch factory waste, etc. All of these represent a very serious form of contamination and which, if they exist in very considerable proportions, are bound to make the work of purification extremely difficult. The first-named, the sulphite waste, is an acid substance which interferes with the bacterial purification of the stream and must be neutralized with some alkaline substance before it can be purified. If it is not present in sufficient quantities to make the water

from cities so that they do not enter into the problem usually presented and as outlined in the forepart of this article.

While the various industries are the principal sufferers from stream contamination, they are also the principal contributors toward it. They must have water in large quantities and they must be provided with an outlet for their wastes. Moreover, certain conditions, such as labor, propinquity of the markets, availability of material, etc., demand that these industries shall be located in or near populated districts. Thus they are prevented from going to remote places

to procure a pure water and they are compelled to use the contaminated supplies invariably found in populated districts. The water supplied by municipalities and water companies ranges in cost from four cents to thirty cents per thousand gallons and such industries as paper mills, bleacheries, silk works, etc., use millions of gallons of water per day. To pay any such tremendous price for water would reduce their profits to nothing. Their very existence depends upon their ability to make the contaminated waters suitable for their requirements, and this problem, while apparently very complex, resolves itself in almost every instance into a comparatively simple one. The solution consists in the treatment of the polluted water with certain chemicals which will produce complete precipitation of the dyes, coagulation of the finer particles of suspended matter, and at least a partial oxidization of the sewage. After the chemical treatment a reasonable period of time to allow for sedimentation and completion of the chemical reactions must take place, after which the water is passed

must have a water that is crystal clear and absolutely colorless. For bleaching cotton a degree of purification not quite so thorough is required while for paper-making it is simply necessary to remove all of the suspended matter and those dyes which would have a tendency to discolor cellulose. The degree of purification attained depends very largely upon the preliminary treatment, or in other words, upon the amount and character of the chemicals employed to exhaust the colors, produce coagulation and oxidize the sewage.

No filter, of course, can remove dissolved substances from water in any appreciable quantity, and to effect a complete removal of many of the most annoying substances which are in solution or so finely divided that they cannot readily be retained by the filter, preliminary treatment should be resorted to. Simple coagulation, however, is only one of its offices.

Preliminary treatment in its broadest sense consists first in the addition of coagulants to exhaust the dyes and to gather together the finely divided particles

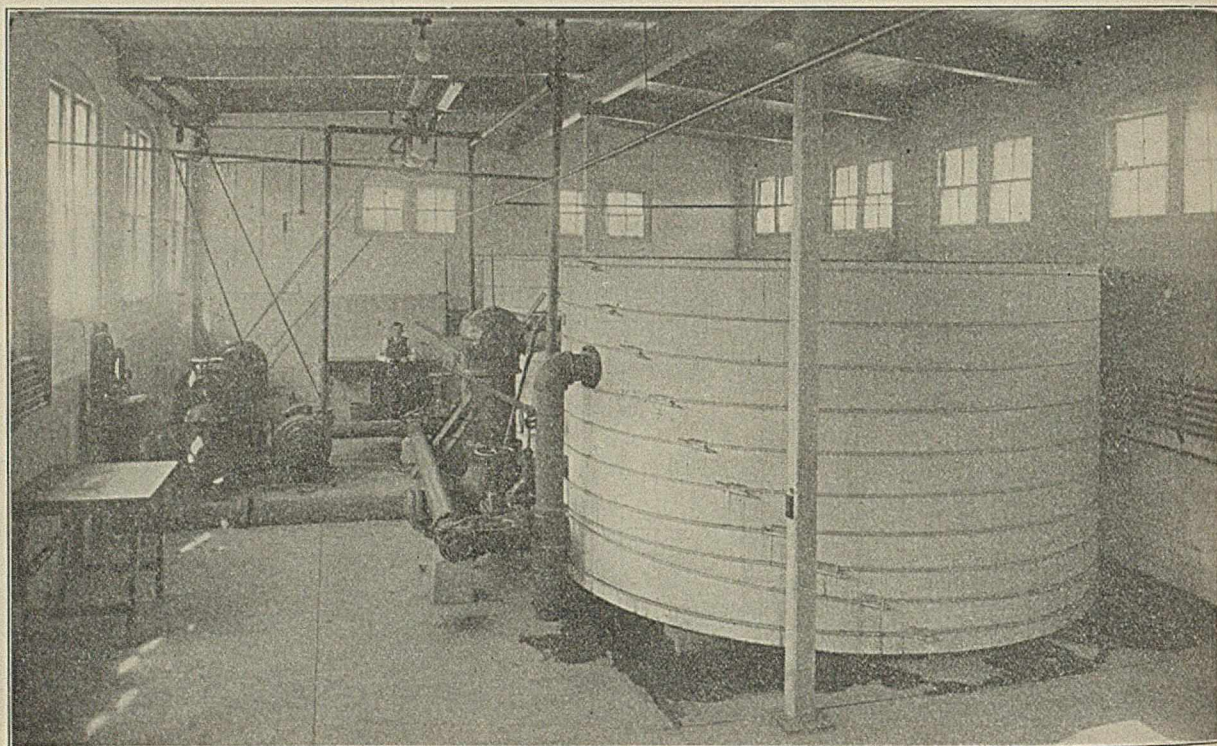


Fig. 2. Filter house: capacity, $2\frac{1}{2}$ million gallons.

through a filter plant of the so-called mechanical type, that is, a filter which can be washed in a few minutes by reversing the flow of water through it. This treatment must be effected in such a manner that the applied chemicals will not leave residual substances prohibitive to the use of the water.

Some industries require a very high degree of purification while others simply require the removal of suspended matter. Silk dye works undoubtedly require the highest degree of purification while cotton bleacheries, cotton and wool dye houses and paper mills come next in the order named. The silk dyer, on account of the extremely delicate shades demanded and the properties of the chemicals employed by him

of matter; the addition of some oxidizing agent to reduce the sewage to an innocuous form, and sedimentation to effect as large a removal of the precipitated matter as is possible before delivering the water to the filters.

The most reliable coagulant that can be used is sulphate of alumina. Other substances have been tried, many of them successfully, but for general efficiency and economy the sulphate of alumina is undoubtedly superior to any other substance. Sulphate of iron followed by lime has been used very extensively but in many cases plants using these substances have reverted to the aluminum sulphate.

Before sulphate of alumina is applied to a water an

analysis, of course, is necessary. Should the water be found to possess no alkalinity it must first be artificially produced, ordinary soda-ash or even building lime being perfectly applicable to this condition. The sulphate of alumina is applied in the form of a solution to the incoming water as it enters the settling basin. It is applied in quantities varying with the degree of pollution, and will range from one to as high as six grains per gallon in extreme cases with an average requirement for polluted waters of two and one-half grains to the gallon.

The chemical action of the sulphate of alumina is very rapid indeed. It almost instantly combines with the alkaline substances in the water to form hydrate of alumina. It also has a direct action upon almost every dye that is found in the stream, and it has a tendency to completely precipitate these dyes when mingled with each other. This effect is sometimes quite surprising because it frequently happens that pure solutions of the dyes themselves which are hardly effected by the sulphate of alumina will, when mingled with the various substances found in the stream, combine to form a general impurity which is quite amenable to treatment by the aluminum sulphate; that is to say, the dyes, mordants, etc., which are used in a dye house and which are not individually susceptible to alum treatment will, when mingled together and in conjunction with the lime existing in the water, the sewage and other industrial waste, form a highly discolored substance which can be completely precipitated by the sulphate of alumina.

In the actual preliminary treatment of the water, the matters precipitated have a tendency to gather together in flocculent masses quite visible to the naked eye. As a rule these substances tend to settle with considerable rapidity so that in three hours' time we find that the water has been rendered passably clear. If sewage, however, is present in any considerable quantity there is a tremendous growth of various forms of bacterial life, some of which possess the property of giving off gases in greater quantity than can be dissolved by the water itself. In fact, the solution of these gases in the water is not a condition to be desired, as many of them have a highly offensive odor. The worst condition of all, however, is the tendency of small bubbles of the gases generated to attach themselves to the matter which has settled and buoy it to the surface, thus preventing the most important action of all—sedimentation. Moreover, in the depth of the sludge the gases of decomposition are generated with such energy that masses several square yards in extent are sometimes brought to the surface where they break up and fall slowly to the bottom again. This process taking place over the entire surface of the settling basin destroys the benefits received from sedimentation, and during warm weather it would be quite possible for the settled water to leave the settling basin in worse condition than it entered.

Furthermore, the liquefying bacteria are also very active under the especially favorable conditions for their growth which exist within the settling basin

and much of the matter that has been precipitated, or in fact that had not been in a liquid form at all, is reduced to a solution through their offices. This action liberates the coloring matter which had been precipitated and the effluent from the filter will show these colors.

Of course, from the manufacturer's standpoint, the removal of the bacteria from the water is something that does not interest him. As a matter of fact, however, his water must be sterile or very nearly sterile to be properly purified as it is quite apparent that the bacteria can completely arrest the purification process. Moreover, if they are not destroyed they will grow in the underdrains of the filters, and even in the piping system throughout the factory, to such an extent as to obstruct the flow of water, so that it is quite apparent that some extremely powerful bactericide must be employed.

By reason of their efficiency and economy there are two substances which immediately present themselves, one calcium hypochlorite and the other sulphate of copper. Of the two, the calcium hypochlorite is far the more preferable, and in fact, copper sulphate is seldom used except in those cases where algae are troublesome. The calcium hypochlorite when used in quantities ranging from 1-5 parts per million not only destroys all of the bacteria that could make any trouble but it also tends to break up the sewage and to decompose many dissolved substances that might by future putrefaction cause great trouble with the water. This substance accurately applied produces the most wonderful results in the settling basins, and a water which possesses a high degree of color, a very offensive smell and much suspended matter will, after three hours' preliminary treatment in the settling basin, with the addition of the requisite quantities of alumina and hypochlorite, flow to the filters very largely clarified, with much of the color, a great deal of the suspended matter and almost all of the odor taken away. In other words, the water has been reduced to a filterable condition, and after passing through the filters it will be as bright, clear, sparkling and odorless as spring water.

These problems of purification are not to be approached without due consideration and a very careful study of the forms of contamination. There may be extraordinary forms of pollution that require some special form of treatment in addition to the usual chemical treatment in the ordinary rectangular settling basin. The presence of very large quantities of sewage makes a problem, which would otherwise be quite simple, very hard to handle. If the sewage contained is very high indeed recourse will have to be made to some of the standard methods of sewage disposal. In such cases possibly the most effective of all would be the Imhoff tank, but even if this were used it would have to be followed by chemical treatment in the usual settling basin.

A very important part of the preliminary apparatus is the chemical feed. It is necessary in almost all instances to apply the coagulants, oxidizing agents, etc., in a very exact manner. The chemical feed to

do this must be an apparatus which is capable of measuring the incoming water and applying to it the exact amount of chemicals required, proportionate to this flow. It often happens that the influx may vary from ten to ninety per cent. and the chemical feed must meet these changes rapidly and accurately. If not enough chemicals are applied the preliminary treatment is a failure. If an overdose of chemicals is applied the water cannot be used, so it is quite evident that this small and apparently insignificant apparatus is of great importance.

The proportion of chemicals required is best determined by means of some simple chemical test that can be conducted by operatives having no chemical knowledge. With regard to the amount of sulphate of alumina required the writer finds that any person of ordinary intelligence can determine the alkalinity of the water by means of *N/50* sulphuric acid, taking 100 cc. of the water to be tested and using erythrosine as an indicator. By conducting the test in the manner above described, each tenth of a cc. of acid consumed in titrating indicates an alkalinity of one part per million, and each grain of sulphate of alumina per gallon applied to the water reduces the alkalinity eight parts per million.

The sulphate of alumina solution is made up of standard strength in wooden tanks, one tank being prepared while the other is in use. Of course, the amount of alum used can always be determined by reference to the chemical feed, but the determination of the alkalinity at weekly intervals makes a very good check upon the laborer who usually attends to the preparation of the alum solution.

The soda solution where required is also made up in the same manner and the test conducted in the same manner. The hypochlorite of lime is made of standard strength in a separate tank with an agitator operated by hand. After it has settled clear the supernatant liquor is drawn into a solution tank from which it is taken by the chemical feed as required. As the quantity of this material used is so small the only test required with this is to make sure that there is no excess of hypochlorite, and so a solution of starch and potassium iodide is used as a qualitative test. If there is any indication of a blue color there is a very great excess of calcium hypochlorite being used and the feed should be very much reduced.

This method of dealing with the situation may not appeal to a chemist but there are many instances in industrial plants where very nice chemical determinations are conducted quite ignorantly but very successfully by people who have no chemical knowledge of what they are about. Where a chemist is employed by the works a more accurate determination can be made at suitable intervals, but the amount of calcium hypochlorite required is so far below that which can actually be consumed by the impurities in the water that an excess could only come from the grossest carelessness imaginable.

After the preliminary treatment of the water is completed the water passes through the filters, which are the most important and by far the most interesting part of the whole apparatus.

These filters must be constructed so that they will remove all suspended matter from the water and can be readily cleaned in a very few minutes' time. They must be capable of handling very large quantities of water, must occupy little space and be so constructed that there is no deterioration of the filtered water as they grow old. This means that the filter beds must wash perfectly every time the current is reversed and that there shall be no permanent concretions of the retained matter. They must also be capable of passing the water through them with a very slight loss of pressure, and economy of operation, next to efficiency, must be a distinguishing characteristic.

Following are the results of filtration upon badly polluted waters:

No. 1.—SAMPLE OF WATER FROM PASSAIC RIVER BELOW PATERSON, N. J.

	Color.	Turbidity.	Alkalinity. Parts per million.	Odor.
Before filtration	deep bluish black	80	23	Musty
After filtration	colorless	0	7	Faint
Coagulant used	2 grains of sulphate of alumina per gallon.			
Sedimentation	2 hours, 15 minutes			

No. 2.—SAMPLE OF WATER FROM DUNDEE CANAL AT PASSAIC, N. J.

	Color.	Turbidity.	Alkalinity. Parts per mil- lion.	Oxygen consumed.	Bacteria per cc.
Before filtration	black	100	23	16.57	8,000
After filtration	colorless	0	3.6	1.83	40
Coagulant used	2½ grains of sulphate of alumina per gallon				
Sedimentation	about two hours				
	Calcium hypochlorite 1 part per million				

No. 3.—SAMPLE OF WATER FROM DAN RIVER AT DANVILLE, VA.

	Color. Hazen scale.	Turbidity.	Alkalinity. Parts per million.
Before filtration	50	4000	12
After filtration	0	5	10
Coagulant used	1 grain sulphate of alumina per gallon and carbonate of soda to neutralize it		
Sedimentation	¾ hour		

The so-called mechanical filter fulfils the above requirements. Unfortunately, this filter is supposed to have been evolved from the older type of slow sand filter, whose action depends principally upon a layer or film of impurities directly upon the surface of the sand. This slow sand filter is capable under average conditions of handling about three million gallons of water per acre per day and when properly taken care of shows a very high bacterial efficiency, but it does not possess a great bacterial efficiency immediately after cleaning or until the surface film gets thick enough to act as a strainer. Also when the rate of three million gallons per acre per day is exceeded materially there are short periods that occur during which the bacteria in the filtered water mount upward to an astonishing degree. Careful investigations have developed the fact that this surface film breaks in places, permitting the water to rush through the sand at those places at a high rate of speed, carrying all manner of impurities through with it. The best way of avoiding this trouble seems to be to keep the rate of filtration below three million gallons per acre per day.

The first successful mechanical filter was developed a good many years after slow sand filtration had be-

come an assured success, and almost coincident with the perfection of this apparatus it was discovered that by the use of alum in the filtration process a very brilliant water could be delivered from the filters. The inventor, with a full knowledge of the theory of slow sand filtration, assumed that the hydrate of alumina formed by the addition of the alum made his surface layer much tougher and permitted a rate of filtration ranging from sixty to one hundred and twenty million gallons per acre per day. This belief in a tenacious surface layer has unfortunately been very largely adhered to by filter manufacturers, but the writer is firmly convinced that this theory is altogether erroneous. In the first place, the hydrate of alumina does not toughen the surface layer. If a water containing nothing but hydrate of alumina is applied to a filter so that it will form a surface layer, a rate of sixty million gallons per acre per day cannot be maintained without serious breaking through, the hydrate of alumina being so unstable that it cannot form a layer of reliable integrity. In the second place a surface layer with fine enough pores in it to retain the bacteria, which range from one twelve-thousandth to one twenty-five-thousandth of an inch on their longest dimensions, and the particles of fine argillaceous matter that give the water an opalescent tint—computed to be about $\frac{1}{100,000}$ of an inch in diameter—could not be forced even under very high pressure to let the water through at anything like the high rate of filtration that the mechanical filter does maintain successfully with only a slight loss of head. Still again we have seen that a surface layer on the slow sand filter breaks through readily at the very slow rate of three million gallons per acre per day, and there is no reason to believe that the mechanical filter acts differently.

With these points in view it must be apparent to every one that the surface layer is not the effective filter, but that some other process beside mere straining is responsible for the high efficiency of the mechanical filter.

A mechanical filter, in spite of its high rate of speed, is constructed of coarser sand of a much more uniform size than that used in the slow sand filter. While there is considerable latitude permissible in the size of the grains in different filters, an average grade of sand which gives interstitial channels about one twelve-hundredth of an inch in cross-section is the size most generally used. The determination of the size of these channels is very easily made in the following manner: For example, we find that twenty sand grains laid in a line cover a space of one inch. This would give for a square inch four hundred grains with a corresponding number of interstitial spaces. Taking the proportion of voids or interstitial spaces in a given quantity of sand, which will be found to be approximately $33\frac{1}{3}$ per cent., we find that in each cubic inch of sand there are twelve hundred channels having a combined area of one-third of a cubic inch, which is equivalent to one twelve-hundredth of an inch for each channel. This

computation is, of course, subject to slight fluctuations, but as above stated the sand is so screened that there is very little variation in the size of the sand grains, and consequently the channels, although quite devious, must maintain a fairly uniform cross-section.

We have already seen that the finer particles of matter that must be retained by the filter range in diameter from one twelve-thousandth of an inch to one one-hundred-thousandth of an inch and we must retain these particles in a medium that has channels one twelve-hundredth of an inch in diameter. In other words, we have a screen with openings ranging from ten to eighty times that of the particles which must be retained. At first sight this appears to be an impossibility but an inspection of the filtered water shows that 99 per cent. or more of these fine particles have been removed. True, the addition of a coagulant has gathered together a great many of these particles into flocculent masses, but these masses have little cohesion and are broken up by the slightest agitation. Besides, a large number of the fine particles are not entrapped in the coagulated matter. Moreover, there are types of filters which run for long periods of time without showing the faintest visible trace of a surface film or blanket so that a hypothetical medium with fine interstices on the surface of the filter can hardly be held accountable for the high efficiency.

A thorough consideration of this rather paradoxical process of filtration brings forth the rather startling conclusion that the so-called mechanical filter is not in the strictest sense of the word a filter at all. We have been accustomed to regard the filter paper of the laboratory as the true type of filter and this to a great extent is true in that the pores in the paper are so fine that they are small enough to prevent large particles passing through.

To a large degree the slow sand filter acts in the same way as the filter paper because the layer of impurities at the surface, being formed of the impurities themselves, has smaller interstices which arrest all that come after.

Some other process must be possessed by the mechanical filter. Although difficult to demonstrate conclusively just what does take place within the depths of the sand bed the following is a plausible theory of the true process. The water delivered to the sand bed contains some more or less finely divided hydrate of alumina and other coagulated substances of a viscid or sticky nature. These particles of matter freely enter the large interstitial channels of the filter bed. In passing through these devious channels they sooner or later come into contact with a sand grain, to which they attach themselves. This may occur very near the surface or not until the matter has been carried several inches into the bed. As the sand is two or more feet deep the probability of any particle passing through such a depth without coming in contact with a sand grain is extremely low. After a few minutes' operation enough adhesive matter has attached itself to the sand grains to give the filter a high efficiency, that is to say, the sand grains have become coated with the adhesive substances derived

from the water so that any particles of matter which are not of a sticky nature would in turn become attached to this substance. This process of adhesion, or entanglement, or whatever we choose to call it, progresses for a period of time, say for some hours, and the channels keep getting smaller and smaller by reason of the quantities of material attached to the sand grains. This reduction in area of the channels first takes place near the surface of the filter. There is no indication on the surface of the sand of any impurities being retained, but if some of it is removed and placed in clear water it will be found that large quantities of matter can be washed from it. If a sample of sand is taken a foot or more below the surface it is found, during the early stages of the run, that there is very little foreign matter in it. In time, however, as the velocity through the upper layer of sand increases, due to the restriction of the area of the channel, particles of the retained matter are torn away from their anchorage and carried deeper into the bed, where, by reason of the greater area, the flow is reduced in velocity so that these particles can again reattach themselves. This process goes on until the voids in the top 12 inches of the sand bed are almost entirely filled with the impurities. At this period the resistance through the filter bed is so great that the velocity of flow cannot be maintained and in a very short time a surface film appears upon the filter, and the appearance of this film with some makes of filters is an indication that the filter bed must be washed, as the filter becomes impervious to water soon after its appearance. Samples of the sand taken from filters at different depths at different periods of operation seem to indicate the correctness of this theory.

The above conclusions have been arrived at after a number of experiments. In the first place, the writer has found that a very shallow filter, six inches in depth, made of the peculiar kind of sand used in mechanical filters, possesses a very low efficiency indeed. In fact it is hardly able to clarify the water. Again, in filtering other substances beside water, fresh cider for instance, that the filter sand has hardly any effect, although a filter paper would make the cider perfectly clear. Other fluids also show poor results.

Puech and Chabal have constructed a number of filters which in certain ways parallel this action of the mechanical filter. They differ in application, however, from the fact that they use a very much coarser medium with much greater interstices, and they filter the water repeatedly through several filters before the requisite degree of purification has been reached. The underlying principals, however, do not differ materially from those possessed by the mechanical filter, but there is a very decided difference in one point which is that the Puech filter has no method of cleansing and consequently the filter medium accumulates great quantities of foreign matter which is not of a sufficiently tenacious form to hold more than a portion of the finely divided matter in the water.

The mechanical filter consists of a suitable tank or container in which is placed the filter bed proper, which, as above described, consists of very carefully

screened sand. Rounded sand is preferable to sharp fresh quartz by reason of the fact that the active movement of the sand grains during the washing process tends to wear the corners off the sharp sand and decrease t in effective size. Underneath the sand bed is placed the strainer system, which is a series of strainers connected to suitable piping, whose office is to conduct the filtered water away from the sand bed and to distribute the wash water uniformly underneath it when the filters are being cleansed. Usually the strainers have orifices or ports in them smaller in size than the sand, but there are certain exceptions to this rule wherein large ports are used and the sand layer is carried upon successive layers of graded gravel. This latter plan is effective for a time but eventually the gravel layers become distributed and let more or less sand pass through, which, of course, enters the strainer piping and is very likely to obstruct it so that only a portion of the filter will wash. Also, sand in the filtered water is frequently very annoying in many industrial applications.

The filter must also be equipped with the necessary piping for reversing the flow of water for washing, filtering to waste and filtering. In the washing process the upward flow of water produces a rapid agitation of the sand grains which may be further increased by means of a revolving rake or by forcing air up through the sand. Occasionally a wash pump as well as a positive blower is required to assist in the above operation. Some filters must be washed with filtered water only while others possess greater latitude and can be washed with either raw or filtered water at will, there being a great advantage in favor of the filter which can use both, as it frequently happens that washing becomes necessary at a time when the supply of filtered water is greatly depleted, and it then becomes necessary to close down the entire plant while enough water wash is being accumulated.

If the filter plant is properly designed and the washing process is thorough, there should be no deterioration whatever of the filter bed, no deterioration of the quality of the effluent as the filter grows older, and no permanent accumulations of foreign matter within the filter bed.

It is inevitable that the streams in thickly populated districts should become the natural channels for industrial wastes. So long as we have industries so long must there be wastes which can be gotten rid of in no other practical way.

There are limitations to the burdens which can be placed upon manufacturers. Laws may be made which will stop the emptying of all wastes into streams, but these same laws will absolutely stop manufacturing, and in view of the fact that with certain very rare exceptions the most polluted streams can be used and reused for manufacturing purposes, the logical solution of the entire matter lays more within the remedial field than the prohibitive one.

THE NEW RESEARCH LABORATORY BUILDING OF THE AMERICAN ROLLING MILL CO., MIDDLETOWN, OHIO.

Received May 1, 1911.

The new laboratory building of The American Rolling Mill Co. marks a forward step in the development of industrial research.

The prime object of The American Rolling Mill Co. is to manufacture the purest ferrite iron that it is possible to produce on the large scale of operation permitted by open-hearth furnace practice. In addition to this, it is the intention to make this commercially pure iron the base of such useful iron alloys as may be demanded by future metallurgical development and discovery. The original attempt to manufacture an iron which should be practically free from carbon, manga-

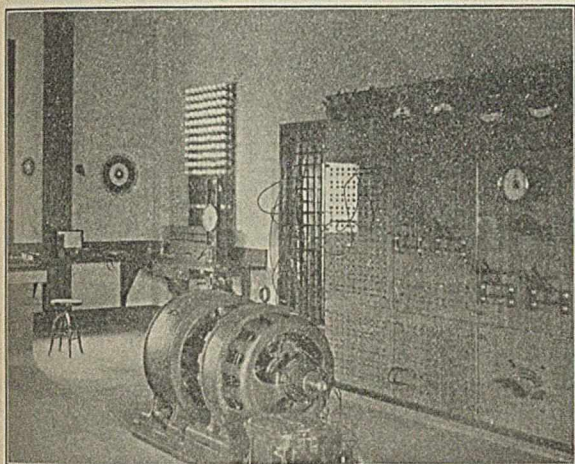


Fig. 1.—Motor generator and switchboard, Research Dept.

nese and the other ordinary impurities found in steel, and still produce a metal unburned and degasified, presented a number of unknown difficulties and obstacles which only systematic investigation could be relied upon to solve. This situation led The American Rolling Mill Co. to organize a Research Department and build and equip a laboratory building in which investigation work could be carried on exclusively, without being burdened with the necessary daily routine of analysis and test. As a result of this determination, the company is now equipped at Middletown, Ohio, with one of the finest exclusively iron research laboratory buildings in the country, if not in the world.

The Electrical Division, Research Department.—Four rooms on the first floor and two in the basement are used by the Electrical Division of the Research Department.

The large main laboratory, taking up the entire width of the building, gives ample space for the main switchboard, motor generator set, and pedestals and benches for general testing. This room is shown in the illustration, Fig. 1. The Standards Room and routine test room, which are adjacent to the main laboratory in the rear, are equipped with benches, pedestals and test or auxiliary switchboards suitable for special work.

The Computation Room which also serves as an

office is adjacent to the main laboratory in front, and is convenient for overseeing the work.

In the basement is located the Storage Battery Room and Shop, which also serves as a terminal room for outside power.

The electric wiring system for the building was laid out to be as simple and flexible as possible. All wires are laid in conduits, and under benches a metal trough is used, which will take care of any temporary cables, which may be necessary for special work, thus keeping the main floor free from obstructions.

Practically all power and distributing wires, terminate in receptacles both on the main switchboard distributing panel and on benches and pedestals, thus making possible many combinations with plugs and cord connection at the main switchboard.

Two 125-volt sets of storage cells are controlled from one panel of the main switchboard, arrangement can be made for series and parallel working, and taps are brought out to receptacles in such a way that almost any voltage within the limit of the set may be obtained.

Another panel on the main switchboard controls the motor generator set, which is of special design for magnetic testing requirements. The motor is of interpole type, 7.5 H.P. capacity, having a speed ratio of 4 to 1. The generator gives a sinusoidal wave form, is 2.5 K.V.A. capacity, and is operated from seventeen and one-half to seventy cycles.

The Electrical Division of the Research Department is equipped throughout for complete tests on steel for magnetic and electrical properties. Modern apparatus is used but old types are retained and can be used at any time.

Permeability of sheets and solid bars can be determined by various methods. Watt loss and ageing tests are made on sheet steel; conductivity and coefficient tests can be made on bars of sheets.

Particular attention is given to the question of standards of precision. The Standards Room, Fig. 2, is

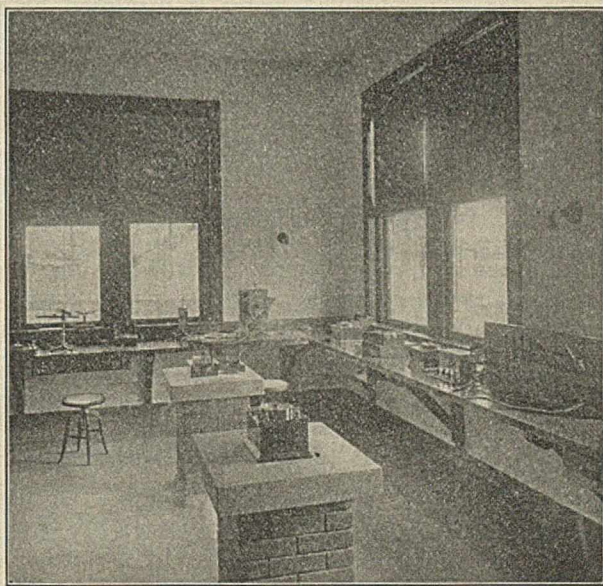


Fig. 2.—Standards room, Research Dept.

equipped for this work only, and here are kept several instruments which are used for standardizing the instruments which are used continually in the laboratory.

Standard samples for various apparatus are kept on file in this room, which are used from time to time in checking up.

Metallurgical Division.—The Metallurgical Division of the Research Laboratory occupies the entire second floor of the building and consists of eight rooms as follows: office, distilling room, dark room, private research laboratory, main chemical laboratory, supply-room, balance room, and microscopical laboratory.

All rooms are heated with low pressure steam and are regulated by the Johnson system of thermostatic regulation to 72° F.

Electric terminals are so arranged in the various laboratories and rooms that any current from one volt up to 220 volts can be obtained at all times.

The chemical laboratories shown in Fig. 3 contain

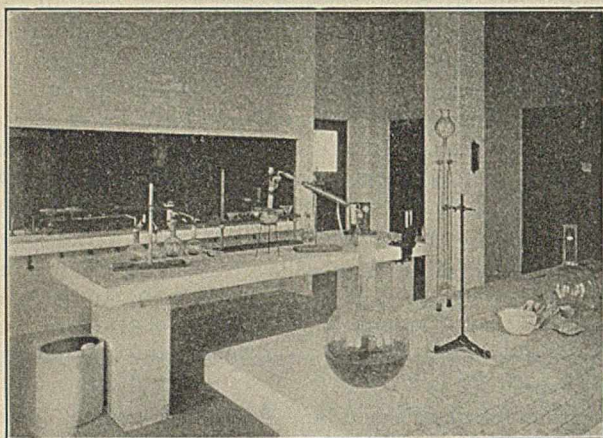


Fig. 3.—Chemical laboratory, Research Dept.

three vitreous enameled sinks connecting with terra cotta pipe to sewer. All sinks are fitted with three faucets, supplying hot and cold city water, and distilled water. The distilled water is furnished by a still in the building, heated by live steam, and has a capacity of ten gallons per hour, the still being located at an elevation of about ten feet above the floor, so as to give a sufficient head. It is connected by block-tin pipe to basement, and to all washstands of the building and tap in the storage battery room.

All gas, air and vacuum pipes in the chemical laboratories are embedded in concrete, the valves being placed beneath the table tops. Lead pipes are run from the laboratories to the basement where connections are made with gasometers from which various gases, such as oxygen, nitrogen and hydrogen can be obtained.

The shelves in the chemical laboratories beneath tables are suspended from the concrete table tops by iron bars.

The supply room shown in Fig. 4 adjoins the balance room on one side, and the main laboratory, being connected by double swinging doors. All shelves in the supply room, balance room and microscopical laboratory are of white carara glass. Supplies are un-

loaded in the supply room from a dumb waiter connecting with the basement storage room.

The balance room is located for a northern exposure, in order that the sun's rays would not interfere with

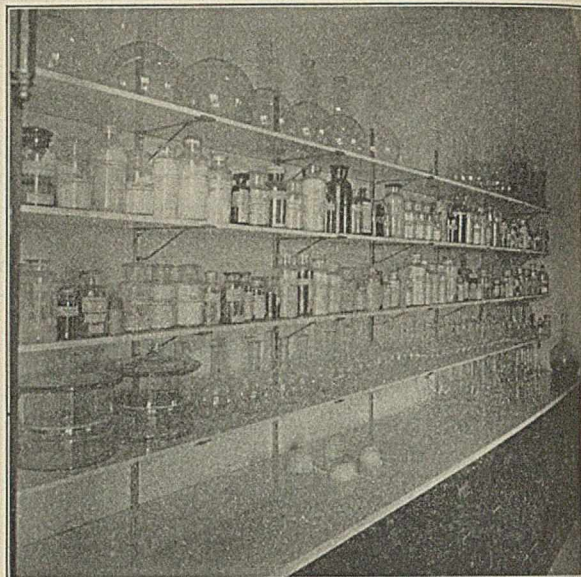


Fig. 4.—Storeroom filled with white glass shelves, Research Dept.

the eyes nor strike the balances so as to cause unequal expansion of the beams. In this room are located two Sartorius balances, one Torsion balance, and Harvard scale.

The dark room is fitted with double vestibule doors so as to exclude light, the bench tops are made of slate and contain the necessary equipment for photographic work. The window lights are double, consisting of the regular sash sliding vertically and glazed with amber colored glass. The other sashes are hinged and open into the room and are glazed with ruby glass. With this arrangement several combinations of light can be secured, *viz.*, daylight, amber, ruby, or a combination of ruby and amber together.

One room is devoted to the Metallurgical Research Laboratory (Fig. 5), the floors, ceiling and table tops

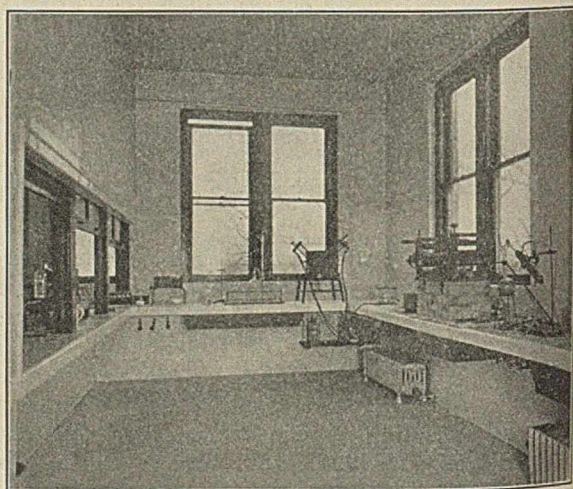


Fig. 5.—Metallurgical laboratory.

in this room being faced with white tile. A hood 17 feet long occupies one side of the room and is lined with slate walls and tile table tops. This hood is partitioned off, the other half being located in the main chemical laboratory. A special feature of this hood is that it has a reinforced concrete outlet for the fumes and has openings on two sides and is also open at the top. The side openings allow the wind to enter, strike a baffle wall where it is deflected upward and creates a very good draught. The outlet is 4 × 8 feet and looks like a burial vault except for the openings. The hood is well lighted with windows glazed with florentine glass.

The main chemical laboratory is lined with white tile throughout, glazed tile for the walls and ceiling, and vitreous tile for floors and table tops. The vitreous and glazed tile were tested before selection.

Two tables, five feet by ten feet, of reinforced concrete faced with tile and supported by brick pedestals, are located in this laboratory, and furnish ample working space for many men. These are in addition to the bench which runs the length of the room on two sides.

The microscopical laboratory contains a reinforced concrete table in the middle of the room, covered with a single slab of white glass weighing 850 pounds. The working benches are also of reinforced concrete construction, covered with white glass.

One room in the basement is used for corrosion tests and is furnished with shelves for crocks, holding various solutions, and at this time several thousand samples are being tested under different conditions.

One accelerated test consists of suspending samples of various materials on half-inch glass rods which pass through bars at the end of iron spokes, which are screwed into a hub. These hubs are all on one shaft, which is run by a small stream of water flowing into buckets on a wheel similar in construction to a water wheel, which when filled with water automatically turn the wheel, Fig. 6.

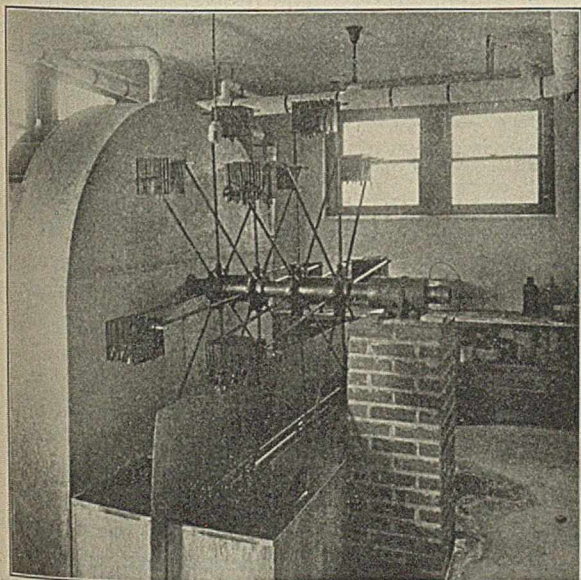


Fig. 6.—Wheel corrosion testing machine, Research Dept., known as the "Ferrous Wheel."

Three different tests are run on the wheel at the same time: one wheel dips the samples in well water, another in distilled water, and one in sea water. The wheel in turning exposes the samples immersed in the sea and well water to the air, where they are dried, while the distilled water samples are dried by burning natural gas which incidentally contributes carbon dioxide from the gas burned.

The apparatus throughout the laboratory is very complete and is of the best that the market affords.

An electric furnace of the electrode type is used in the Metallurgical Department, which is also equipped with an electric hot plate, silica tube furnaces, etc.

In the microscopical laboratory (Fig. 7) is a com-

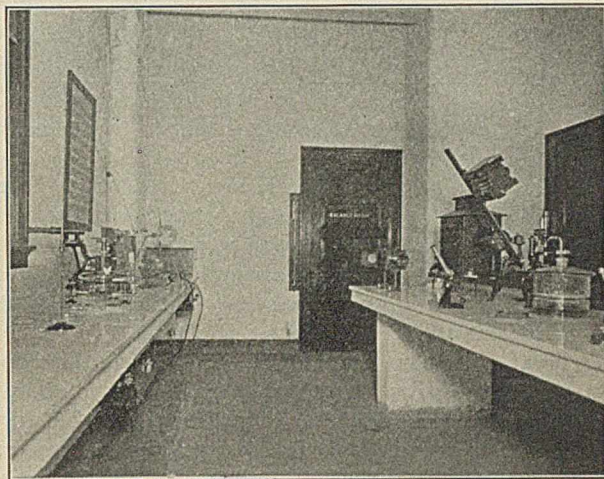


Fig. 7.—Metallographic laboratory, Research Dept.

plete equipment for the microscopical examination of metals, and in this room is a spectrometer of the latest model for studying the gaseous impurities of iron and steel.

Hardness tests are made by the Shore scleroscope.

In the physical test division which is located in the basement of the Research Laboratory, the most modern equipment for the physical testing of iron and steel is installed. This includes a Riehle 100,000-pound tensile testing machine, the Landgraf-Turner alternating impact testing machine, a complete equipment for preparing samples, etc.

AN ELECTRIC FURNACE FOR ZINC SMELTING.¹

By FRANCIS A. J. FITZGERALD, Consulting Chemical Engineer, Niagara Falls, N. Y.

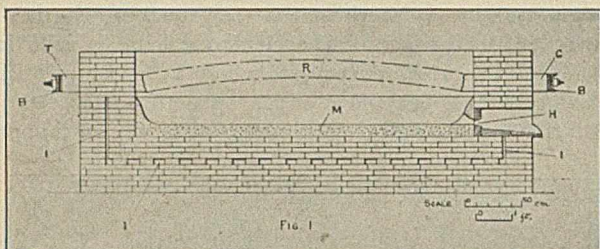
There is no branch of metallurgy which is apparently more suited to electric furnace treatment than that of zinc smelting. Moreover, the electric furnace possesses certain characteristics which make it specially applicable to the conditions of zinc smelting. It has long been known that when zinc sulphide and metallic iron are strongly heated the following reaction takes place,



but the reaction does not seem to be complete unless

¹ Abstracted from a paper presented before the Congress of Technology at the Massachusetts Institute, Boston.

there is a relatively large excess of iron, or unless the temperature of the reaction is very high. Imbert, however, discovered¹ that by using suitable "dissolvents" this objection to the process is overcome. Imbert, for example, found that ferric oxide and iron sulphide mixed together in the proportion of one part and three parts respectively formed a very fluid bath at a temperature between 1000° and 1100° C., and that



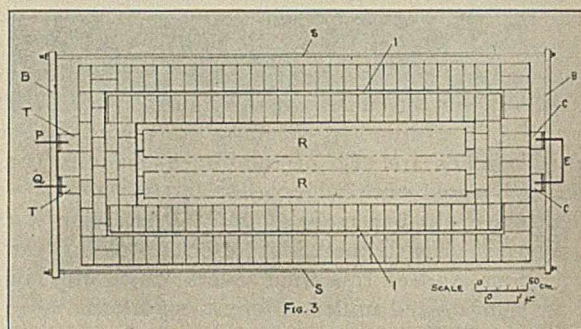
this bath would "dissolve" six parts of blende. When the blende is "dissolved" in a bath in this way the reaction with iron mentioned above takes place with the greatest ease, is complete, works at a comparatively low temperature and as a residue produces two distinct substances—a slag consisting of the gangue from the ore and a ferrous matte which may be used for the regeneration of iron, etc.

(A great many experiments were made with this process and the results were highly satisfactory, except that it was very difficult to construct a suitable furnace for the purpose.) Obviously working the process in the ordinary zinc retort furnace would not be satisfactory, for the process should be carried out with a much larger unit than a zinc retort. When it comes to applying fuel heat to such a process numerous diffi-

Process. One of these furnaces of 150 kilowatt capacity was constructed and worked under the author's supervision in Hohenloehutte, Upper Silesia, with highly satisfactory results.

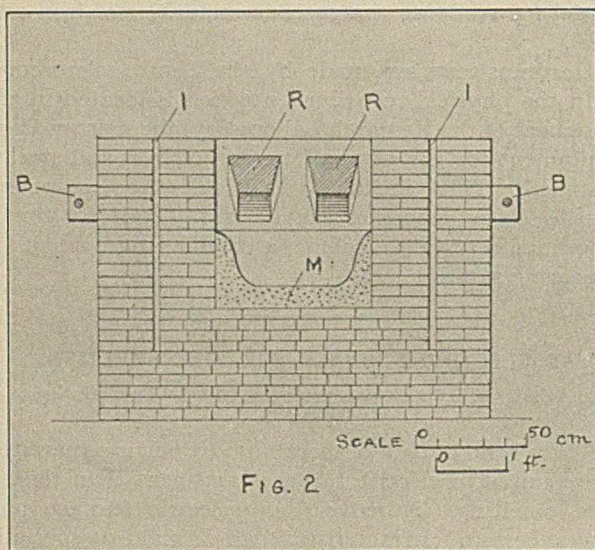
In order to design a satisfactory furnace it was necessary to keep certain points in view: The furnace must be gas-tight; the temperature must admit of careful regulation; the construction must be rugged so as to stand severe usage; the heat losses must be reduced to a minimum since electrically generated heat is always expensive.

In Figs. 1, 2 and 3 are shown respectively a longitudinal section, transverse section and plan of the furnace with the cover removed. The walls of the furnace are double with air-spaces I which are designed to prevent the loss of heat by conduction through the walls. The furnace is provided with carbons, T, T, C and C, the two former serving as terminals which are connected to the source of current by means of cable indicated by P and Q, while the two latter are simply connector



terminals which form the other terminals of the two sections of the resister R, R, and are connected by E. Bearing on the terminals T, T and the connector terminals C, C are channels B, B which are connected with each other by the tension rods S, S. The channels are, of course, insulated from the terminals. The furnace is lined with a suitable refractory M and is provided with a tap-hole at H. The resister of the furnace is built up of a series of corrugated plates, which are illustrated in Fig. 4, the figure on the right showing an end view of the plate, while the one on the left shows the shape in which the plates are cut as viewed from the front. In Fig. 5 is shown a view of the plates set up so as to form a resister. Considering one of the plates it is to be noted that the thickness is not the same from top to bottom, but increases from the bottom up so that when put in place they form an arch of very long radius as shown in Fig. 5. Because of the interlocking of the plates this arch form is not necessary, but seems to be desirable in the preliminary assemblage and is also utilized to produce a somewhat greater current density along the lower surface of the resister. The cover of the furnace, which is not shown in the illustration, carries feeding tubes by means of which the ore mixture may be fed into the bath below the resister.

The peculiar construction of the resister plates has two purposes: to give a sufficiently high resistance to the resister and at the same time to form an interlocking device so that even if no arch form is given to the



culties arise which are sufficiently plain without mentioning them in detail. This naturally led to the idea of using an electric furnace, and many experiments with various kinds were made. Finally Mr. John Thomson and the author designed a furnace which was used on a large scale in the working of the Imbert

¹ U. S. Patent 875,589, Dec. 31, 1907.

resister yet it will not fall down. A furnace was built with plates having these dimensions:

Length at top.....	405 mm. 16 inches
Length at bottom.....	255 mm. 10 inches
Width.....	165 mm. 6.5 inches

The two sections of the resister contained 71 plates each. This when cold had a resistance of 0.200 ohm and when running at the full capacity of 150 kilowatts, and with a temperature in the furnace of 1400° C., the resistance was 0.0375 ohm. This resistance is due almost altogether to the contact resistance between the plates, for by calculating the resistance of the carbon itself we find that it would not amount to more than 0.00064 ohm.

In order to regulate the rate of generation of energy in the resister there must be some means of varying the voltage at the terminals of the furnace. At Hohenlohehutte, as well as in the FitzGerald and Benie Laboratories where these furnaces have been worked, this is done by means of a transformer with several taps brought out from the primary coils which allow the voltage on the secondary circuit to be varied from 50 to 100 volts in 2.5-volt steps, and from 100 to 200 volts in 5-volt steps.

It will be seen that the weakest part in this furnace is the carbon resister, due to the fact that if working in an oxidizing atmosphere the resister will be destroyed. In the particular work for which it was designed, however, there would be no danger of this because the furnace is filled with vapor of metallic zinc. During the process of heating the furnace, or at any time when zinc vapors were not generated, there would be danger of burning through air leaking in; but this is easily overcome by keeping a reducing

The furnace is a highly efficient one. In one of the earlier models where the heat insulation was far from being satisfactory careful determination of all heat losses were made. When working at temperatures between 1250° and 1260° C. the total heat losses were 33 kilowatts, and when working at temperatures between 1400° and 1450° C. the heat losses were 42 kilowatts. Consequently when the furnace is working at full capacity, 150 kilowatts, the thermal efficiency at 1250° is 78 per cent. and at 1425° C. is 72 per cent. No exact determinations of the efficiency of later models have been made, but it is known to be much higher than those given above.

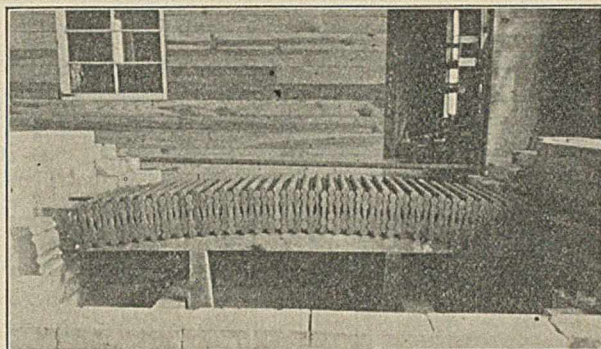


Fig. 5.

The metallurgical end of the problem has not been completely worked out, but the satisfactory working of the furnace has been clearly demonstrated, and furnaces built on similar principles have been used experimentally with great success in the melting of aluminum, copper, brass, etc. This is thought to be of some interest, as a development in the use of electric furnaces using the heat generated by the passage of an electric current through a resister. There is a tendency in electric furnace work to employ the arc which is often a mistake because of the difficulty in regulating the temperature. Finally, the furnace described above from its construction lends itself readily to adaptations which permit of using the combined heat effects of fuel and electricity, and it is thought that a great future is in store for furnaces of that type.

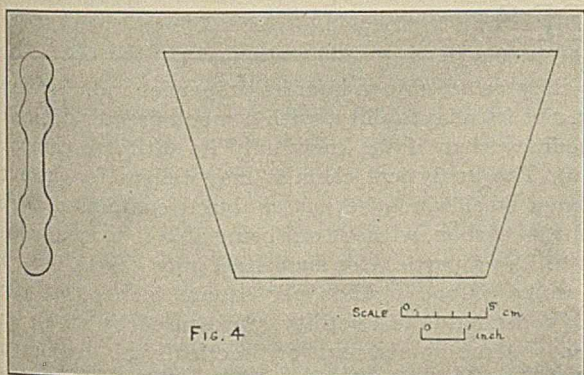


FIG. 4

atmosphere in the furnace slightly above external pressure. It has been found by actual experiment that a furnace of this type running continuously for two months showed no appreciable wear of the resister.

The regulation of temperature in this furnace is most satisfactory. In the Hohenlohehutte experiments thermo-couples of pyrometers were placed in several parts of the furnace to study the temperature conditions carefully. It was found that the most accurate regulation of the temperature in the furnace was possible, the workman in charge adjusting the rate of generation of energy in the resister so as to keep the needle of the pyrometer stationary.

A RADIATOR FOR PLATINUM CRUCIBLES.

By W. M. THORNTON, JR.

Received March 16, 1911.

The accompanying drawing illustrates a very simple radiator for the evaporation of solutions to dryness in platinum crucibles. P is the platinum crucible, held in position by the Hoskins chemists' triangle M (a special nickel alloy). The ends of the Hoskins' triangle are cut off at a point about midway their length and bent upwards. The Hoskins triangle is supported by the walls of the nickel crucible N at a height that will hold the platinum crucible with its bottom and sides about equidistant from the bottom and sides of the nickel crucible. The outer crucible is supported by a triangle of nickel wire, R, which in turn rests on a tripod, T, of iron (coated with aluminum

paint). By placing a small flame under the outer crucible the inner crucible is uniformly heated by hot air, and its contents can be rapidly brought to dryness without danger of spattering. After the cessation of fumes the lid can be placed on the nickel crucible and the platinum crucible baked at an even and moderately high temperature if desired. The apparatus in use by the author is constructed of a "rein nickel" crucible of 100 cc. capacity and a 1½-inch Hoskins triangle. These dimensions serve very well for platinum crucibles

of 20 or 25 cc. capacity. The following advantages are claimed for the apparatus:

1. It can readily be constructed of materials obtainable by any chemist at small cost.

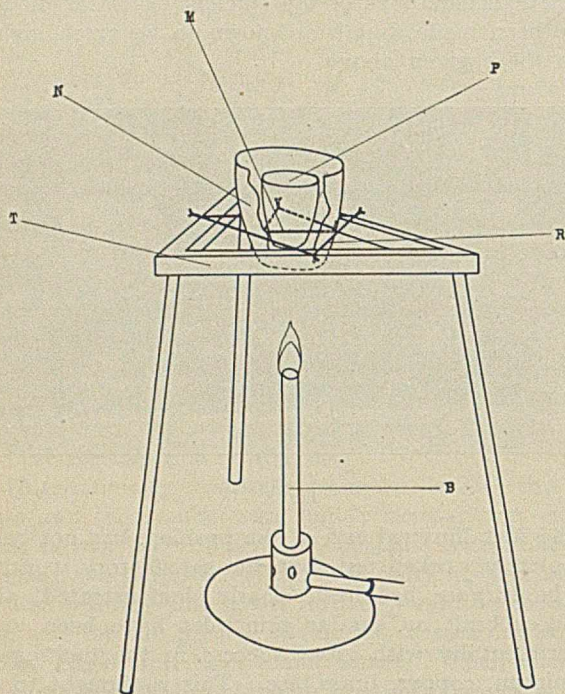
2. Nickel serves as an excellent material for a radiator because of its high conducting and radiating power. It is also very resistant to burning and rusting; and, hence, is very durable. The Hoskins triangle is made of a very refractory alloy in which platinum vessels can be held and heated with impunity.

3. Since the shape of the rein nickel crucible is approximately the same as that of the ordinary platinum crucible, all parts of the latter can be supported equidistant from the corresponding parts of the former thus securing uniform heating.

The author has found the above form of radiator especially useful in the analysis of some highly titaniferous rocks from Nelson Co., Virginia, in the laboratory of the Virginia Geological Survey. In separating the silica at 100° C. the titanium always hydrolyzes in large measure and precipitates on the separated silica. When the silica is subsequently determined by loss on evaporation with hydrofluoric and sulphuric acids, there is a considerable amount of solid titanium sulphate remaining. In conducting these evaporations on the hot plate, superheated steam and other vapors accumulated below a solid crust and much trouble was experienced on account of spattering. When the radiator was used, however, and with proper adjustment of the flame, spattering became a very rare occurrence.

The above description is given with the hope that it may prove of help to other chemists who may find it to their advantage to resort to a like expedient.

VIRGINIA GEOLOGICAL SURVEY,
UNIVERSITY OF VIRGINIA.



ADDRESSES.

METALLOGRAPHY AND ITS INDUSTRIAL IMPORTANCE.¹

By ALBERT SAUVEUR, Professor of Metallurgy in Harvard University.

Received April 17, 1911.

Twenty years ago the science of metallography was practically unknown and it is only within the last fifteen years that it has been seriously considered by metal manufacturers and consumers as a valuable method of testing and investigation. That so much has been accomplished in so short a time is highly gratifying to the many workers, practical or scientific, who have contributed by their efforts to the progress of metallography.

To realize the practical importance of metallography, it should be borne in mind that the physical properties of metals and alloys, that is, those properties to which these substances owe their exceptional industrial importance, are much more closely related to their proximate composition than to their ultimate composition, and that microscopical examination reveals, in part at least, the proximate composition of metals and alloys, whereas chemical analysis seldom does more than reveal their ultimate composition. It will bear repeating that from the knowledge of the proximate composition of a certain industrial metal

or alloy we are able to infer its properties and, therefore, predict its adaptability, with a much greater degree of accuracy than if we knew only its ultimate composition. The analytical chemist may tell us for instance that a steel which he has analyzed contains 0.50 per cent. of carbon, without our being able to form any idea as to its properties, for such steel may have a tenacity of some 75,000 pounds per square inch or of some 200,000 pounds, a ductility represented by an elongation of some 25 per cent. or practically no ductility at all; it may be so hard that it cannot be filed or so soft as to be easily machined, etc. The metal microscopist on the contrary on examining the same steel will report its structural, *i. e.*, its proximate, composition, informing us that it contains approximately 50 per cent. of ferrite and 50 per cent. of pearlite, and we know at once that the steel is fairly soft, ductile and tenacious, or he may report the presence of 100 per cent. of martensite and we know that the steel is extremely hard, very tenacious and deprived of ductility. Which of the two reports is of more immediate practical value, the chemist's or the metallographist's? Surely that of the metallographist. Nor is it only in the domain of metals that we find such close relationship between properties and proximate composition, for, on the contrary, it is quite true of all substances. How many

¹ Abstracted from a paper presented at the Congress of Technology, April 11, 1911, Boston, Mass.

organic bodies, for instance, have practically the same ultimate composition and still are totally unlike in properties because of their different proximate composition, *i. e.*, different grouping and association of the ultimate constituents! If we were better acquainted with the proximate composition of substances many explained facts would become clear to us. Unfortunately the chemist too often is able to give us positive information in regard to the proportion of the ultimate constituents only, his reference to proximate analysis being of the nature of speculation. Ultimate analysis has reached a high degree of perfection in regard to accuracy as well as to speed of methods, and analytical chemists have built up a marvelous structure calling for the greatest admiration. Their searching methods never fail to lay bare the ultimate composition of substances. But how much darkness still surrounds the proximate composition of bodies and how great the reward awaiting the lifting of the veil! The forceful and prophetic writing in 1890 of Professor Henry M. Howe naturally comes to mind. Speaking of the properties and constitution of steel, Professor Howe wrote:

"If these views be correct, then, no matter how accurate and extended our knowledge of ultimate composition, and how vast the statistics on which our inferences are based, if we attempt to predict mechanical properties from them accurately we become metallurgical Wigginses. . . .

. . . ; ultimate analysis never will; proximate analysis may, but by methods which are not yet even guessed at, and in the face of fearful obstacles.

"How often do we look for the coming of the master mind which can decipher our undecipherable results and solve our insoluble equations, while if we will but rub our own dull eyes and glance from the petty details of our phenomena to their great outlines their meaning stands forth unmistakably; they tell us that we have followed false clues, and paths which lead but to terminal morasses. In vain do we flounder in the sloughs and quagmires at the foot of the rugged mountain of knowledge seeking a royal road to its summit. If we are to climb, it must be by the precipitous paths of proximate analysis, and the sooner we are armed and shod for the ascent, the sooner we devise weapons for this arduous task, the better.

"By what methods ultimate composition is to be determined is for the chemist rather than the metallurgist to discover. But, if we may take a leaf from lithology, if we can sufficiently comminute our metal ('ay, there's the rub!'), by observing differences in specific gravity (as in ore dressing), in rate of solubility under rigidly fixed conditions, in degree of attraction by the magnet, in cleavage, luster, and crystalline form under the microscope, in readiness of oxidation by mixture of gases in rigidly fixed proportions and at fixed temperatures, we may learn much.

"Will the game be worth the candle? Given the proximate composition, will not the mechanical properties of the metal be so greatly influenced by slight and undeterminable changes in the crystalline form, size, and arrangement of the component minerals, so

dependent on trifling variations in manufacture, as to be still only roughly deducible?"

The above was written before the days of metallography or at least when metallography had barely appeared in the metallurgical sky and when no one yet had fancied what would be the brilliant career of the newcomer. Metallography has done much to supply the need so vividly and timely depicted by Professor Howe, precisely because by lifting a corner of the veil hiding from our view the proximate composition of metals and alloys it has thrown a flood of light upon the real constitution of these important products. Has the game been worth the candle? Will any one hesitate to answer in the affirmative Professor Howe's question?

Professor Howe with his usual acumen was conscious of the fact that proximate analysis, while likely to reveal a great deal more of the constitution of metals than ultimate analysis ever could, might still leave us in such ignorance of their physical structure as to throw but little additional light upon the subject. His fear was certainly well founded and surely if the proximate composition had been obtained by chemical analysis it would indeed have told us little of the structure or anatomy of the metals. In the domain of proximate composition chemistry can not do more for the metallurgist than it does for the physician. Chemistry does give invaluable information without which both the physician and the metallurgist would be in utter darkness, but it throws little or no light upon the anatomy of living or inanimate matter. Its very methods which call for the destruction of the physical structure of matter show how incapable it is to render assistance in this, our great need. The parallel drawn here between metals and living matter is not fantastic. It has been aptly made by Osmond who said rightly that modern science was treating the industrial metal like a living organism and that we were led to study its anatomy, *i. e.*, its physical and chemical constitution; its biology, *i. e.*, the influences exerted upon its constitution by the various treatments, thermal and mechanical, to which the metal is lawfully subjected; and its pathology, *i. e.*, the action of impurities and defective treatments upon its normal constitution.

Fortunately metallography does more than reveal the proximate composition of metals. It is a true dissecting method which lays bare their anatomy, that is, the physical grouping of the proximate constituents, their distribution, relative dimensions, etc., all of which necessarily affect the properties, for two pieces of steel for instance might have exactly the same proximate composition, that is, might contain, let us say, the same proportion of pearlite and ferrite and still differ quite a little as to strength, ductility, etc., and that because of a different structural arrangement of the two proximate constituents; in other words because of unlike anatomy.

It is not to be supposed that the path trodden during the last score of years was at all times smooth and free from obstacles. Indeed the truth of the proverb that there is no royal road to knowledge was constantly and forcibly impressed on the mind of those

engaged in the arduous task of lifting metallography to a higher level. Its short history resembles the history of the development of all sciences. At the outset a mist so thick surrounds the goal that only the most courageous and better equipped attempt to pierce it and perchance they may be rewarded by a gleam of light. This gives courage to others, and the new recruits add strength to the besieging party. Then follows the well-known attacking methods of scientific tactics and strategy, and after many defeats and now and then a victorious battle the goal is in sight—but only in sight and never to be actually reached, for in our way stands the great universal mystery of nature: What is matter? What is life?

Nevertheless there is reward enough for the scientist in the feeling that he has approached the goal, that he has secured a better point of vantage from which to contemplate it. The game was worth the candle. And if scientific workers must necessarily fail in their efforts to arrive at the true definition of matter, whatever be the field of their labor, they at least learn a great deal concerning the *ways of matter*, and it is with the ways of matter that the material world is chiefly concerned. Hence the usefulness of scientific investigation, hence the usefulness of metallography.

Like any other science with any claim to commercial recognition, metallography has had first to withstand the attack and later to overcome the ill-will and reluctance of the so-called "practical man" with a decided contempt for anything scientific. He represents the industrial Philistine clumsily standing in the way of scientific application to industrial operations. Fortunately, while his interference may retard progress, it cannot prevent it. Had he had his own way neither the testing machine, nor the chemical laboratory, nor the metallographical laboratory, nor the pyrometer would ever have been introduced in iron and steel works.

In metallography, as in other fields of research, American workers, with very few exceptions, have been quite willing to let Europeans perform the arduous and generally unrewarded task of the pioneer, being content to wait, before entering the field, until practical results were fairly in sight. Such course, which is never to be commended, becomes intolerable when accompanied, as it so frequently is, by the coarser boasting attitude of the man believing himself smarter than his neighbor whom he regards in the light of the cat drawing the chestnut from the fire. America, barring brilliant exceptions like Richards at Harvard and Noyes at Tech, does not as yet do her share of the pioneer's work in investigations which do not give evident indications of quick commercial returns. The unselfish, nay self-sacrificing spirit of the true scientist is of far rarer occurrence in the United States than it is in Europe and especially in France. America has not yet produced a Pasteur nor a Berthelot, intellectual giants, profound scientific thinkers, whose conception of the duty of the scientist as a man is so lofty that they have despised the wealth within their easy reach to devote themselves unreservedly to the betterment of their country or rather of the world, for they

are morally so great that the entire world becomes their fatherland: Humanity claims them.

Speaking in 1904 of the practical value of metallography in iron- and steel-making, I wrote the following which it may not be out of place to reproduce here: "History, however, must repeat itself, and the evolution of the metallographist bids fair to be an exact duplicate of the evolution of the iron chemist; the same landmarks indicate his course: distrust, reluctant acceptance, unreasonable and foolish expectation from his work, disappointment because these expectations were not fulfilled, and finally the finding of his proper sphere and recognition of his worth. The metallographist has passed through the first three stages of this evolution, is emerging from the fourth and entering into the last. For so young a candidate to recognition in iron- and steel-making, this record is on the whole very creditable."

We may say to-day that he has definitely entered the last stage and that the adverse criticisms still heard from time to time, generally from the pen or mouth of ignorant persons, are like the desultory firing of a defeated and retreating enemy.

In the United States alone the microscope is in daily use for the examination of metals and alloys in more than two hundred laboratories of large industrial firms while metallography is taught in practically every scientific school or technical school.

THE HYGIENE OF THE WHITE LEAD INDUSTRY.

By ALICE HAMILTON, M.A., M.D., Illinois Commission on Occupational Diseases.

Received April 13, 1911.

The Illinois Commission on Occupational Diseases made a study last year of the poisonous trades of Illinois, among which the lead trades hold by far the most important place. In the course of this work it was my task to investigate personally the white lead factories, and I visited ten such places in and near Illinois, eight using the Old Dutch Process, one the rapid modification of this process known as the Carter Process, and one the Mild or Rowley Process. During the summer and autumn I had an opportunity to see some white lead works in England, Belgium and Germany, and to compare the hygienic conditions in the white lead industry in those countries with the conditions in our own.

Like any American I went to Europe prejudiced in favor of my own country. It is true I knew that there was an admirably planned system of government control of this dangerous trade in Europe but I had been led to believe that such control was absolutely necessary in the older countries, that hand-work, the employment of women, the wretched physique of the workmen made necessary a sort of protection which would be absurdly superfluous here. I was destined to find that the reverse is true, that not only is the foreign workman protected against the dangers of work in white lead, but the dangers are not nearly so great with European methods as with American. In the following pages I will try to give briefly the difference between the methods used here and in Europe.

As far as the construction of European white lead and color works is concerned compared with ours, I should say that their best was not as good as our best, nor their worst as bad as our worst. Nowhere did I see a white lead plant as admirably built as some American factories, with their concrete walls and floors. On the other hand, the most antiquated and economically managed factories there cannot be as bad as some of ours are, because the law insists upon certain essentials in structure. For instance, there is a factory in Chester which is 143 years old and looks it. The buildings are low and shabby, irregular and dark, but the stacks are built of brick, glazed on the outside, the floors are of stone or of sheet iron, the water supply throughout is adequate so that the floors may be repeatedly flushed, the lavatories, bathrooms and lunch-rooms are what they should be, all of these details being controlled by the Home Office. A manufacturer may let his plant run down in any other way, but he may not let it become a dangerous place to work in. In Germany the same thing is true, in Belgium it is only partially true. State control there does not seem so strict.

The standard of cleanliness is not as high as it is in our best factories, though of course it is never allowed to fall as low as it does in some of our worst.

One thing which state control brings about in Europe is the complete separation of dusty from non-dusty operations. You will never see there, as you sometimes see here, dry packing or mixing carried on in the same room with the filling and labeling of white paint kegs.

Machinery has reached a high point of development, a fact which came to me as a surprise for I had repeatedly been told that I should find hand-labor everywhere in Europe. There are some places where processes are still done by hand which can be done mechanically, but in the best factories hand-work has been superseded by machinery as much as it has with us. For instance at Debbaudet Bros., in Brussels, where the process is more nearly like ours than in any other place I saw, there is as little hand-work as possible and there are all sorts of most ingenious devices which I have never seen in any other place. In the red lead department of Cookson's, in Newcastle-on-Tyne, machinery is used to the same extent as it is here and in Leyendecker's, in Cologne, it is much more highly developed, human labor seems almost eliminated.

For those who are not familiar with the Old Dutch or Stack Process for making white lead it may be best to give a brief description of this process as carried on in the United States. Pig lead is melted and cast mechanically in the form of "buckles," thin plates with open spaces and cross-bars, in shape resembling old-fashioned shoe buckles. These are conveyed to the stack house, a more or less open building divided into compartments or stacks, with concrete or wooden partitions. Here the buckles are placed in earthenware pots which contain dilute acetic acid and laid in rows upon a bed of spent tan-bark and covered with boards. Another layer of bark is placed on these boards and then another layer of pots and so, on until

the stack is full. It is then left untouched for about 90 days when the acetic acid vapor together with the CO_2 from the fermenting tan-bark has converted the lead into the basic carbonate, white lead. Uncovering and emptying the pots of white lead is a dusty and very dangerous piece of work. These "corrosions" are then carried in trucks, by hand or by crane, to the "dump" which is a large opening, with usually a very inadequate exhaust system, into the separating apparatus. Once inside the separator the lead is not a source of danger for the machines are tightly enclosed, and only the repairing machinist need run any risk in this part of the process. The separating is effected by means of rollers and screens, and the final products are white lead powder which is discharged into water, and fragments, large and small, of "old lead" or uncorroded buckles which are covered with white lead and very dusty to handle. In some American factories it is customary to remelt these and they are usually shoveled into open trucks, wheeled to the casting-room where they may be dumped to lie on the floor till they are needed or put at once into the kettle. In other places the "old lead" is given a second corrosion in the stacks. All this handling of dry fragments is dangerous for the men.

After it has passed through water mills, bolting machines and settling tanks, the white lead is pumped into great drying pans which stand one over the other in a hot room. At the end of about five days the water has passed off and the powder is ready to be shoveled out and conveyed to the barrels or the oil mixers. This is the most dangerous spot in an American white lead factory, and although I have seen some effort made to diminish the dangers I have never seen a drying room which was even moderately safe. The other dangerous jobs are the barrel-packing, which is mechanical but always accompanied by dust, heading up barrels, filling chasers (oil and lead mixers) which in some factories are well covered and free from danger, and the work in the dust-collecting room which is always attended with risk. In a well-managed American white-lead factory there are always some dusty, dangerous processes; in a carelessly managed one there may be no spot in the factory where it is really safe to work. Dry sweeping is the rule in almost all the American factories I have seen.

In England and Europe the Old Dutch Process has developed differently in many details.

Nowhere are buckles cast, always long strips, sometimes solid, sometimes with three or four holes, sometimes with depressions like a long waffle. They are often eighteen inches long and an inch thick. At Locke-Lancasters each strip weighs four pounds. The pots are small and the strips are either piled in layers on top of them or they are bent on themselves and laid edgewise on the top. English factories do not set stacks with cores from former corrosions, they always send these to the melting pot, but in the Brussels factory the cores are used to make the top layer of each set of pots. This is, of course, a disadvantage from the hygienic point of view, although the danger is lessened by drenching them before they are handled.

The Old Dutch Process is used in Belgium and almost everywhere in England. At Cookson's, in Newcastle, I found both Stack and Chamber processes in use, and the management much more enthusiastic for the latter. In Germany it is all Chamber Process, which means that the strips of lead are hung in large chambers into which steam, acetic acid vapors and CO_2 are conveyed by pipes.

It was only in the filling of the stacks that I saw women employed anywhere and this was in an old factory in Chester, where they still have women carry baskets of tan-bark up ladders to the stacks. Their employment is prohibited in any part of the work where white lead is handled, and though many manufacturers told the Parliamentary Commission that they would be driven out of business if such a law were passed, they seem to have been agreeably disappointed.

In Germany and England stacks and chambers must be thoroughly watered before they are emptied, so that there will be no dust. From then to the final drying, all the process is wet. The big corroded strips are picked up and laid in wooden trays and then are carried on trucks to the separator. As a further precaution against dust each tray is rapidly plunged into water, "baptized" they call it, or sprayed with water, before being emptied into the separator. Separation is done by washing and does seem very simple, far simpler than our dry method. Sometimes it is done by hand, as in one of Locke-Lancaster's plants where 15 tons are separated in a day, in others it is done by mechanical crushing in water. But it consists simply in washing the white light powder from the heavy solid core which falls to the bottom, while the water and white lead pass on, first through metal sieves, then through two sets of granite stone mills, then through silk sieves to the settling tanks.

From the point of view of the hygienist this method is so much better than ours that one longs to see it adopted here. I cannot, of course, speak of it from any other point of view, although to an outsider like me it does seem economical and sensible. There are no small particles to be gotten rid of as from our corroded buckles, only large solid cores. And they do not aim at anything like complete corrosion. Locke-Lancaster's foreman stated that 36 per cent. to 50 per cent. corrosion was what they expected.

From here the process varies in different factories. In some of the less advanced English plants, the product of the last settling tank, now a thick soup, is ladled into shallow trays which are carried to the shelves of the drying rooms. In the best factories, such as Cookson's, Locke-Lancaster's, and Leyendecker's, it is pumped by means of compressed air into a vacuum receiver where it is forced through filter presses, and all but 16 per cent. of the water removed. This paste then is partly used for the making of pulp lead, in England, or sold as it is in Germany where pulp lead is never sold. The rest is put into shallow trays and these are laid on trucks which are wheeled into drying cells. A high temperature is maintained here, and after three days the white lead is dry. Then the trucks are wheeled out, the workman only opening one door at a time, and not stepping inside the cell.

The trays are then lifted one by one and emptied through a small opening which is variously made but always protected by a hood and an exhaust. The cleverest arrangement I saw was in Brussels where the tray was set on a shelf into which it fitted tightly. This was tipped over under a hood, and then tipped back again. Cookson's has a different drying process which they worked out independently, in their effort to get away from the dangers of the old-fashioned stoves. They shovel the paste into furnaces, and the furnace room is beautifully clean and well-ventilated. The furnace is emptied by means of a long-handled shovel which passes through a canvas bag. The top of the bag is fastened to the edge of a hood with an exhaust, which is right over the door of the furnace, and the bottom falls over the truck into which the dry powder is being shoveled. There is absolutely no escape of dust.

The dry white lead as I saw it was much harder, more porcelain-like than ours is, and the Europeans insist that you cannot get it bone-dry by our method.

You can see what an enormous contrast there is between their methods and ours as far as danger is concerned. In the best factories, handling of the dry product is accompanied by practically no dust; in the worst the dust is slight in amount, while I have never seen an American drying-room which was even moderately dust-free.

Barrel-packing is done as it is here, in most places, and again I should say that it is nowhere as careless or dirty a process as I have seen it here, and nowhere as clean as I saw it in one American factory. In Belgium I saw an interesting device. The barrel—stronger and better built than ours—is already headed up and the lid has a round hole some six inches in diameter. Into this is fastened one end of a strong rubber tube, the other end of which is hanging from the bottom of the white lead hopper. As the powder falls into the barrel it is shaken down because each barrel stands on a platform which is made to jump up and down by means of compressed air. I saw a whole roomful of barrels in process of filling and not a particle of dust. These of course need no heading-up, another great advantage. Heading-up is considered dangerous work, and all sorts of devices are being experimented with. In Germany, as in some of our factories, each barrel is lined with strong paper which is folded down over the top before the lid is put on. In an English factory they are trying a lid with expanding leaves, which fits into place without hammering. I may add that no European country will allow shipment of leaky barrels or barrels smeared with white lead dust. In England the manufacturers are in favor of the Home Office forbidding the sale of dry white lead. They consider the objections to pulp lead a mere matter of prejudice. In Belgium the state allows the sale of dry white lead only to certain accredited color houses.

All chasers are enclosed and provided with exhausts, and "enclosed" does not mean that there are large windows in the sides which are habitually left open as is often the case here.

The process in Belgium differs from those I have described, and is more like the American because separation is done dry, and the stacks are not sprayed

before stripping. However, the buckles or rather strips, are lifted by hand, not dumped, and are carried in trays to the separator. I have already described the clever arrangement for preventing dust at the separator opening. The dry cores drop out from the separator under a falling lid with a good exhaust. They are taken in covered trucks—no open trucks of dry corosions are found anywhere—and are used to set stacks, being put on top of the layers of blue lead. Dust collection is not needed in English and German factories, but in Belgium it is necessary, and in one place I saw it done in a very novel way. There is a tightly-built little brick house in one of the rooms and the dust which enters it is driven by means of fans against some curtains of heavy felt which hang from the ceiling and are kept wet by means of a spray of steam. The moist white paste is scraped off these curtains, which never are allowed to get dry, so that the dust house is really not dusty at all. It seems to me the simplest and certainly the safest device I have ever seen.

As to the hygiene of the white lead industry, many of the processes I have been describing have been devised in the effort to do away with the dangers inherent in the work, and here Cookson's led the way. In fact, the Home Office rules of 1883 were modeled largely on the practice obtaining then in Cookson's plants. That seems to me a very proud record for a commercial house.

The study of the past 30 years has shown that lead enters the body through inhalation and swallowing, not through the skin to any important extent. The English lay more stress on inhalation than the Germans, claiming that lead is absorbed by the blood vessels of the lungs, while the Germans think that what is breathed into the mouth is swallowed.

Of course the methods of protection are founded upon these facts and resolve themselves into suppressing the dust and seeing to it that the workman is free from white lead when he eats his lunch and when he goes home and that he does not carry it into his mouth while at work by chewing tobacco.

The abolition of dust I have already described. The care of the workman's person consists in supplying washing and mending his working clothes, supplying head-covering and sometimes shoes. At Leyendecker's all the men wear wooden shoes while at work, which is a splendid protection against the damp, cold floors.

Everywhere the men are provided with proper washing facilities and, not only that, but they must, by law, be given sufficient time to wash up, and all those who are engaged in the dustier processes must bathe every day. There is a bathing record kept, and it is a case of no bath, no pay. A man must show his bath receipts, so to speak, before he receives his wages. In the less dusty processes the workman need bathe only once a week.

Washing arrangements there are not as luxurious as they are here. On the other hand they are very much more carefully planned. The Englishman does not waste his money on luxuries, so you will not find as beautiful sanitary equipment there as you may

find in this country, but the Home Office sees to it that he gives the employees what they need. The men have usually individual towels, numbered with each man's number to prevent stealing. There are long porcelain-lined sinks with no stoppers, so that a man must wash in clean running water. Usually big cans of soft hand soap are provided. There are sprays for the head attached over the sink, and long nail brushes are fastened to the wall just above the basins. The great difference between our arrangements and these does not lie in equipment, but in the fact that the foreign workman's personal cleanliness is compulsory, his employer is held responsible for it; the American workman (usually a Slav, Italian, Greek or negro) may wash or not, as he sees fit.

The lunch-rooms are not at all luxurious but there is always provision for heating food. Europeans insist that it is very important in white lead factories that the men should not go to work fasting, for nothing so favors lead-poisoning as that, and there is no better safeguard against it than the presence of food in the stomach. So we find always in England and on the Continent a half-hour given in the morning for breakfast. American employers if they inquired would find that their foreign-born workmen, and so many of them are foreign-born, need that pause for breakfast, for they are not accustomed to the hearty breakfast that fits the American workman to keep at work till noon. Another thing that struck me over there was the strict prohibition of tobacco-chewing. Wherever I have been in this country in white lead or red lead, or dry color establishments, or paint factories, I have asked the foreman whether he encouraged tobacco-chewing among his men, and I think there have hardly been more than one or two exceptions to an affirmative answer. Many a time the foreman says he teaches his men to use it. I find also that it is the opinion held by practical painters that the constant expectoration keeps the mouth free from lead dust. Tobacco-chewing is forbidden in Europe and in England because they say that the plug of tobacco is carried in a man's dusty clothes, his working clothes, and that it is taken out with lead-smearing fingers and passed into his mouth often through a lead-smearing mustache. The rules as to this are very strict. I was in one lead establishment with an inspector from the Home Office, and he wanted to test a certain exhaust and asked for a match. The foreman had none but one of the workmen had. The inspector told me later that as he was on a visit of courtesy he did not follow up the match episode. I asked him what he meant, and he said that any workman who had a match about him no doubt had some tobacco too, and that he always investigated such incidents.

Medical inspection is required by law over there. It is gratifying to know that many American white lead factories now have medical care for their men, but they have not yet taken the next logical step, which is that the medical inspector be told to weed out the men who are unduly susceptible to lead poison. A certain number of men cannot stand exposure to lead. Hirt, a great German authority, says that about 20 per cent. of all lead workers are over-susceptible and should

never attempt to do such work. The English and German physician examines all applicants for work and rejects the weakly and anemic. It is also the rule that a man once really leaded shall not return to a dangerous part of the work. Here, I find in a great many places that a man drops out because he is poisoned and goes home or to a hospital, and when he has recovered he is allowed to go back to exactly the same sort of work.

Of course in many ways it is much easier to manage men who are of the same nationality as their foreman and who speak the same language, as is the case in most foreign factories. On the other hand, I was told that the Italian help employed in one English factory were more docile than the Englishmen, who are sensitive about their individual rights and do not like to be controlled as far as personal habits go. It would certainly seem possible to make our men as amenable to discipline in the matter of cleanliness as in the matter of other factory rules.

It may be asked, What is the result of all this elaborate regulation in England and Europe? I have been told by American manufacturers that there is actually less lead-poisoning here than over there. Fortunately it is possible to answer that quite definitely. In Cookson's plant in Newcastle where 182 men are brought in contact with white lead, the most rigid weekly medical examination did not reveal one case in the year 1909 to 1910. In Locke-Lancaster's place there was not one case among 90 men for the five years between 1903 and 1908; there was one in 1909.

Let us look at our factories now. I can give partial statistics of six places which manufacture white lead, and when I say partial, I mean that in none of these factories is the whole truth about the men known. Three of them have the physicians examine all of the men employed in handling lead, but do not follow up those who quit work—the English and German laws require this to be done—a third factory has a physician see only those men who complain or whom the foreman suspects of illness, the other two have no medical inspection and the only way I have been able to find any cases has been through hospital records, and the men who go to hospitals are only the very severely poisoned, who have no families to care for them.

These are the statistics:

In Factory No. 1, medical examination showed one man in eight to be at the time suffering from plumbism.

In Factory No. 2, one man in nine.

In Factory No. 3, 28 per cent. of all employees have been leaded.

In Factory No. 4, where medical examination is only on complaint, 25 cases occurred among about 200 men, or one man in eight.

The two factories which have no medical inspection¹ are sending to a public hospital three cases and four cases respectively a month. This would mean 36 cases for one during the year and 48 for the other, but we know that not one-half of the leaded men go to the hospital and that the actual figure would be so much larger.

¹ One has recently engaged a physician to examine all the men regularly.

In the whole district of Newcastle-on-Tyne there were employed last year in the white lead works, 1320 persons and only five suffered from lead-poisoning, or one for every 264 employed. In Illinois last year there were from 425 to 450 men employed and we discovered sixty-three cases of lead-poisoning, or one for every seven men employed. This is a startling contrast and one that should make the American manufacturer stop and think.

POTASH FROM FELDSPAR.

By B. HERSTEIN, Technical Expert of the Tariff Board.

Received February 8, 1911.

The recent controversy between the German producers and the American importers of potash salt, a controversy which involved also the governments of both countries, has brought out forcibly the monopolistic privileges enjoyed by Germany through the sole possession of potash deposits and has emphasized the fact that most of the other nations, our own pre-eminently included, have to depend entirely upon that country for their supply of this absolutely indispensable plant food.

Irrespective of the economic aspect of the questions involved—and this is big enough even though we are accustomed to figure in big units—it must be admitted that the situation created by such a condition is far from satisfactory, and has naturally led numerous investigators to work on the subject.

It seems to have become an established fact that of the very few mineral deposits in which the United States, otherwise so bountifully provided, are deficient, potash is agriculturally available, *i. e.* soluble, form is one. However, potash in the form of insoluble silicate or aluminate makes up no inconsiderable part of the weight of feldspar and similar rock formation, and of these the supply in this country is practically limitless. As a plant food, however, the potash in this natural form is not assimilable and therefore of little value. The gist of all the many proposals so far made to secure from domestic sources the necessary potash salts required for agricultural purposes has consequently centered in the use of these rocks as raw material, differing only in the form proposed to render the potash available. The literature on the subject is fairly abundant and easily found in patent, technical or scientific publications.

As far as the chemistry of the problem is concerned the field seems to have been covered fairly well, and in submitting an additional proposition in this direction, the fact is not overlooked that taken separately the individual features of this proposition may present little novelty, emphasis being laid on their combination, which is absolutely essential, and appears not to have been suggested before. Those who have given the subject more than casual thought know also that the problem is more than chemical and more than commercial, and the plan is submitted here solely with the intention of broadening the legitimate scope of discussion by presenting possibly new and

important features towards a solution to a complicated problem.

The chemical reaction involved in the process as proposed needs no further elaboration, having been proved in practice; it is in fact being used in somewhat modified form as an analytical method for the determination of alkalis in silicates. It consists in heating the finely ground feldspar with calcium chlorid eventually under addition of some limestone, whereby the silicate is decomposed with the formation of alkali chlorides—readily removable—and calcium silicate or aluminate. The process differs, as can be seen, from the well-known Lawrence Smith method only by the fact that the calcium chloride is used here directly, while in the other the silicate is heated with a mixture of ammonium chlorid and calcium carbonate, which reagents form calcium chlorid as an intermediate product and thus bring about the decomposition of the silicate. Experiments have shown that the reaction can be carried through and decomposition of the feldspar accomplished with little more than the theoretical amount of calcium chlorid if the ingredients are intimately mixed and the temperature well regulated and maintained for a sufficiently long time. Increasing temperature requires a corresponding excess of calcium chloride.

Cushman, working along the same lines without adding limestone, seems to have made the same experience and rejects the process merely because it is too expensive, as indeed it would be if there were no other considerations, to mitigate and outweigh this otherwise justifiable injunction.

In the first place, the calcium chlorid required for the reaction is a waste by-product obtained in huge proportions in the manufacture of soda ash and salt. It is less than valueless and the owner, if assured of a continuous outlet, could well afford to let it go at a nominal price.

Secondly, the residue left after the potash has been removed, by aqueous extraction or otherwise, contains all the essential elements of a cement into which it could be transformed by ignition, supplementing the deficiency of calcium oxid with limestone, if required. No previous grinding would be necessary in this instance, since with the temperature kept reasonably low, the mass does not clinker and disintegrates easily in water. Moreover, both the silica and the alumina of the original feldspar have been rendered extremely reactive and should therefore readily form cement on the subsequent operation.

Another way to carry out the process would be to combine the two stages into one, *i. e.*, add limestone and an excess of calcium chlorid to the finely ground feldspar and heat the mass to clinkering, whereby the potassium chlorid would be driven out by the higher temperature and could be collected in a suitable way. The heat prevailing in a rotary cement kiln should prove amply sufficient to produce this result. The cement clinker would be formed simultaneously with the distillation of the alkali chlorid and would need only final grinding. In this form the process would not differ materially from

the ordinary way of making cement except in the presumed condensation of the alkali chlorid.

The plan as outlined, if feasible in any form, would accomplish:

1. The utilization of the valueless waste product, calcium chlorid, which at present is but a source of annoyance and expense.

2. The production of cement.

3. The production of potash salts for both industrial and agricultural purposes—a combination of three important features which should bring the proposition within the range of practicability.

The plan is embryonal, of course, as any plan of this character, based mostly on *a priori* consideration, must be. The problems involved are vast and touch materially the interests not only of great industries but presuppose also careful consideration and coöperation on the part of different sciences: chemistry, engineering, geology and—not the least—economics. The difficulties militating against the realization of any proposition to utilize the gigantic stores of potash compounds lying unavailable in the feldspar and similar rocks are great and should not be underestimated. A review of the more important objections may help to a better conception of the subject.

First, as to the supply of the principal raw material itself. Feldspar, it has been stated, is most abundant in many of the states and will undoubtedly be found in others. But, unfortunately, the deposits are compact only in isolated instances, more frequently, however, they are contaminated with quartz and the mineral requires picking before it can be put to its proper use. Also the percentage of K_2O varies within wide limits, some being as low as 5 per cent. and even under, others about 10 per cent., and some considerably above this figure. An average yield of 6 per cent., or 120 pounds of K_2O per ton, would probably be a safe limit to calculate upon; and this would be obtained in the form of potassium chlorid. This is not the most desirable and therefore not the highest paid form of potash for agricultural purposes, yet it is used very extensively. The above yield would correspond to 190 of KCl per ton of feldspar, the money value of which on this side of the Atlantic is at present, according to the price set by the German syndicate, \$4.50.

This sum is contingent upon one factor which requires consideration. The valuation of potash salts, at least for the export trade, is fixed, quite arbitrarily it seems, by the German commission entrusted with this task according to the law passed last Spring by the German Reichstag, which abolished all competition for trade between the individual mine owners. The monopoly is most complete and it is fair to assume that we are paying monopoly prices irrespective of the cost of production. The fact that individual operators contracted to furnish potash salts for some years to come to American importers at prices considerably lower than those fixed later by the commission, seems to support this interpretation, and the potash value of \$4.50 per ton of feldspar holds true

only as long as the Germans see fit to maintain their present prices.

As a potash proposition alone any attempt to utilize our feldspar as raw material offers therefore little attraction because a return of \$4.50 per ton would barely more than cover the cost of the raw materials themselves, *viz.*, feldspar, calcium chlorid, limestone and coal. But each ton of feldspar is assumed in the plan also to produce five and possibly six barrels of cement of an average value of \$4.80, which would bring the total returns up to \$9.30 per ton of feldspar. Is this sum sufficient to pay all the expenses and allow also some interest on the large investment that would be required? In answer to this it could be pointed as a parallel that cement is now selling at not much more than about \$4.50 per ton, and yet seems to pay at that price for the raw materials, cost of operation, etc., and only quite recently it has been stated by no less an authority than Dr. McKenna that the actual cost of materials and labor is about 12 cents per 100 pounds of cement. The \$4.50 obtained for the potash would, therefore, have to cover only the additional cost of the feldspar, the cost of some 200 to 250 pounds of calcium chlorid, a small additional charge in operation, and the interest on the additional investment required to provide for the collection of the potash salts. All evaporation, it is figured, is to be done by the waste heat of the kilns. Another item of extra expense would undoubtedly be found in the heavier freight charges because the raw materials would have to be brought together from different localities which is not the case in the cement industry.

An important factor to be considered is, to what extent such an undertaking would influence the cement industry, which already faces serious competition on the part of iron and steel manufacturers. Our present consumption of cement may be said to be about 65,000,000 barrels per year, but is rapidly increasing. The calculation as given above assumes for every ton of 80 per cent. KCl made, a production of 44 barrels of cement. Last year's imports of potassium chlorid alone amounted to over 160,000 tons, which, on the above basis, would be equivalent to 7,040,000 barrels of cement. Could such vast quantities be gradually added to a market which seems already overprovided, without creating an alarming disturbance? Can it be expected that within reasonable time things would adjust themselves to the new conditions, or could this new industry be established and maintained only by inflicting serious losses upon one already existing?

In the face of these difficulties it must be candidly admitted that from a purely commercial point of view, *i. e.*, as a question solely of profit and loss, the proposition as outlined above is not very alluring; nor for that matter any proposition so far advanced looking towards the utilization of the potash in the feldspar. The investment required and the risk assumed are unproportionately large compared with

the eventual stake. But the problem is not purely commercial, should not and cannot be considered so without ignoring the larger economic questions involved. The days of extensive agriculture—an anachronism under any condition in an age of chemistry such as ours—have passed in this country through natural limitations, and the years to come must see in the United States a rapid development of intensive agriculture if we don't want to become dependent upon other nations for some of our food supply and face all the serious consequences which such a condition implies. This means a more extensive use of fertilizers, more phosphates, more sulphuric acid, more nitrogenous compounds, and more potash salts. Our phosphate deposits are enormous. One-half of the sulphuric acid made in this country, or at present over 1,000,000 tons, goes into agriculture, and while the larger part is made from imported pyrites, there is more sulphur driven into the air in our western smelters than all our requirements call for, not counting the rich and readily accessible sulphur deposits in Louisiana. The fisheries and the slaughter-houses furnish vast quantities of nitrogenous matter which are being steadily increased by the gradual enlargement of the numbers of by-product coke ovens. With the rational development of water powers the fixation of atmospheric nitrogen on a large scale is only a matter of little time in this country. No fear need therefore be entertained on that score. For potash salts alone, every pound of it, we must depend on imports, paying at present yearly about \$8,000,000, a sum which is bound to go on increasing, even if the Germans should forego the temptation to raise prices, which always goes with monopolistic possession. To prevent this we would be absolutely helpless, unless through the adoption of some plan for utilizing the latent potash in the rocks we devise some means of checking such tendencies. By creating a new industry and developing our dormant resources more useful employment would be provided, which are other considerations of importance not to be neglected in any economic appreciation of the situation.

The problem as a whole, though fairly clear in its outlines, is yet far from being sufficiently concrete to promise any development from individual initiative alone. It is too broad and involves too many far-reaching questions of science, industry and national husbandry to admit of a solution on the part of any single person. It is a national question and should be treated as such. If any advance is to be made at all, it can come only from an authoritative body of men commissioned to investigate the whole field of the potash supply question in this country, a commission to include men of science with minds practical enough to distinguish between the economically feasible and visionary or impossible, and men of business capable of weighing a question from a viewpoint broader than merely that of profit and loss.

RESEARCH AS A FINANCIAL ASSET.¹

By WILLIS R. WHITNEY, Director, Research Laboratory, General Electric Co., Schenectady, N. Y.

Received April 26, 1911.

It is only in our century that there could be much significance to such a title as "Research as a Financial Asset." This is an industrial century, and, whether we are proud of it or not, we are an industrial people. For some reasons it may be thought unfortunate that so large a proportion of man's energies should be devoted solely to the industries. In some eras we find that there was a predominance of art over industry; in others, literature was predominant; in still others, war and conquest. Once territorial discovery and acquisition predominated, and now, in our own times, the principles of community interest have so greatly developed that we are accustomed to seeing many people who, instead of directly producing their own necessities of life, are more generally repeatedly producing some one little article which contributes in the lives of others. This we recognize as a natural tendency to higher efficiency. Our intricate and delicately balanced system of work is becoming continually more complex, but is certainly still covered by the elemental laws of demand and of survival. New discoveries in our day are largely mental, instead of geographical, and the old battles of conquest have become wars with ignorance. They are struggles to overcome inefficiencies, attempts to broaden the common mental horizon, as our ancestors broadened their physical horizon. Very few people realize the rapidity with which technical advances are being made. Few realize how the way of this advance has itself advanced. I might make this more clear by an illustration.

Consider for a moment the increasing uses of chemical elements and compounds. New combinations in alloys, medicines, dyes, foods, etc., etc., and new uses and materials are being produced daily. For a more simple comparison, consider only the advances in our technical uses of the metallic chemical elements.

Copper, iron and five other metals were known and used at the time of Christ. In the first 1800 or 1900 years of our era, there were added to the list of metals in technical use (pure or alloyed) about eight more, less than two per centum. There has been so much industrial advance made within the past twenty to thirty years that fourteen new metals have been brought into commercial use within this period. This is almost as many in our quarter-century as in the total preceding age of the world. Of course this rate, as applied to metals, apparently cannot continue, but there is no reason to question the possibility of the general advance it indicates. For centuries a single metal was made to serve for all uses which that metal could fill. Then two metals divided the field, each being used where it was preferred for any reason. Alloys began to displace metals to a limited extent. While the engineer still uses iron for his railroad, iron for his buildings and iron for his tools, these irons are different and have been specially developed for those uses. The electrical engineer prefers copper for his conductor,

certain irons for the frames of apparatus, other special irons and steels for the shafts, the magnetic fields, etc., and the specialization to best meet specific wants is still under way. I suppose that this kind of complex development is largely responsible for research laboratories.

A research laboratory is a place where men are especially occupied with new problems, presumably not too far in advance of technical application. By this group devoting its entire attention to the difficulties of meeting already well-defined necessities, or of newly defining and meeting together, the efficiency of those processes is increased. Men specially trained for this very purpose are employed and they are usually just as unfitted for successfully manufacturing as those who efficiently reproduce are of discovering or inventing. It is merely an extension of the principle of the maximum efficiency. A man with his entire attention devoted for months or years at a time to the difficulties of a single problem should be better able to reach a solution than the man who can devote only irregular intervals to it. He should then also be the better prepared for a second problem.

A research laboratory is also a place equipped with apparatus especially designed for experimental work. In a busy manufacturing plant, if a foreman has an idea pointing towards an improvement of his product he frequently has great difficulty in finding the time, the necessary idle apparatus, the raw materials and the incentive to try it. In the laboratory all of these are combined and there is added a system of coöperation of permanently recording results and an atmosphere of research.

The mathematics of coöperation of men and tools is interesting in this connection. Separated men trying their individual experiments contribute in proportion to their numbers, and their work may be called mathematically additive. The effect of a single piece of apparatus given to one man is also additive only, but when a group of men are coöperating, as distinct from merely operating, their work raises with some higher power of the number than the first power. It approaches the square for two men and the cube for three. Two men coöperating with two different and special pieces of apparatus, say a special furnace and a pyrometer, or an hydraulic press and new chemical substances, are more powerful than their arithmetical sum. These facts doubtless assist as assets of a research laboratory.

When a central organization, such as a laboratory, has access to all parts of a large manufacturing plant and is forced sooner or later to come into contact with the various processes and problems, the various possibilities and appliances, it can hardly fail to apply, in some degree, the above law of powers.

As a possible means of illustrating the almost certain assistance which one part of a manufacturing plant may give another when they are connected by experimenting departments or research laboratories and how one thread of work starts another, I will briefly review part of a single fairly connected line of work in our laboratory. In 1901 the Meter Depart-

¹ Presented before the Congress of Technology at the Fiftieth Anniversary of the Granting of the Charter of the Massachusetts Institute of Technology.

ment wanted electrically conducting rods of a million ohms resistance. These were to be one-quarter inch diameter by one inch length. In connection with this work we had to become fairly familiar with published attempts at making any type of such high resistances. Some kind of porcelain body containing a very little conducting material seemed a fair starting formula after the resistance of almost all kinds of materials had been considered. Our own porcelain department was of great help in showing us how to get a good start. We learned how and what to mix to get a fair porcelain, and we found that small quantities of carborundum or of graphite would give us the desired resistance about once in a hundred trials. The rods could be made, but the difference in their resistance when taken from the porcelain kiln and when they were made as nearly alike as we could make them, was often so many thousand-fold that something new had to be done to make a practical success. A small electric furnace was then devised for baking the rods and this was so arranged that the rate of rise of temperature, the maximum temperature reached and the duration of heat at any temperature was under control and was also recorded. The desired result was obtained and this work was thus finished. It gave us a certain stock of knowledge and assurance.

At that time a very similar problem was bothering one of the engineering departments. Lightning arrester rods, part of the apparatus for protecting power lines from lightning, were needed. Their dimensions were $\frac{3}{4} \times 6$ " and they needed to have a definite but, in this case, low resistance, and could apparently not be baked in a porcelain kiln. The usual temperature variations in such a kiln are so great that in practice many thousand rods were repeatedly fired and afterward tested to yield a few hundred of satisfactory product. All the cost of making an entire batch would have to be charged against the few units which might be found satisfactory, and in many cases there were none good in a thousand tested. It was evident that regulation and control of temperature was necessary. This was found to be impracticable in case any considerable number were to be fired at one time, as the heated mass was so great that the rods near the walls of the retort received a very different heat-treatment from those near the middle and were consequently electrically different. This was still the case even when electrically heated muffles were used. This difficulty led to experiments along the line of a heated pipe, through which the rods could be automatically passed. Some time was spent in trying to make a practical furnace out of a length of ordinary iron pipe, which was so arranged as to carry enough electric current to be heated to the proper baking temperature. Troubles here with oxidation of the iron finally led to substitution of carbon pipes. This resulted in a carbon tube furnace, which is merely a collection of six-foot carbon pipes, embedded in coke powder to prevent combustion, and held at the ends in water-cooled copper clamps, which introduce the electric current. By control of this current the temperature could be kept constant at any point desired. When this was combined with a constant rate of mechanical feed of

the air-dried rods of porcelain mixture, a good product was obtained. For the past seven years this furnace has turned out all the arrester rods, the number produced the last year being over 100,000 units.

In this work we were also forced to get into close touch with the electroplating department. The rods had to be copper-plated at the ends, to insure good electrical contact. The simple plating was not enough. This introduced other problems, which I will pass over as I wish to follow the line of continuous experiment brought about, in part, at least, by the single investigation. The electric furnace consisting of the carbon tube packed in coke was a good tool for other work, and among other things we heated the carbon filaments for incandescent lamps in it. We were actuated by a theory that the high temperature thus obtainable would benefit the filament by removal of ash ingredients, which we knew the ordinary firing methods left there. While these were removed, the results did not prove the correctness of the theory, but rather the usefulness of trying experiments. It was found by experiment that the graphite coat on the ordinary lamp filament was so completely changed as to permit of a hundred per cent. increase in the lamp life or over 20 per cent. increase in the efficiency of the lamp for the same life, so that for the past four or five years a large part of the carbon lamps made in this country have been of this improved type. This is the Metallized, or "Gem" lamp. Naturally, this work started a great deal of other work along the lines of incandescent lamp improvement. At no time has such work been stopped, but in addition to it, the new lines of metallic filament lamps were taken up. In fact, during the past five or six years, a very large proportion of our entire work has been done along the line of metallic tungsten incandescent lamps. In this way we have been able to keep in the van of this line of manufacture. The carbon tube furnace has been elaborated for other purposes, so as to cover the action under high pressures and *in vacuo*. Particularly in the latter case a great deal of experimental work has been carried out, contributing to work such as that connected with rare metals. In such a furnace, materials which would react with gases have been studied to advantage. Our experience with the metallized graphite led to production of a special carbon for contact surfaces in railway signal devices, where ordinary carbon was inferior, and suggested the possibility of our contributing to improvements in carbon motor and generator brushes. On the basis of our previous experience and by using the usual factory methods, we became acquainted with the difficulties in producing carbon and graphite motor brushes with the reliability and regularity demanded by the motor art. Furnace-firing was a prime difficulty. Here again we resorted to special electrically heated muffles, where the temperatures, even below redness, could be carefully controlled and automatically recorded. This care, aided by much experimentation along the line of composition, of proportionality between the several kinds of carbon in the brush, etc., put us into shape to make really superior brushes. The Company has now been manufacturing these for a couple of years, with especial reference to particularly severe

requirements, such as railway motors. In such cases the question of selling price is so secondary that we can and do charge liberally for delicacy and care of operation in the manufacture.

This carbon work naturally led to other applications of the identical processes or materials. Circuit breakers, for example, are now equipped with a specially hard carbon contact, made somewhat as motor brushes are made.

It is not my intention to connect all of the laboratory work to the thread which seemed to connect these particular pieces of work, but rather to show the possible effect in accumulating in a laboratory experiences which might affect an inventory.

Among other considerations which appeal to me is one which may be worth pointing out. Probably almost every manufacturing plant develops among its workmen, from time to time, men who are particularly endowed with aptitude for research in their line. They are usually the inventors of the company. They are often discoverers in spite of opposition. They are always trying new things. They are almost of necessity somewhat inefficient in the routine production. In many plants they are merely endured, in a few they are encouraged. To my mind their proper utilization is a safe investment. A research laboratory assists in such a scheme. Sooner or later such a laboratory becomes acquainted with this type of men in a plant and helps them in the development of their ideas.

It is not a perfectly simple matter to measure the value of a research laboratory at any one time. In the minds of some, the proper estimate is based on the profit already earned through its work, which otherwise would not have been earned by the company. This is a fair and conservative method which in our generation ought to be satisfactory when applied not too early to the laboratories. It does not take into account what we may call the good-will and inventory value, both of which should be more rapidly augmenting than any other part of a plant. The experience and knowledge accumulated in a general research laboratory is a positive quantity. In our own case we expended in the first year not far from \$10,000, and had little more than expectations to show for it. Our expenses rapidly rose and our tangible assets began to accrue. Perhaps I can point to no better criterion of the value of a research laboratory to our company than the fact that its force was rapidly increased by a company which cannot be particularly interested in purely academic work. Our annual expenditures passed the \$100,000 mark several years ago. My own estimate of the value would probably be greater than that of others, for I am firmly convinced that proper scientific research is practically required by the existing conditions of our technical age.

Without going into exact values, which are always difficult to determine, consider for a moment the changes which incandescent lighting has witnessed in the past ten years. In this field our laboratory has been active, in contributing to both carbon and to metallic filaments. Moreover, all of the improvements in this field have been the product of research laboratories of trained

men. In the case of our metallized carbon filament, which has now been in use several years, the efficiency of the light was increased by about twenty per cent. Among the carbon lamps of last year these were sold to the extent of over a million dollars.

A broader, but admittedly less accurate impression of changes recently produced may be gained by considering the economy now possible on the basis of our present incandescent lamp purchases in this country and that which would have resulted if the lamps of only ten years ago were used in their stead. On the assumption that the present rate of lamp consumption is equivalent to about eighty million 25-watt tungsten lamps per year, and on the basis of one and a quarter watts per candle power as against 3.1 of the earlier lamps and charging power at 10 cents per kilowatt hour, we get as a result a saving of \$240,000,000 per year, or $\frac{2}{3}$ million per day. Naturally, this is a saving which is to be distributed among producers, consumers and others, but illustrates very well the possibilities. It is interesting to note that we are still very far removed from a perfect incandescent illuminant, when considered from the point of view of maximum theoretical light efficiency.

I see from advertisements that 65,000 of the Magnete arc lamps, originally a product of the laboratory, are now in use. These must have been sold for something near \$2,000,000. The supplying of electrodes which we make and which are consumed in these lamps should amount to about \$60,000 per year.

Our study of the properties of the mercury arc produced our rectifier, which has been commercially developed within the past few years. Of these, about 6,000 have been sold. As they sell for not far from \$200 per set, it is safe to say that this also represents a sale of over a million dollars. The advantage of these outfits over other available apparatus must also be recognized as not far from \$200 for each hour through which those already sold are all operating.

In such a complex field as insulations and molded materials there have been many changes produced. As far back as 1906 we were using annually, in a certain apparatus, 30,000 specially drilled and machined soapstone plates, which cost \$1.10 each. As the result of experiments on substitutes for such material, it was found that they could be molded by us in the proper shape, with holes in place and of a material giving increased toughness, at a greatly reduced cost. As the result of this fact, the price of the purchased material was reduced to us from \$1.10 to 60 cents which in itself would have paid for the work. But further developments proved that the new molded material could be made for 30 cents, which the foreign material could not equal, so we have since produced it ourselves. This caused a saving of approximately \$24,000 annually for this one molded piece. I have heard of other cases where prices to us have gone down, when we have obtained a little promise from our experimental researches.

In considering the research laboratory as a financial asset there is another view which might not be visible at first sight. It is the question of the difference between the value of the useful discovery when purchased

from competitors in the business and when made by one's own company. It is not usually pleasant to have to purchase inventions after their value is known, no matter from whom, but to have to pay a competitor for such a discovery is doubly irksome. One is naturally unduly fearful of its value to the competitor, and he, in turn, is overestimating another's power to use it. The purchaser's profit is apparently limited to the differences between his efficiency of operating it and that of the original owner.

I was recently informed by an officer of another large manufacturing company, where much chemical work is done and which established a research laboratory several years ago, that the most important values they got from their laboratory was the assurance that they were keeping ahead and are at least prepared for the new, if they cannot always invent it themselves. Incidentally, he said that from one part of their research work they had produced processes, etc., which had saved \$800,000 a year. They are at present spending in their several research departments a total of about \$300,000 a year.

We hear frequent reference to the German research laboratories, and a brief discussion may be in place. For the past fifty years that country has been advancing industrially beyond other countries. Not by new opened territories, new railroads, new farm lands, new water power cites, but by new technical discoveries. In fact, this advance may be said to be largely traceable to their *apparent* overproduction of research men by well-fitted universities and technical schools. Every year a few hundred new doctors of science and philosophy were thrown on the market. Most of them had been well trained to think and to experiment; to work hard, and to expect little. The chemical manufactories began to be filled with this product and it overflowed into every other calling in Germany. These well-educated young men became the docents, the assistants and the professors of all the schools of the country. They worked for \$300 to \$500 per year. They were satisfied so long as they could experiment and study the laws of nature, because of the interest in these laws instilled into them by splendid teachers. This condition soon began to make itself manifest in the new making of things—all sorts of chemical compounds, all kinds of physical and electrical devices. I might say that pure organic chemistry at this time was academically most interesting. Its laws were entrancing to the enthusiastic chemist and consequently very many more doctors were turned out who wrote organic theses than any other kind. What more natural than that organic chemistry should have been the first to feel the stimulus? Hundreds, and even thousands of new commercial organic products are to be credited to these men and to that time. All the modern dyestuffs are in this class. Did Germany alone possess the raw material for this line? No! England and America had as much of that. But Germany had the *prepared men* and made the start.

It seems to me that America has made a start in preparing men for the research work of its industries. For example, it is no longer necessary to go abroad to

get the particular training in physical chemistry and electrochemistry which a few years ago was considered desirable. Advanced teaching of science is little, if any, more advanced in Germany to-day than it is in this country. In my opinion the quality of our research laboratories will improve as the supply of home-trained men increases, and that the laboratories of this kind will be increasingly valuable when analyzed as financial assets. I am certain, too, that the industries will not be slow in recognizing the growing value of such assets. They merely want to be shown.

Probably in most industries there are what I may call spots particularly vulnerable to research. For example, the efficiency of steam boilers, based upon the heat energy of the coal used and the efficiency of the engine using the steam, are continually being raised. We may expect, until the maximum calculable efficiency is reached, that this advance will continue. The reason is not far to seek. It is a vulnerable spot. Improvement is possible. A small increase in efficiency of power plant is an ever-continuing profit. Great numbers of steam power plants exist and so inventors are influenced by the fact that new improvements may result in enormous total economies. Every rule of the game encourages them. I can make this clearer by illustrations.

Artificial light is still produced at frightfully poor efficiency. Electric light from incandescent lamps has been greatly improved in this respect, but there is still room for greater economies. It is still a vulnerable spot.

In the case of iron used in transformers, we have another such vulnerable spot. A transformer is practically a mass of sheet iron, wound about with copper wire. The current must be carried around the iron a certain number of times and the copper is chosen because it does the work most economically. No more suitable material than copper seems immediately probable, nor is there any very promising way of increasing its efficiency, but in the iron about which it is wound there is a vulnerable spot. The size of the iron about which the copper is wound may possibly be still much further reducible by improvements in its quality. In other words, we do not yet know what determines the magnetic permeability or the hysteresis of the iron, and yet we do know that it has been greatly improved in the past few years and that it can still be greatly improved.

Let us make this vulnerable point a little clearer by considering the conditions here in Boston. I assume there are approximately 50,000 kilowatts of alternating current energy used here. Nearly all of this is subject to the losses of transformers. If the transformers used with this system were made more than ten years ago, they probably involve a total loss, due to eddy and hysteresis, of about \$1000 per day, at the ten-cent rate. Transformers as they are made to-day, by using improved iron, are saving nearly half of this loss, but there still remains over \$500 loss per day, to serve as a subject for interesting research work.

It should also be noted that Boston uses only a very

small fraction of the alternating current energy of this country.

Consider for a moment two references to the sciences and industry in Germany and England. Dr. O. N. Witt, professor in the Berlin Royal Technical High School, reporting to the German government in 1903, says: "What appears to me to be of far greater importance to the German chemical industry than its predominant appearance at the Columbian World's Fair, is the fact which finds expression in the German exhibits alone, that industry and science stand on the footing of mutual deepest appreciation, one ever influencing the other," etc. As against this, Prof. H. E. Armstrong, of entirely corresponding prominence and position in England, says of England: "Our policy is the precise reverse of that followed in Germany. Our manufacturers generally do not know what the word research means. They place their business under the control of practical men, who, as a rule, actu-

ally resent the introduction into the work of the scientifically trained assistants. If the English nation is to do even its fair share of the work of the world in the future, its attitude must be entirely changed. It must realize that steam and electricity have brought about a complete revolution, that the application of scientific principles and methods is becoming so universal elsewhere that all here who wish to succeed must adopt them."

So long as motors burn out, so long as subways are tied up by defective apparatus, so long as electric motors can run too hot, so long as street cars may catch fire from so-called explosions of the current, so long as the traffic of a whole city can be stopped by a defective insulation or a ten-cent motor brush, there will probably be the equivalent of research laboratories somewhere connected with the electrical industries, where attempts will be continually made to improve.

SCIENTIFIC SOCIETIES

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

THIRD SEMI-ANNUAL MEETING.

JUNE 21ST TO 24TH, 1911.

CONGRESS HOTEL, CHICAGO.

PROGRAM.

WEDNESDAY, JUNE 21ST.

Meeting at Congress Hotel, 10.00 A.M.

Address of Welcome.

Business Session.

Reports of Officers and Council.

Reports of Committees.

Special Report of Committee on Chemical Engineering Education: Dr. Samuel P. Sadtler, *Chairman*.

Discussions by several Professors of Chemical Engineering.

Luncheon.

Excursion, 1.30 P.M.

Visit to Plant of Swift & Company, Union Stock Yards.

EVENING SESSION.

Held at Armour Institute, 8.00 P.M.

Address of President Frerichs: "Method of Attacking Chemical Industrial Problems." (Illustrated by drawings and photographs.)

THURSDAY, JUNE 22ND.

Visit to Glucose Works at Argo, Ill., 9.30 A.M.

Luncheon at Congress Hotel.

Automobile Sight-seeing Trip, 3.00 P.M.

Subscription Dinner at Congress Hotel, 7.30 P.M.

FRIDAY, JUNE 23RD.

Session at Congress Hotel, 9.30 A.M.

Reading of Papers.

"Industrial Chemical Calculations, by Professor Joseph W. Richards.

"Rapid Determination of Tin in Food Products," by Edward G. Gudeman.

"Distillation on the Continuous System," by Charles L. Campbell.

"A New System of Lead and Silver Lining," by Charles L. Campbell.

"The Institute and the U. S. Patent System," by William M. Grosvenor.

Luncheon.

Excursions (Alternative), 1.00 P.M.

Carter White Lead Company, West Pullman.

Semet-Solvay Coke Ovens of the By-Products Coke Corporation, 112th St. and Torrance, South Chicago.

Evening Session at Congress Hotel, 7.30 P.M.

"Manufacture of Gelatine," by Ludwig A. Thiele.

"The Practical Value of Calorific Tests on Anthracite Coal," and "Two Methods of Testing Asphalt," by S. F. Peckham.

Final Business Session.

SATURDAY, JUNE 24TH.

Excursions: Gary Plant of the Indiana Steel Company, Gary, Ind.; Universal Portland Cement Co., Buffington, Ind.

Permits have also been obtained to visit the Illinois Steel Company Works, South Chicago, where eleven blast-furnaces are in operation, besides open-hearth, Bessemer and open-hearth by an electric process. A portion of the furnaces are supplied with dry-air blast. There are large rolling mills for all varieties of structural steel. Standard Oil Refinery at Whiting, Indiana.

Adjournment.

Local Committee of Arrangements:

A. Bement, *Chairman*, 206 So. La Salle St., Chicago.

P. C. Brooks, *Secretary and Treasurer*, Hegewisch, Ill., Oscar Linder, T. G. Wagner.

J. C. OLSEN, *Secretary*,

Polytechnic Institute,

Brooklyn, N. Y.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.

The Annual Convention of the American Institute of Electrical Engineers, for 1911, will be held in

Chicago, Ill., on Monday to Friday, June 26, to 30, 1911. The Institute headquarters will be at the New Hotel Sherman, northwest corner of Clark and Randolph streets. There will be a reception on Monday evening, and the technical sessions will open on Tuesday morning. The Convention Committee will have charge of the local arrangements. The members of this committee are as follows: Louis A. Ferguson, *Chairman*; W. L. Abbott; B. J. Arnold; H. M. Byllesby; W. Lee Campbell; T. P. Gaylord; William B. Jackson; J. W. Johnson; John D. Nies; W. P. Sidley; B. E. Sunny; Fay Woodmansee; P. B. Woodworth; J. G. Wray.

It is many years since the annual convention was held in Chicago, and the committees are arranging to make it both profitable and interesting to the members and their guests.

The following is a partial list of the papers that will be presented:

PROGRAM.

"Economical Design of Direct-Current Magnets," by R. Wikander.

"Catenary Span Calculations." by W. L. R. Robertson.

"Currents in Inductors of Induction Motors," by H. Wiechsel.

"Multiplex Telephony and Telegraphy by Means of Electric Waves Guided by Wires," by Major G. O. Squier.

"Electrolysis in Reinforced Concrete," by C. E. Magnusson and G. H. Smith.

"Induction Motor Design," by T. Hoock.

"The High Efficiency Suspension Insulators," by A. O. Austin.

"The Electric Strength of Air II," by J. B. Whitehead.

"Electrification Analyzed, and Its Application to Trunk Line Roads," by W. S. Murray. (Abstract of paper presented before Institute meeting at Toronto on April 7.)

"Telegraph Transmission," by F. F. Fowle.

"The Cost of Transformer Losses," by R. W. Atkinson and C. E. Stone.

"The Costs of Railway Electrification," by B. F. Wood.

"Induction Motor for Single-Phase Traction," by E. F. W. Alexanderson.

"Magnetic Properties of Iron at 200,000 Cycles," by E. F. W. Alexanderson.

"Electric Storage Batteries," by Bruce Ford.

"The Characteristics of Isolated Plants," by P. R. Moses.

"Elevator Control," by T. E. Barnum.

"Limits to the Use of Resistance Materials."

Two papers on educational topics.

Some of these papers are printed in the current issue of the Proceedings. The others will appear in the June and July issues. Full details regarding the convention, including the program and transportation arrangements, will be published in the June Proceedings.

AMERICAN CHEMICAL SOCIETY.

INDIANAPOLIS MEETING.

The forty-fourth annual meeting of the American Chemical Society will be held in Indianapolis, Indiana, June 28th to July 1st, inclusive. A meeting of the Council will be held at 2.30 P.M. on Tuesday, June 27th.

Hotel headquarters will be the Claypool Hotel, but the meetings themselves will all be held at the German House, which is not a hotel but a German club house. The smoker will be held at the German House, where lunches will also be served. The building is one of the most suitable in Indianapolis and has been leased for the occasion. The fact that it has the atmosphere of a club will add very greatly to the attractiveness of the meeting.

The Indiana Section is making a special effort to entertain the members, and the outlook at present is for one of the largest and most successful meetings the Society has ever held.

Mr. Harry E. Barnard, of the Indiana State Board of Health, is chairman of the Local Committee and Mr. H. A. Schwarz, 522 Tibbs Ave., Indianapolis, is chairman of the Local Publicity Committee. Either one of these gentlemen will be glad to place himself at the disposal of any of the members of the Society to give them information as to local conditions and the special attractions of the meeting itself.

The Entertainment Committee is planning an interesting program, which will be an undoubted success, and special attention is being paid to preparations for the entertainment of ladies at such times as they cannot participate in the regular program. Many manufacturing plants will be visited and many papers of importance read.

The following is a rough draft of the program, which will undoubtedly be changed to meet new conditions that may arise.

WEDNESDAY, JUNE 28TH.

Morning—General meeting.

Afternoon—Division meetings.

Evening—Smoker.

THURSDAY, JUNE 29TH.

Morning—Division meetings.

Afternoon—Visit to Eli Lilly Co., where the Pharmaceutical Division will hold a meeting and assist in dedicating the new laboratories.

Evening—Automobile ride to the Country Club: luncheon, lawn fete, dancing; music, etc.

FRIDAY, JUNE 30TH.

Morning—Division meeting.

Afternoon—Visit to manufacturing plants.

Evening—Banquet.

SATURDAY, JULY 1ST.

Morning—Unfinished division meetings and visit to plants.

Afternoon—Unfinished division meetings and visit to plants.

INTERNATIONAL CONGRESS.

President Taft has appointed the following as the official representatives of the respective bureaus of the federal government on the Organizing Committee

of the International Congress of Applied Chemistry: *Department of the Treasury*—Dr. Reid Hunt, Hygienic Laboratory, Marine Hospital Service; Dr. A. B. Adams, Internal Revenue Service. *Department of the Interior*—Mr. George Steiger, Geological Survey; Dr. George S. Ely, Patent Office; Professor Nathaniel W. Lord, Ohio State University, Columbus, O., to represent Bureau of Mines. *Department of Agriculture*—Dr. H. W. Wiley, Chief, Bureau of Chemistry; Dr. C. F. Langworthy, Office of Experiment Stations; Professor W. W. Cooke, Biological Survey; Mr. William L. Hall, Forest Service; Dr. Frank E. Cameron, Bureau of Soils; Professor W. J. Humphreys, Weather Bureau; Dr. R. H. True, Bureau of Plant Industry; Dr. Marion Dorset, Bureau of Animal Industry; Dr. W. F. Hillebrand, Chief Chemist, Bureau of Standards.

The Pennsylvania Legislature has passed a concurrent resolution, providing for the appointment of a chemist to officially represent the Commonwealth of Pennsylvania at the Eighth International Congress.

The Preliminary Announcement, dated March 6, 1911, has been translated into French under the auspices of the Association des Chimistes du Sucrier et de Distillerie; into German under the auspices of the Verein Deutscher Chemiker; and into Italian under the auspices of the Instituto Chimico and is being distributed by these societies. The Society of Chemical Industry has undertaken to distribute the Announcement to all the chemists of the British Empire.

A pamphlet addressed specifically to American manufacturers, showing them how their business interests may be benefited by cooperation with the Congress, is in preparation and will be ready for distribution by the middle of May.

Under the leadership of the Verein Deutscher Chemiker, ten technical societies have already begun

an organization for Germany along the lines of the American organization for the Congress; in England, the Society of Chemical Industry has taken the initiative along similar lines.

SOCIETY FOR ENGINEERING EDUCATION.

The nineteenth annual meeting of the Society for the Promotion of Engineering Education will be held at Pittsburg, Pa., on Tuesday, Wednesday and Thursday, June 27th, 28th and 29th. The headquarters will be at the Carnegie Technical Schools.

At the meeting special attention will be given to the reports of the Committees on the Teaching of Mathematics to Engineering Students and to Entrance Examinations for Technical Schools.

Particulars regarding the meeting can be obtained from Professor H. H. Norris, Cornell University, Ithaca, N. Y.

SOCIETY CHEMICAL INDUSTRY.

ANNUAL GENERAL MEETING, 1911.

The annual General Meeting will be held in the Montgomery Hall, Sheffield, at 10.30 A.M., on Wednesday, July 12, 1911. A program of the proceedings will be issued later.

MEETING OF SOUTHERN ASSOCIATION.

The annual meeting of the Southern Fertilizer Association will be held at Atlantic City, N. J., July 17, 1911. Already there are indications of a very large attendance of the members of this organization.

An Academy for Silk Industry is being erected in Nagana, Japan, and an Academy for Mining and Metallurgy in Akita.

EDUCATIONAL

PRATT INSTITUTE EXHIBIT.

The annual exhibition of the students of Pratt Institute was held on June 1st, 2nd and 3rd in the buildings of the Institute in Brooklyn.

In the School of Science and Technology, which is the division of the Institute especially concerned with the training of young men in industrial and technical lines, the various classes were at work in the shops and laboratories during the exhibit, and thus an excellent opportunity was given those interested to inspect not only the results of the students' work, but also the methods of instruction and the general facilities for conducting this kind of training.

A special feature of the exhibition was the opening of the new tannery of the Institute, recently installed to provide for the courses in Tanning and Leather

Chemistry which are to be conducted in co-operation with the National Association of Tanners.

On May 5th, New York University celebrated the 100th anniversary of the birth of John William Draper who was professor of chemistry in New York University. Dr. John J. Stevenson, emeritus professor of geology, presided and gave a short résumé of Draper's life and work. Dr. Arthur B. Lamb, director of the chemical department, exhibited some of Dr. Draper's original instruments which were used in producing the first daguerreotypes.

In the near future the New York Section of the American Chemical Society will have a celebration befitting the importance of Draper's work.

Harvard University has raised the \$50,000 necessary to complete the \$100,000 Wolcott Gibbs Memorial Laboratory Fund which was started by Dr. Morris Loeb and Mr. James Loeb, of New York, by a donation of \$50,000. It is expected that \$65,000 will be expended on the construction and \$35,000 on the maintenance of the building.

Professor Julius O. Stieglitz, of the University of Chicago, and Professor B. B. Boltwood, of Yale University, have been elected to membership in the National Academy of Sciences, and Professor Ernest Rutherford, of the University of Manchester, has been elected a foreign associate.

Miss Caroline L. Hunt (32 Eliot St., Jamaica Plain, Mass.) is preparing a life of the late Prof. Mrs. Ellen H. Richards and will appreciate receiving any material such as letters photographs, etc., which might be of assistance in preparing the biography.

On April 4th, Professor Coblenz formally resigned his chair as Professor of General Chemistry in the New York College of Pharmacy, which he has occupied for many years, to assume the duties of a new position with the firm of E. R. Squibb & Sons.

Dr. F. W. Woll, Professor of Agricultural Chemistry at the University of Wisconsin, will represent the

University at the Centennial celebration of the University of Christiania, Norway, in September.

Harry J. Sears and Alice R. Berger have been appointed instructors in chemistry at Stanford University, and Dr. Robert E. Swain has been promoted to be professor of physiological chemistry.

Dr. J. W. Turrentine, instructor in physical and electrochemistry at Wesleyan University, has been appointed scientist in the laboratory of the Bureau of Soils, U. S. Dept. of Agriculture.

The Bessemer gold medal of the Iron and Steel Institute of London for this year will be awarded to Prof. Henri Le Chatelier, the French metallurgist.

The University of Edinburgh will confer its doctorate of laws on Prof. Ernest Rutherford, of the University of Manchester.

Dr. Elmer Ellsworth Brown, U. S. Commissioner of Education, has been elected chancellor of New York University.

Prof. William A. Noyes has been elected President of the Illinois State Academy of Science.

NOTES AND CORRESPONDENCE.

THE INVENTOR OF CELLULOID.

In a recent review¹ of a work on celluloid, the statement appears that "it is not surprising that there should be some mistakes, errors, and omissions. In the first chapter, the invention of celluloid which belongs to Daniel Spill, of Hackney, England, is credited to Hyatt," the inference being that Spill and not Hyatt was the inventor of celluloid. This is not a question of the expression of individual opinion—to which all are entitled—for the statement that the invention of celluloid belongs to Spill is an error of fact, readily disproved by historical data, which data, in the interests of accuracy, is appended herewith.

As the result of conversations with his friend John Taylor, who patented the manufacture of cellulose nitrates in England (Eng. Pat. 11,407, 1846) for Schönbein, who is credited with their discovery, Alexander Parkes began experiments with pyroxylin in Birmingham at the laboratory of Elkington, Mason & Co., where he was then employed, which experiments resulted in there being granted to him E. P., 2,359, 1855. This was followed by E. P. 1,123, 1,125, 1856, and later by E. P. 2,675, 1864; 1,313, 2,733, 3,163, 1865; 1,564, 1,592, 2,709, 1866; 865, 1,695,

1867; 1,366, 1,614, 1868; 983, 1881; F. P. 71,871, 1866, all of which contained pyroxylin. His product—to which the name Parkesine was given—in its more successful forms comprised pyroxylin, camphor and alcohol, with and without vegetable oils, and is fully described in *Jour. Soc. Arts*, 1865, No. 683, Dec. 15, p. 81, and by Lewthwaite in his process for "Coating Fabrics with Parkesine" (E. P. 741, 1868; U. S. P. 103,209, 1870). After Parkes' Company suspended operations in 1867, the first patent (E. P. 1,816, 1867) of Daniel Spill, appeared, which he followed by others (E. P. 2,666, 1867; 3,984, 1868; 3,102, 1869; 180, 787, 1,017, 1,626, 2,649, 1870; 1,739, 1875; F. P. 85,369, 1869; 88,898, 1870). Spill gave to his product one name only, *i. e.*, Xylonite, or Cotton Xyloidine, taking the name "xyloidine" from Braconnet's term for the nitrated starch discovered and described by him in 1833.¹ His last process was patented in 1875 (E. P. 1,739), and two years later the British Xylonite Company was formed, taking its name from the word "Xylonite" which Spill originated to designate his product. After Spill had been granted his four United States patents (91,377, 91,378, 97,454, 1869; 101,175, 1870) the U. S. branch chose a name as near xylonite as possible without infringing on the parent name,

¹ THIS JOURNAL, 3, 194 (1911).

¹ *Ann. chim. phys.*, 52, 290 (1833); *Pogg. Ann.*, 29, 176 (1833).

namely zylonite. The writer has read in detail all the testimony of all the suits in which the American Zylonite Co. participated, in none of which is claim laid to the use of the word "celluloid."

In 1863, John Wesley Hyatt was a printer in Albany, New York, and hearing of a prize of ten thousand dollars offered by Phelan & Collender, a New York City firm, for the patent rights for a satisfactory process for the manufacture of a billiard ball containing no ivory, began experiments in billiard ball manufacture. Mr. Hyatt told the writer, in 1910, that, until required by his attorneys to modify certain claims in his then pending U. S. P., 91,341, 1869, he had not heard of the work with pyroxylin of Parkes, Spill, Berard (E. P. 607, 1856; 1,883, 1,884, 1857), Thistlewaite (E. P. 1,159 1856), MacIntosh and Rhodes (E. P. 734, 1859), Barnwell and Rollason (E. P. 945, 1859; 2,249, 1860), Mennons (E. P. 2,775, 1860), Henry (E. P. 1,454, 1860), Cartright (E. P. 365, 1863), Cutting (E. P. 1,636, 1854), Pierson (U. S. P. 65,267, 1867), Seely (U. S. P. 79,261, 1868), Kendall and Trested (U. S. P. 86,841, 1869) or others in the pyroxylin patent field. J. Hyatt started out by applying to the problem certain principles of heat and great pressure, fully described in his earlier U. S. Patents (31,461, 1861; 35,652, 1862; 50,359, 1865; 76,765, 1868; 88,633, 88,634, 89,582, 91,233, 91,234, 91,235, 1869). His experiments reached such a stage of success that he called his brother Isaiah Smith Hyatt, then an editor at Rockford, Ill., and the latter in Albany in 1868 or the early part of 1869, gave to the product the name celluloid, from "cellulose" and "oid" meaning "like," this being the origin of the word. The word celluloid, as expressing a distinct product, was therefore the invention of the Hyatts, and the product was first made by them at the factory of Osborn, Newcomb & Co., on Eagle St., Albany, N. Y. This firm name was soon changed to the Hyatt Manufacturing Co., then to the Albany Billiard Ball Co., the firm under the latter name being in active existence in Albany to-day. Just as the company formed to exploit Spill's English xylonite patents was named the British Xylonite Co., and to work his U. S. patents of zylonite was known as the American Zylonite Co., so the firm organized to manufacture celluloid was termed the Celluloid Co. Celluloid as a name was registered as a trade mark in the United States Patent Office Jan. 14, 1873, as No. 1,102, and again in 1883.

When the Cellonite Manufacturing Company was restrained from the use of the word "cellonite" because it sounded so much like celluloid (U. S. Circuit Court—District of New Jersey, decided July 12, 1887; Patent Office Gazette, Vol. 41, Nov. 8, 1887, p. 693) Judge J. Bradley in handing down the decision stated: "The word 'Celluloid' had never been used before, except . . . by Isaiah S. and John W. Hyatt, by whom the word was coined," and "that the word 'Cellonite' is sufficiently like it to produce the mischief which is within the purview of the law."

Spill was not even the first to describe the use of camphor and alcohol with pyroxylin—the combination which induces plasticity. While it is true that

Spill brought suit in the United States to restrain certain manufacturers from the use of an ethyl alcohol solution of camphor, and came personally to the United States to prosecute those suits and won; and while it is also true that Spill sued again to restrain the same company from the use of a methyl alcohol solution of camphor, it is also true that the second suit was lost to Spill on the ground that Parkes in his patents above quoted, and not Spill, was the pioneer in the use of camphor in alcohols as solvents for the cellulose nitrates. The second suit being lost, the first decision was appealed and reversed, all of which is given in detail in 22 Blatchford C. C. R. 441.

In all the works on celluloid of which the writer is aware, and specifically Joseph Ertel, p. 9; Fr. Böckmann, p. 2; L. Andes, p. 10; and Masselon, Roberts and Cillard, p. 2, the statement occurs that celluloid was discovered by the Hyatt Brothers in Newark, N. J. in 1869. As mentioned above, this statement is untrue in that the product was discovered in Albany, and Mr. John W. Hyatt informed the writer that he had never been to Newark until in the early seventies.

F. C. WORDEN.

CELLULOID FROM ACETYLCELLULOSE.

Up to the present, acetylcellulose found application only as a varnish for coating objects where non-inflammability and certain electric properties were required. The main use was for the manufacture of cinematograph films, which did not burn even after ignition. Altogether, it has been impossible to make objects from it more than one-fourth of a millimeter in thickness.

Dr. A. Eichengrun has now discovered (*Zeitschrift für angewandte Chemie*, 1911, 366) a method of making celluloid of any shape, color and thickness, using acetylcellulose instead of nitrocellulose. In this manner, he has produced an incombustible substitute for celluloid which he calls "Cellon." His invention seems to be laid down in his French Patent 412,797 of January 20, 1910, and British Patent 1441 of January 19, 1910, the essence of which is:

"Certain types of cellulose acetate, notably these which are soluble in acetone, are soluble on heating, in mixtures of liquids, *e. g.*, methyl alcohol and benzene, neither of which have any solvent action alone. On cooling these solutions, the ester may either remain in solution or separate out in the form of long felted filaments. The separation may be prevented by adding to the solution any of the ordinary solvents of cellulose acetate, in which it is soluble in the cold, *e. g.*, glacial acetic acid, acetone, etc., in which case the solution remains liquid or becomes syrupy on cooling. Or else, there may be added a substance having an influence analogous to that of camphor in nitrocellulose, in which case the solution sets to a continuous mass on cooling. Suitable bodies are methylacetanilide, ethyltoluenesulphonate, trichloraniline, etc. If a very concentrated mass be desired, the cellulose acetate may be dissolved in alcohol and benzene, freed from impurities by filtration and allowed to deposit by cooling; the liquid is then poured

off and the precipitated cellulose acetate worked up with a camphor substitute. One of the numerous examples of the process runs as follows: 1 kilo of cellulose acetate is dissolved in 2 kilos of methyl alcohol and 1 kilo of toluene at 80° C.; 150 grams of methyl-acetanilide are added to the solution and 100 grams of epichlorhydrin. The liquid is filtered hot and on cooling sets to a solid mass, which may be sliced, moulded, or pressed through orifices. In various ways plastic masses having all the technical properties of celluloid may be prepared."

SACCHARIN IN FOOD.

FOOD INSPECTION DECISION 135.

At the request of the Secretary of Agriculture, the Referee Board of Consulting Scientific Experts has conducted an investigation as to the effect on health of the use of saccharin. The investigation has been concluded, and the Referee Board reports that the continued use of saccharin for a long time in quantities over three-tenths of a gram per day is liable to impair digestion, and that the addition of saccharin as a substitute for cane sugar or other forms of sugar reduces the food value of the sweetened product and hence lowers its quality.

Saccharin has been used as a substitute for sugar in over thirty classes of foods in which sugar is commonly recognized as a normal and valuable ingredient. If the use of saccharin be continued it is evident that amounts of saccharin may readily be consumed which will, through continual use, produce digestive disturbances. In every food in which saccharin is used, some other sweetening agent known to be harmless to health can be substituted, and there is not even a pretense that saccharin is a necessity in the manufacture of food products. Under the Food and Drugs Act articles of food are adulterated if they contain added poisonous or other added deleterious ingredients which may render them injurious to health. Articles of food are also adulterated within the meaning of the act, if substances have been mixed and packed with the foods so as to reduce or lower or injuriously affect their quality or strength. The findings of the Referee Board show that saccharin in food is such an added poisonous or other added deleterious ingredient as is contemplated by the act, and also that the substitution of saccharin for sugar in foods reduces and lowers their quality.

The Secretary of Agriculture, therefore, will regard as adulterated under the Food and Drugs Act foods containing saccharin which, on and after July 1, 1911, are manufactured or offered for sale in the District of Columbia or the Territories, or shipped in interstate or foreign commerce, or offered for importation into the United States.

FRANKLIN MACVEAGH,

Secretary of the Treasury.

JAMES WILSON,

Secretary of Agriculture.

CHARLES NAGEL,

Sec. of Commerce and Labor.

WASHINGTON, D. C., April 26, 1911.

USE OF SACCHARIN.

The experiments of the Referee Board of Consulting Scientific Experts of the Department of Agriculture show that the continued use of saccharin for a long time in quantities of over $\frac{3}{10}$ of a grain is liable to impair digestion.

Considering that saccharin is 550 times as sweet as cane sugar, $\frac{3}{10}$ of a gram possesses the sweetening power of 165 grams of cane sugar. It is hardly conceivable that any one person would daily digest such an amount of saccharin in food and beverage, and without having studied in detail the experiments carried out by the scientists of the Referee Board, the conclusion seems to be justified that saccharin—as has been the case in Europe—has been sacrificed to the agrarian interests of the country. But in spite of all restrictions the consumption of saccharin for technical uses is enormous in Europe.

In Germany, for example, the production of artificial sweeteners and their importation has been forbidden by the law of July 7, 1902. The existing factories were bought out by the government and received an indemnity of about five million marks.

The price of cane sugar did not rise in consequence of this arbitrary removal of the dangerous competitor, but an immense amount of smuggling of saccharine from Switzerland and Belgium into Germany and Austria was the result. From April 1, 1904, to December, 1910, over 11,000 k. of saccharin were confiscated at the Swiss-Austrian border and 444 smugglers were arrested and convicted. Much larger quantities were of course surreptitiously brought into Germany, and a train running by night time from Switzerland into Germany is called the "Saccharin Train" because so many smugglers are traveling on it.

In Zurich alone there are 129 persons who make the smuggling of saccharin a specialty, and these people exercise the greatest ingenuity in concealing saccharin. In one case they hid in each of 30 barrels of herrings, which were to be forwarded across the frontier, a tin can containing 25 k. of the sweetener. Again, they filled champagne bottles with the material, and in another instance they packed tin tubes containing saccharin into cans in which sesame oil was shipped.

The sweetener thus marketed is employed by householders exclusively who refuse to believe that saccharin is injurious to health, and who prefer to use the sweetener on account of its sweetness.

The Editor of the Journal of Industrial and Engineering Chemistry:

With the enlargement of the policy of the JOURNAL and the effort of the Industrial Section of the American Chemical Society to be of greater value to its members as well as to the public at large, it might now be well to take into consideration one of the most vital points of interest, especially to the younger members, *i. e.*, the question of finding the particular line of employment for which each is suited.

I do not mean by this to refer to the man who is habitually out of a job but first to the young man who

is just starting out in life. He should have a better opportunity to make a selection than is, as a rule, offered. Secondly, there is the class, to which many ambitious young men belong, which consists of those who have positions which are not suited to their training or which they have outgrown and in which there is no further chance for advancement.

It appeals to many men, with whom I have discussed the subject, that, by acting as a clearing-house for members of the Society, who wish a change of employment and for the corporations, who wish to employ chemists, the Society would be serving a good cause and further the interests of the greater number of its members.

This problem is already solved, but to a very small extent, by the "want ads" which can be inserted in the *Journal of the American Chemical Society*.

The opportunity possessed by the Society is unique in that among its members are numbered those most prominent in each of the various fields of chemistry, and that any one of its members seeking employment can be vouched for by some one who is a specialist in his own line and who therefore knows the true value of the man. In this manner the recommendations should carry a weight which is not carried by other forms of recommendation and result in placing the right man in the right place a much greater number of times than is at present the case.

I am much interested in a plan of this nature and hope that it may be taken up officially by the Society as a whole. In the meantime I should like to hear from any one interested in any way whatsoever.

RAYMOND C. BENNER.

UNIVERSITY OF ARIZONA,
TUCSON.

WORLD-WIDE FIGURES.

Through study and observation of the volcanic outflow the geologist knows approximately the composition of the earth's crust to a depth of 10 miles below sea-level. As Frank W. Clarke, of the United States Geological Survey, says in the "Data of Geochemistry:" "This thickness of 10 miles represents known matter." The vastness of the figures which it is necessary to employ in the discussion of this 10-mile lithosphere, as it is termed, transcends ordinary human comprehension.

The volume of the lithosphere, including the continents elevated above the sea, is 1,633,000,000 cubic miles.

A cubic mile of average rock weighs 12,800,000,000 tons.

The volume of the ocean is 302,000,000 cubic miles.

The atmosphere is equal in weight to 1,268,000 cubic miles of water, which, however, is only one two-hundred-and-thirty-eighth of the volume of the ocean; yet this would be sufficient to raise the level of the ocean 45 feet on all shores and to submerge an important part of the continents.

One per cent. of the water of the ocean would cover all the land areas of the globe to a depth of 290 feet.

The salt in the ocean would make 4,800,000 cubes

each 1 mile in dimensions, which, if spread over the United States would form a layer 1.6 miles high.

In comparison with this outer 10-mile section of the earth's crust the thin sheet of organic matter on the surface—the prairie and valley soils, the alluvial bottoms and the rich tablelands by whose products man lives—becomes a mere film, a skin.

CONDENSITE, A NEW ACID- AND ALKALI-PROOF PLASTIC MATERIAL.

Under this name, a new phenol-formaldehyde product is to be placed on the market, the properties of which are claimed to be superior to all similar substances heretofore introduced. Condensite is soluble in alcohol and can be employed like shellac for varnish purposes, etc.

By simple heating, Condensite is converted into the insoluble variety ready for use as a plastic material. It can be perfectly moulded, it sets rapidly without any air holes. Its electric properties are excellent. It possesses great tenacity, is tasteless and odorless.

The product is manufactured by the Condensite Company of America, in Glen Ridge, N. J., and is the invention of J. W. Aylsworth, who has spent a lifetime in Edison's laboratories as research chemist. Mr. Edison has reserved for himself the exclusive rights for using the new material for phonographic purposes. Mr. Frank L. Dyer, the attorney of the Edison interests, is the treasurer of the company and Mr. Kirk Brown its president. Mr. Aylsworth, the inventor, is a director in the company and will act as its consulting chemist.

AMERICAN TIN-PLATE INDUSTRY.

From information supplied by the Bureau of Statistics it appears that during the first eight months of the fiscal year 1911 both the tin imports and the tin-plate exports of the United States exceeded all previous records for a similar period. The total imports of pig tin, of which England and the Straits Settlements are the chief sources of supply, amounted in the eight months ending with February, 1911, to 68,000,000 pounds (compared with 66,500,000 pounds in the same months of the preceding fiscal period), valued at \$23,500,000, and will probably approximate in value \$35,000,000 for the full fiscal year. The exports of tin and terne plates in the eight elapsed months of the current fiscal year aggregated 24,250,000 pounds (in contrast to 15,000,000 pounds in the corresponding period of 1910), valued at \$880,000, and the total exportation for the complete fiscal year is estimated at \$1,333,000.

ALCOHOL FROM SAWDUST.

The problem of the utilization of sawdust for the conversion of cellulose into sugar and the subsequent production of alcohol by fermentation has been economically solved.

A plant established at Georgetown, S. C., has been

running successfully for over one year, producing more than 2,000 gallons of ethylic alcohol per day. The capacity of the plant is about 5,000 gallons daily.

The process carried out at Georgetown is founded on the Ewen-Tomlinson inventions which have been patented in all the civilized countries. The works in Georgetown are partly owned by the Du Pont Powder Co., and the alcohol there produced is used in their manufacture of powder.

ALABAMA COKE.

There were 43 coke-making establishments in Alabama in 1910, the same number as in 1909, but the total number of ovens increased from 10,061 in 1909 to 10,132 in 1910, exclusive of the 60 Koppers ovens under construction at the close of 1910. Of these, 9,614 ovens were in operation in 1910, with an average production of 338 short tons each. In 1909 the average production per oven was 330 tons.

The following table shows the growth of the coke-making industry in Alabama:

	Short tons.
1880.....	60,781
1890.....	1,072,942
1900.....	2,110,837
1905.....	2,576,986
1906.....	3,034,501
1907.....	3,021,794
1908.....	2,362,666
1909.....	3,085,824
1910.....	3,249,027

INCREASED LEAD PRODUCTION IN 1910.

The production of refined lead in the United States in 1910, as shown by an advance statement issued by the United States Geological Survey, was 470,380 tons, an increase over the figures for 1909 of 22,268 tons.

The following are the States which smelted or refined lead in excess of 10,000 tons:

	1909.	1910.
	Short tons.	Short tons.
Missouri.....	142,650	161,659
Idaho.....	97,183	99,924
Utah.....	64,534	57,081
Colorado.....	29,326	35,685

GROWTH OF CEMENT INDUSTRY.

Few mineral products can show so rapid an increase in output as Portland cement. The production for 1909, according to the United States Geological Survey, was the greatest in the history of the industry, being 65,399,889 barrels, valued at \$52,797,973. In 1900 the production was only 17,231,150 barrels, in 1902 it was 25,753,504 barrels, in 1905 it was 31,675,257 barrels, in 1906 it was 51,000,445 barrels, and in 1908 it was 52,910,925 barrels.

PUMICE.

The value of the pumice produced in the United States in 1909 was \$33,439 and that of the pumice imported was nearly three times as great, according to the figures recently published by the United States

Geological Survey. The native supply comes principally from deposits in Harlan and Lincoln counties, Nebr. Pumice is an acidic volcanic rock, which may be in either massive or finely comminuted form.

ENDOWMENT COMMITTEE.

Mr. Hyde announces the completion of the organization of the Endowment Committee as follows:

B. T. Babbitt Hyde, Chairman, 11 Broadway, New York.

Arthur L. Day, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

Wm. L. Dudley, Vanderbilt University, Nashville, Tenn.

A. D. Little, 93 Broad Street, Boston, Mass.

E. G. Love, 80 East 55th Street, New York.

Theo. B. Wagner, 746 Marquette Terrace, Chicago, Ill.

GENERAL NOTES.

The annual dinner of the Utah Society of Engineers was held at the Commercial Club, Salt Lake City, Thursday, April 20, 1911. Addresses were made by President John Dern, of the American Mining Congress, and by various members of the Society. The following officers were elected to serve for the year 1911-1912:

President, M. D. GROSH.

First Vice-President, C. F. MOORE.

Second Vice-President, E. H. BECKSTRAND.

Secretary, R. B. KETCHUM.

Treasurer, A. S. PETERS.

W. C. EBAUGH,

Secretary U. S. E.

Swift & Co., Chicago, are building a cottonseed oil refinery at Harvey, opposite New Orleans, La. The buildings, which are on the river front, located on a tract of 37 acres, are nearing completion, and include an oil refinery, 115 × 52 feet, brick and concrete construction, fireproof throughout, part of which is four and the other three stories high; the packing and shipping building, 128 × 61 feet, two stories high; cooper shop, 64 × 64 feet, two stories high; boiler and engine room, 79 × 40 feet.

The plant will be ready for operation about the middle of June, and will employ a large number of hands.

On April 13th, Prof. Wm. B. Alwood, enological chemist of the Bureau of Chemistry, U. S. Dept. of Agriculture, sailed for Spain to investigate viticultural conditions in Spain, France, Germany and Italy. While in Europe Dr. Alwood will read several papers on the chemistry of American grapes before the International Viticultural Congress when it meets at Montpellier.

The Union Phosphate Co., Union City, Ga., will

expend \$20,000 on improvements and additions to their buildings. The main building will be increased to 70 × 300 feet. When the additions are completed, the capacity will be 100 tons of acid phosphate daily. J. G. Eubanks is the president of the company, which has a capital stock of \$150,000.

Work has begun on the foundation of the new fertilizer plant, 114 × 135 feet, on the site purchased by the Central Chemical Co., Hagerstown, Md., in the northern suburbs along the Cumberland Valley Railway. The new plant when completed will have a capacity of 20,000 tons a year.

On April 28th, the Arbuckle Bros. Sugar Refinery in New York City was destroyed by fire causing a loss of about \$400,000. Nothing is known as to the cause of the fire except that it followed an explosion in the char house.

On April 11th, Henry Pemberton, former Vice-President of the Pennsylvania Salt Manufacturing Co., died in Philadelphia at the age of 85 years. Mr. Pemberton was well known as a manufacturer, scientist and author.

Dr. G. D. Rosengarten has been elected by the Executive Committee of the Division as Chairman of the Industrial Division of the American Chemical Society in place of Dr. George C. Stone, resigned.

The Mitchell Varnish Works have moved their plant from Newark, N. J., to Camden, N. J., where they also have their offices.

The Casein Co. of America is erecting a plant in Hagerstown, Md., for the manufacture of dry milk powder.

CONSULAR AND TRADE NOTES.

NITRATE INDUSTRY OF CHILE.

Minister Henry P. Fletcher, Santiago, submits the following data relative to the nitrate industry of Chile, based upon a report recently issued by the Nitrate Propaganda Association:

The production of nitrate in Chile for the years 1908, 1909, 1910, and 1911 (estimated), and the increased production in each year over the one preceding, were as follows, in quintals of 101.6 pounds each:

Years.	Production. Quintals.	Increase over preceding year. Quintals.	Years.	Production. Quintals.	Increase over preceding year. Quintals.
1908	41,751,284	1910	52,500,000	7,705,535
1909	44,794,465	3,043,181	1911 (estimated)	55,000,000	2,500,000

These figures are slightly higher than those given in official statistics. In 1910 there were shipped to the United States over 12,000,000 quintals, as against 8,000,000 in 1909.

The increase in exportation over the preceding year was 1,804,989 quintals in 1909 and 4,369,196 quintals in 1910; the increase in consumption was 4,559,769 quintals in 1909 and 6,814,052 quintals in 1910.

The figures relative to the stocks of nitrate on the coast December 31, 1910, prepared by a special commission, show a total of 9,916,278 quintals.

A Reuter dispatch from Santiago de Chile estimates the production of nitrates for 1911 at 55,000,000 quintals and the world consumption at 53,860,000 quintals, and states that nine establishments are nearing completion which will produce 11,000,000 quintals a year.

DUST-PROOF CEMENT BAGS FOR AUSTRALIA.

Consul General John P. Bray, Sydney, reports that differences have arisen between the local cement manufacturers and the Wharf laborers at Sydney, over handling cement in bags, the dust from which the laborers claim injures their health. The wharf laborers have virtually refused to handle bagged cement, which seriously hampers the trade.

The output of the leading cement factory is about 36,000

bags per week, of which 8,000 to 10,000 bags are shipped to other Australian States. Recognizing that immediate steps must be taken to save this interstate market, the company has made a trial shipment of cement in bags lined with paper. It is stated that the present cost of these paper-lined bags makes their use almost prohibitive, but that, if the experiment proves successful, arrangements will be made to make such bags by machinery.

As this matter may interest manufacturers in the United States, some of whom produce bags of paper stock strong enough to convey coal, it is suggested that they correspond with the company in question (address may be secured from the Bureau of Manufactures).

LITHOPONE IN GERMANY.

Consul General Robert P. Skinner reports that lithopone is manufactured in some 12 factories, of which three are in Silesia, two in the Duchy of Brunswick, one in Thuringia, two in Nassau, three on the lower Rhine, and one in Bavaria. The capacity of these factories per annum varies between 1000 carloads at the most important and 100 at the smallest.

In addition to its various uses in the paint trade, lithopone is also being employed in the manufacture of many rubber articles, linoleum, oilcloth, sealing wax, and artificial stone. The consumption of lithopone will increase steadily, although there is no doubt an overproduction at this time.

GERMAN INCANDESCENT-LAMP INDUSTRY.

Official statistics of the production of incandescent lamps, now being compiled in connection with the new Government tax upon lighting apparatus, have so far been made public only for the six months from October 1, 1909, to March 31, 1910. The following table gives the total number of the various kinds of incandescent lamps manufactured and imported.

Kind of lamp.	Produced.	Exported.	Imported.
Filament:			
Carbon.....	13,994,323	8,397,756	566,115
Metal.....	17,828,730	12,303,719	141,407
Nernst burners, etc.....	253,456	141,965	418
Burners for mercury-vapor lamps.	4,541	1,617	79

MINERAL PRODUCTION OF BRITISH COLUMBIA.

The total mineral production of British Columbia for 1910, compared with 1909, as shown in Government reports, was as follows:

Articles.	1909.	1910.
Gold:		
Placer.....	\$477,000	\$482,000
Lode.....	4,924,090	5,198,505
Silver.....	1,239,270	1,282,500
Lead.....	1,709,259	1,480,000
Copper.....	5,918,522	4,972,500
Zinc.....	400,000	184,000
Total.....	14,668,141	13,599,505
Coal.....	7,022,666	9,800,000
Coke.....	1,552,218	1,284,000
Building materials, etc.....	1,200,000	1,500,000
Grand total.....	24,443,025	26,183,505

DECLINE OF INDIAN INDIGO.

Consul General Wm. H. Michael, Calcutta, reports that during 1896 India's indigo industry had reached its greatest prosperity. Exports of 20,981,744 pounds were valued at \$17,848,370.

By adhering to old methods of cultivation the Indian planter has permitted the more progressive synthetic dye manufacturer to surpass him, and in 1906 Indian indigo exports had fallen to 3,920,000 pounds, valued at \$2,333,333. Since then the decline has been continuous. During the fiscal year ended March 31, 1910, it had fallen to 2,022,832 pounds, with a valuation of only \$1,172,718, and this year it will, no doubt, be still lower.

LARGE GRAIN CROPS IN ROUMANIA.

The Roumanian consular officer in London states that the total value of grain production in his country for 1910 was \$253,000,000 or \$20,000,000 greater than for 1906, when crops were very abundant. The wheat crop alone was worth about \$100,000,000 and the corn crop about \$60,000,000. He adds that Roumania will have to provide the largest share of corn for European requirements this year.

BOOK REVIEWS.

Nitrocellulose Industry. By EDWARD C. WORDEN. Vol. I [Vol. II in press], 565 pp., 148 illustrations. D. Van Nostrand Company, New York, 1911. Price, \$5.00

The first volume of this work comprises the following subject matter: Cellulose, its sources, properties and modifications; Cellulose Nitrates, their history, properties and analysis; Manufacture of Nitrocellulose; Solvents treating especially of fusel oil, amyl acetate and camphor; Paint Removers and Turpentine Substitutes; Pyroxylin Solutions and Lacquers including their preparation, properties and uses; Imitation Leather; Pyroxylin Coated Enamel and Patent Leather; Artificial Filaments describing the Chardonnet, Cuprammonium and similar processes together with the spinning, properties and uses of artificial silk.

Obviously it would be impossible for one person to be personally familiar with all the processes outlined above, and in treating the subject the author has drawn freely from the journal and patent literature. In the chapter on Solvents and Non-Solvents and that on Pyroxylin Coated Enamel and Patent Leathers, however, he writes from his own experience and especially in the first mentioned chapter, contributes much that is valuable.

In this chapter, which is typical, a careful account is given of the first work done on solvents and their development up to the present time. This account is accompanied by notes in smaller type, often covering over half the page, in which an unusually complete bibliography is given with short reviews of the subject matter of the references in most cases. Also elaborations are given in the notes of the text above, enabling the reader to get more specific information where desired.

To consider the chapter on solvents more in detail, a very clear idea of the uses and functions of the various solvents of pyroxylin is given under the heading "Classes of Solvents." Under the heading "Acetone,"

a lucid explanation is given of the parts played by the different ingredients of a pyroxylin solution. Here, as in the rest of the work, the commercial side of the question is kept steadily in view and the cost of a solvent is considered along with its other properties; thus the use of benzene in lowering the cost of solutions is well set forth in the statement of "Stevens' Law."

The sub-headings of the above chapter, as in the case of many of the other chapters, are not logical or well chosen. For example, the first few paragraphs differ from most of the other paragraphs in the book in having no heading at all and gradually change from a historical account of solvents to a discussion of their relations to each other in their action on nitrocellulose. Thus some valuable data would be lost by a reader making use of the headings in heavy type. Where the headings are given, they are often misleading as, to give a further example, phenyl acetate follows the paragraph of non-solvents along with the headings "Chloroform," "Carbon tetrachloride," etc.

This same haphazard arrangement is also noticeable in the matter contained in the different chapters, a paragraph on methyl alcohol being included in the chapter on fusel oil which, may it be said parenthetically, makes itself prominent by the extraordinary statement that acetone-free methyl alcohol is a non-solvent of industrial cellulose nitrates.

Besides putting subjects out of their logical place much matter is included which is irrelevant in a book on the nitrocellulose industry; for example, there is a whole chapter on paint removers, a sketch of the tanning industry in Chapter XII and an account of cuprammonium and other non-nitrocellulose filaments in Chapter XIII. Thus a wonderfully complete but not very well digested pile of facts is brought together, which, although they may be located by

means of the excellent index, make the book cumbersome and tedious to read in many places.

Included in this vast amount of information are many excellent descriptions of technical processes, accompanied by illustrations of apparatus. These include numerous nitrating processes, methods and contrivances for making pyroxylin solutions, the refining of fusel oil and manufacture of amyl acetate, leather-coating compounds and machinery for applying them, and the manufacture of artificial filaments.

Not nearly as valuable are the analytical methods given for the determination of nitrogen, the analysis of mixed acid and the assay of amyl acetate, also Redpath's method of acid calculation, all of which need editing by one who has made use of them in factory practice. It would be better to give an outline of the methods than to give actual procedure which is incomplete and misleading.

Viewed in perspective, the various faults here mentioned do not detract seriously from what is undoubtedly the most valuable and complete work on the subject of nitrocellulose yet published. The student and general reader will find much of interest in the historical accounts and the descriptions of the manufacture of many familiar articles, while the technician will find the bibliography and résumés of patent and journal references invaluable. C. M. JOYCE.

Elementary Chemistry for Coal-mining Students. By L. T. O'SHEA, M.Sc. (Sheffield), B.Sc. (London). Professor of Applied Chemistry in the University of Sheffield. 12mo., 319 pp. Longmans, Green and Co. 1911. \$1.80 net.

This very readable volume has been the gradual outgrowth of many years of lectures, delivered before audiences composed largely of students of coal-mining, ignorant of chemistry, which may explain the semblance of crudity and lack of continuity occasionally to be found in the text. This crudity, or lack of precision in the formulation of laws and the statement of facts, is apparently intentional and should be no drawback, as the audience for whom the work is primarily intended would be largely incapable of appreciating fine distinctions, and would be but confused by them. The lack of continuity may be attributed to the lecture origin of the work. It would appear that many of the chapters have originally been lecture themes, and even though arranged in logical sequence, there is often but little connection between them.

While this book is termed a work on chemistry, it is really a compilation of data pertinent to the science of coal-mining, the pure chemistry being secondary to, and explanatory of, these data. The text is so worded, and the chapters so arranged, that the facts of most importance are kept largely free from chemical theory, so that their salient points may be readily grasped, without entering into the pure chemistry. This chemical theory is profusely illustrated by the description of well chosen experiments.

The mining profession at large owes a debt of gratitude to the author of this estimable work for

the many valuable facts and tables, which have been carefully gleaned from a great mass of literature. Perhaps some slight idea of the wealth of information stored in this volume may be gathered from a brief résumé of its more important chapters.

In the chapter on the atmosphere, besides the usual statements regarding its composition and constituents, the spontaneous ignition of coal is treated of at length. The theoretical consideration of the origin of this evil and its remedy are dealt with. Extinctive and irrespirable atmospheres are made the subject of another section of this chapter, in which very interesting tables are given, showing the percentage composition of atmospheres extinctive of the flames of various burning substances. The physiological action of atmospheres depleted in oxygen is also briefly treated.

A chapter is devoted to a very thorough and concise discussion of gas, and atmospheric pressures, with a description of the various types of barometer, and water gauge, used for the measurement of these pressures. It may be noted here that the mathematical considerations throughout the book are simple and uninvolved, and may be readily followed by the least initiated.

Following the usual chapter on water and its composition is found a chapter on pure chemistry, treating very simply of atoms and molecules.

The chapter on sulphur is remarkable for nothing save that a brief outline of the physiological action of hydrogen sulphide is given, and that the "iron disulphide" associated with coal is described as iron pyrites, no mention being made of the presence of marcasite.

Under carbon, tables are given showing the composition of various cokes and charcoals, as well as analyses of samples of fire-damp.

The chapter dealing with flame and the safety-lamp is full and well written. Cuts are given showing the appearance of different shaped flames burning different fuels in atmospheres containing varying quantities of methane. The conditions to be fulfilled by an efficient safety-lamp are clearly stated with a description of the more important types of this lamp and their advantages and drawbacks.

The subject of coal is treated fully and clearly. As might be expected, much stress is laid on the description of the coking of coal and the by-product oven, which is amplified by a special chapter discussing these by-products and their recovery.

The subject of explosives is especially well handled. The physical effect of high and low explosives, when detonated, and their dynamic testing is detailed. A section is devoted to the length of flame from explosives, while the requirements to be fulfilled by such bodies when used in coal mines are discussed, as well as the subject of "permitted explosives" with the tests to which these are subjected. The general consideration of safety in handling of explosives forms the topic of another section, while throughout the chapter many analyses of these substances are quoted.

In the chapter on explosion in gases, the description of several colliery disasters are abstracted. The whole subject is roughly divided into two types, that of a pure fire-damp explosion, and that of a fire-damp explosion continued and magnified by coal dust.

The mechanics of the propagation of flame through an explosive mixture of a combustible gas and air is lucidly explained. The various experiments carried on in England to ascertain the explosibility of coal dust are described.

The book is concluded by a chapter dealing with the physical consideration of the effects of pressure and temperature on gases, another on chemical calculations, and several appendices of useful tables.

EDWIN M. CHANCE.

Zur Kenntnis der Cellulosearten. VON DR. WALTER SCHULZ. Introduction by Dr. Carl G. Schwalbe. Verlag von Gebrüder Borntraeger, Berlin. 1911. 100 pp., 3 illustrations. 3 Mks., 20 Pf.

The identification of cellulose fibers is usually accomplished by the aid of the microscope and very seldom by strictly chemical means. Even in these cases the investigation is usually done by micro-chemical methods. The author in this book has collected the latest chemical methods for the determination of the various intermediate decomposition products of cellulose and the various constants used in testing sulphite cellulose.

The work of the author can be divided into two parts: Part I deals with the methods of production and characterization of the intermediate decomposition products of cellulose, such as the vegetable parchment, the Guignet cellulose, the amyloid of Flechsig, the acid cellulose of Ekström, etc. The end-products of the hydrolysis of cellulose have also been considered as to methods, yield, etc.

Part II describes the physical-chemical methods as tried out by the author for determining the various constants of sulphite cellulose.

The author has added in this little work a valuable addition to our knowledge of the little-known field of cellulose chemistry and cellulose testing.

O. KRESS.

Composition and Heat Treatment of Steel. By E. F. LAKE. x+252 pp., 143 illustrations. \$2.50. McGraw-Hill Book Company, New York. Second Edition, Revised and Corrected.

This book is not worthy of a review, yet it would be unfair to say that it is of no value. It is fair, however, to say that many of the sentences and paragraphs are loosely constructed and their meaning vague and obscure. Many of the statements are in error and truths stated correctly in one part of the volume are contradicted in another part.

To point out all the errors and put the seemingly intended thought of the author in plain simple language would make a volume larger than the book itself.

The following quotation will serve to illustrate the character of the book:

Page 1, paragraph 3: "In making steel, the opera-

tion begins by making pig iron from the iron ore, which is a natural iron rust or a combination of iron and oxygen. The oxygen is removed by combining iron ore, coke, and limestone in a furnace, as shown in Fig. 2, and heating to a high temperature by injecting superheated air into the bottom of the furnace. The coke is burned by the oxygen in the air; a part of it aids in maintaining this high temperature while the rest is useful in removing the oxygen."

Page 13, paragraph 4, discussing blown metal: "Except for the impurities which poison the metal, namely phosphorus, sulphur, oxygen and possibly nitrogen, it has become for all practical purposes a pure metal that is very brittle. This makes it necessary to add certain ingredients that will toughen, strengthen, and harden it so as to make it useful and workable."

Page 64, paragraph 5: "Carbon unites with chemically pure iron in all proportions up to 4 $\frac{1}{2}$ per cent. The capacity of the iron for carbon can be increased by using manganese, and when a high percentage of manganese is added to steel the carbon content can be raised to 7 or 8 per cent."

Page 73, paragraphs 4 and 5: "Manganese is not only useful to cleanse the bath of impurities, but it has other properties that aid in making steel better. The amount that can be left in the steel varies with the amount of various other ingredients that are added to the metal, and this is especially so of carbon. In effect it behaves in practically the same manner as carbon, as also does nickel. With a given carbon content the introduction and increase of manganese causes a series of structural changes similar to those that occur in carbon steels, that only contain small percentages of manganese.

"While the action of these three elements upon iron is of the same kind, it is not of the same strength, as the equivalent of 1% of total carbon, that contains the maximum amount of hardening carbon, is 7.25 per cent. of manganese and 17.55 per cent. of nickel. All three of these cause a structural change in the metal from pearlite, that includes the sorbitic, to martensite, that includes the troostitic, and then to the polyhedral structure, and with none of them is a special carbide formed. Chromium has an analogous effect, but not as complete, as a double carbide of iron and chromium forms and this is not maintained in solution in the iron without tempering."

Page 75, part of paragraph 3: "Many contradictory statements have been made as to the effect of silicon on steel. When the silicon is high in Bessemer steel it is an indication that the metal has been blown too hot, and the metal is apt to be brittle. The percentage varies considerably, according to the heat of the charge, and this causes irregularities which may account for the difference of opinion. The melting point and specific weight of pig iron are governed chiefly by the silicon and the carbon, which are the principal elements."

Page 78, paragraph 3: "In the rolling mills phosphorus does not show any bad effect, as the heat under which the steel is worked seems to overcome this,

but when the metal has become cooled and is subjected to sudden shock or to vibrational stresses, it breaks very easily. The lower the temperature and the higher the atmosphere the easier will the breaks occur. This has led to the term 'cold-shortness' as applied to the effect of phosphorus on steel."

Page 121, paragraph 2: Direct Steel Castings. "In this process the metal is taken direct from the furnace to a heated mixer where the proper materials are added to make the required quality of steel. The metal can be kept liquid as long as desired in the mixer, and its chemical properties adjusted by the addition of different materials. The mixer is kept full by transferring metal from the furnace. When the metal is wanted for casting the mixer is tapped and the metal run into ladles, from which it is poured into the molds as in other castings."

Page 193, paragraph 7: "Cementite is the carbide

of iron, and is expressed by the following formula: Fe_3C , which means ferrite—which is pure iron—3 atoms for every one atom of carbon. It is the second constituent in importance in steel—ferrite being first—and is very hard and brittle. Practically all the carbon is present in this form, and it usually crystallizes in thin flat plates. Cementite does not exist in pure iron, which contains no carbon, and of itself contains about 6.6 per cent. of carbon, which is about one-fifteenth of it."

I have never before read in any book such a conglomerated mass of facts and misinformation.

The binding and paper of this book are good; the print clear and well defined; the illustrations are excellent.

It is to be regretted that the publishers should have permitted such a book to go out without the exercise of greater editorial skill.

WILLIAM BRADY.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

METAL AND ORE PRODUCTION.

In an advance chapter of "Mineral Resources of the United States," by Waldemar Lindgren, of the United States Geological Survey, covering the metal production of the United States for 1909, the Survey has adopted the common-sense plan of reducing all values to a single unit of measure, namely, the short ton of 2,000 pounds. The comparative figures for 1908 and 1909 are issued in this form, covering the production of the different metals, and also the crude metalliferous ores. They show at a glance the quantities of metals and ores produced and their relative quantitative importance.

Mr. Lindgren also includes, in this statement, the large quantities of imported ores, unrefined bullion, etc., which are refined in this country, thus adding to the figures of production from domestic ores as stated in the usual tables. In 1909, for instance, the total production of domestic ores of gold, as stated in the gold chapter of "Mineral Resources," was \$99,673,400. The total production, however, including gold refined from foreign ores, matte, etc., was \$126,099,632.

Comparison of the 1908 and 1909 figures thus stated shows in most items a marked increase. Pig iron increased from 17,678,080 tons, valued at \$248,733,369, in 1908 to 28,638,883 tons, valued at \$411,544,773, in 1909. Of copper 568,981 tons, valued at \$150,210,984, were produced in 1908, as against 695,510 tons, valued at \$180,832,600, in 1909. The platinum production in 1908 was 0.026 ton, valued at \$14,250, which increased in 1909 to 0.039 ton, valued at \$28,440.

The chapter also states the production of crude ores from domestic ores, a showing which has not been attempted in any prior year, and also gives figures on the concentrates of several metals. It is interesting to note that while the production of crude zinc and zinc-lead ores in the United States in 1909 was 10,679,608 tons, the production stated in zinc concentrates was only 715,300 tons.

The crude ore mined in 1908 was 85,627,624 tons and in 1909 it was 112,056,302 tons. An estimate is made of the volume of gold-bearing placer gravel washed in 1909, which is stated to be 80,000,000 cubic yards in the United States, with an average value of 12 cents a cubic yard, and 4,418,000 cubic yards in Alaska, with an average value of \$3.66 a cubic yard.

CLAY PRODUCTS IN FAVOR.

The year 1909 was a record breaker for clay products—bricks, tile, pottery, etc.—The value of the output being \$166,321,213, as compared with \$133,197,762 in 1908. The value was higher than that of 1907 (\$158,942,369). The United States Geological Survey has just issued an advance chapter of "Mineral Resources of the United States" for 1909—"Clay-Working Industries," by Jefferson Middleton—which shows the year to have been a remarkably prosperous one in this important industry. In brick and tile products every item except fancy brick, sewer pipe, and stove lining increased in value. In the pottery industry every item showed an increase. The imports of pottery showed a gain of less than 1 per cent., although the domestic product gained 23.53 per cent. and the exports of high-grade domestic pottery likewise increased. The exports of all clay products increased 22.24 per cent. Every State and Territory except Alaska, but including Porto Rico, is a producer of burned clay, and 42 States showed gains.

The following are the 10 States with highest recorded production for 1909:

State.	Brick and tile.	Pottery.
Ohio.....	\$16,929,885	\$13,416,356
Pennsylvania.....	19,403,944	1,782,769
New Jersey.....	9,380,958	7,791,136
Illinois.....	13,505,898	838,555
New York.....	10,270,227	1,887,209
Indiana.....	6,744,295	900,928
Missouri.....	7,367,061	73,122
Iowa.....	4,846,706	51,990
California.....	4,312,590	124,575
West Virginia.....	1,159,627	2,350,470

The great growth shown in some of the clay-working industries during the last decade is interesting. Common brick increased from \$38,621,514 in 1900 to \$57,251,115 in 1909; vitrified paving brick from \$4,764,124 to \$11,269,586; front brick from \$3,864,670 to \$9,712,219; drain tile from \$2,976,281 to \$9,799,158; sewer pipe from \$5,842,562 to \$10,322,324; and fireproofing from \$1,820,214 to \$4,466,708.

NATURAL GAS PRODUCTION FOR 1909.

The chapter on natural gas from "Mineral Resources of the United States for 1909" can now be had of the United States

Geological Survey by application to the Director at Washington. The industry surpassed in 1909, both in the quantity and value of the gas produced, the record of any previous year, the estimated value being \$63,206,941, as against \$54,640,374 in 1908. Although the returns are unusually late, it is believed that as a result of coöperation with the Census Bureau they are more complete than those of any previous year. The report discusses the production in considerable detail and gives the output by States covering a long period of years. In 1909 Pennsylvania led with an output valued at \$20,475,207, West Virginia came next with \$17,538,565, Ohio was third with \$9,966,938 and Kansas was fourth with \$8,293,846. No other State produced as much as \$2,000,000 worth.

INCREASE IN GOLD AND SILVER PRODUCTION.

A report on the production of gold and silver in the United States in 1909, by H. D. McCaskey, of the United States Geological Survey, has just been issued as an advance chapter of the Survey's volume "Mineral Resources." The figures agree with those of the Director of the Mint, being the result of coöperation between the two bureaus, and are therefore final for both. The gold production was valued at \$99,673,400 and the silver at \$28,455,200, an increase over the figures for 1908 of \$5,113,400 for gold and \$404,600 for silver. The report includes figures and detailed statements of production by States, and comparisons of the total output for the last three decades. It also includes the statistics of imports and exports as well as tables of ore production.

SEVEN MILLION DOLLARS FOR MINERAL WATERS.

The sales of mineral water in the United States during 1909, according to the United States Geological Survey, represented a value of \$6,894,134, a slight increase over the figures for 1908. The quantity sold was 64,674,486 gallons and the average retail price was 11 cents a gallon. In addition to this quantity over 6,000,000 gallons were estimated to have been used in the manufacture of soft drinks. The tables given in the report show a steady increase in the production of mineral waters for the last 25 years, the figures for 1885 being 1,312,845 gallons. The value of the imports of mineral water in 1909 was \$1,085,177, with an average of 31 cents a gallon.

The report shows the production by States with names of springs and other details.

QUALITY OF ILLINOIS RIVER WATERS.

The United States Geological Survey has just published another edition of its exhaustive report on the quality of the waters of Illinois (Water Supply Paper 239). While this report is of first interest to the people of Illinois, it contains much information on steam pollution, the treatment of impure waters for municipal engineering and other industrial uses, the cost of differing degrees of purification for different purposes, and similar subjects having a general application and interest. The volume is now available for distribution and can be obtained on request to the Director, United States Geological Survey, Washington, D. C.

NATURAL GAS IN TRINIDAD.

The island of Trinidad, according to the United States Geological Survey, is well supplied with natural gas, large supplies of which are reported to be going to waste. This gas, if piped to Port of Spain, would undoubtedly be a great source of revenue. The gas is under great pressure, the discharge from a well at Guayaguayana being said to be about 1,000,000 cubic

feet a day. Every oil well drilled on the island thus far has produced large quantities of gas in addition to the oil.

Examination of the Raw Materials, Products and By-products of the Sugar Industry. By R. FRUEHLING. Brunswick, 8vo., 535 pp. \$3.75.

The Analysis of Paints and Painting Materials. By GARDNER and SCHAEFFER. 1911. L. 8vo., 109 pp. \$1.50. D. Van Nostrand Co.

Commercial Peat: Its Uses and Possibilities. By FREDERICK F. GISSING. 1911. 8vo., 200 pp. \$2. J. B. Lippincott Co.

A Text Book of Physics. By HURST & LATTEY, 1911, D. Van Nostrand Co. 8vo., 648 pp. \$3.00

Micro-organisms and Fermentation. By ALFRED JORGENSEN, 1911. 8vo., 500 pp. \$4.50. D. Van Nostrand Co. 4th Edition.

Electrical Nature of Matter and Radioactivity. By HARRY C. JONES. 1911. 8vo., 219 pp. \$2. D. Van Nostrand Co. 2nd Edition.

A Manual of Dyeing. By KNECHT, RAWSON & LOEWENTHAL, 1911. L. 8vo., 531 pp. \$12. J. B. Lippincott Co. 2nd Edition.

A Text Book of Botany and Pharmacognosy. By HENRY KRAEMER. 1911. 8vo., 888 pp. \$5. J. B. Lippincott Co. 4th Edition.

Technical Mycology. By FRANZ LA FAR. 1911 8vo., 327 pp. \$4.50. J. B. Lippincott Co.

Handbook of Biochemistry. By E. LAMBLING, Paris. 1911. 8vo. \$2.

Text Book of Electrochemistry. By M. LE BLANC, Leipzig. 1911. \$1.75.

Acetylene: The Principles of its Generation and Use. By LEEDS & BUTTERFIELD. cr. 8vo., 411 pp. 1911. \$2.75. J. B. Lippincott Co. 2nd Edition.

Radium in Biology and Medicine. By E. S. LONDON 1911. Leipzig. L. 8vo., 199 pp. \$1.50.

A Treatise on Electrometallurgy. By WALTER G. McMILLAN. 1911. cr. 8vo., 459 pp. J. B. Lippincott Co.

Drying Machinery and Practice. By THOMAS G. MARLOW. 1910. L. 8vo., 388 pp. \$5. D. Van Nostrand Co.

The Construction and Working of Internal Combustion Engines. By R. E. MATHOT. 1910. 8vo., 576 pp. \$6.60.

The Non-metallic Minerals. By G. P. MERRILL. 1911. 8vo., 444 pp. \$4. John Wiley & Sons.

Blast Furnace Practice. By J. J. MORGAN. 1911. 12mo., 53 pp. 75c. J. B. Lippincott Co.

Catalysis. By W. OSTWALD. Leipzig. 1911. 50c.

White Paints and Painting Materials. By W. G. SCOTT, The Modern Painter: Chicago. 8vo., 493 pp. 1911.

Qualitative Chemical Analysis. By WILFRED W. SCOTT. 8vo., 176 pp. \$1.50. D. Van Nostrand Co. 1911.

Chemistry of Food Nutrition. By HENRY C. SHERMAN. 12mo., 355 pp. \$1.50. 1911. MacMillan Co.

The Organic Chemistry of Nitrogen. By N. V. SIDGWICK. Roy. 8vo., 428 pp. \$3.75. Oxford. 1911.

Modern Assaying. By J. REGINALD SMITH. cr. 8vo., 145 pp. \$1.50. 1911. J. B. Lippincott Co.

- Ceramic Literature. By M. L. SOLON. 649 pp. \$15. J. B. Lippincott Co. 1911.
- Year Book of Radioactivity. By J. STARK. Leipzig. \$5.00. 1911.
- An Elementary Text Book of Physics. 4 Vols. 12mo., 1042 pp. \$6.25. 1911. J. B. Lippincott Co.
- Preparation of Colloidal Solutions of Inorganic Substances. By T. SVEDBERG. 8vo., 507 pp. 1911. Th Steinkopf, Dresden.
- Outlines of Inorganic Chemistry. By F. SWARTS. L. 8vo., 578 pp. \$3.75. 1911.
- The Theory of Ionization of Gases. By JOHN S. TOWNSEND. 8vo. 99 pp. \$1.25. D. Van Nostrand Co. 1911.
- Acetylene. By J. H. VOGEL. Leipzig. L. 8vo., 294 pp. \$4.25. 1911.
- Mycology of Milk. By H. WEIGMANN. Leipzig. L. 8vo., 267 pp. \$1.75. 1911.
- A History of the Theories of Ether and Electricity. By E. Z. WHITTAKER. L. 8vo. 488 pp. \$4.50. 1910. D. Van Nostrand Co.
- Foods and their Adulteration. By H. W. WILEY. 8vo., 640 pp. \$6.00. 1911. 2nd Edition. Blakiston's.
- Text Book of Analytical Chemistry. By H. WOEBLING. Berlin. L. 8vo., 479 pp. \$2. 1911.
- Logarithms and Tables for Chemists. By C. J. WOODWARD. 12mo., 70 pp. D. Van Nostrand Co. 1910.
- Tests for Coal Tar Colors in Aniline Lakes. By GEORGE ZERR. 8vo., 228 pp. \$5.50. J. B. Lippincott Co. 1911.
- Kunststoffe, or Artificial Substances. Edited by DR. RICHARD ESCALES, Munich. A journal devoted to the use of refined or chemically produced substances. The following subjects will be considered: artificial silk, natural and artificial rubber, rubber substitutes, celluloid, artificial leather, linoleum and oil cloth, artificial resins (Bakelite), casein products, etc. Dr. Leo H. Baekeland and Dr. Arthur D. Little are among its contributors.
- International Journal of Metallography. Edited by W. GUERTLER. First issue February, 1911. Subscription, \$5 per volume. (Two vols. per year). Gebrüder Bornträger.
- More Recent Cyanide Practice. By H. FOSTER BAIN. 1910. 8vo., 424 pp. D. Van Nostrand Co. \$2.
- Chemistry and Biochemistry of the Lipoids. By J. BANG. Wiesbaden. L. 8vo. \$1.50.
- Text Book of the Illuminating Gas Industry. By W. BERTELSMAN. Stuttgart. 1911. L. 8vo. \$5.50.
- The Metallurgy of Lead. By HENRY F. COLLINS. 1911. L. 8vo., 558 pp. J. B. Lippincott Co. \$6.
- Constitution of the China Alkaloids. By E. COMANDUCCI. Stuttgart. 1911. L. 8vo., 166 pp. \$1.25.
- The Chemistry and Testing of Cement. By CECIL H. DESCH. 1911. 8vo., 277 pp. D. Van Nostrand Co. \$3.
- An Introduction to Bacteriological and Enzyme Chemistry. By GILBERT J. FOWLER. 1911. 328 pp., 8vo. \$2.10. Longmans, Green & Co.
- Collected Essays on Colloids and Absorption. By J. M. VAN BEMMELEN. T. Steinkopf, Dresden. L. 8vo., 274 pp. \$3.75. 1911. (German.)
- Almanac for the Chemical Industry, 7th Ed. By H. BLUECHER. F. Siemenroth, Berlin. L. 8vo. 1362 pp. \$4.00. 1911. (German.)
- Modern Industrial Chemistry, 7th Ed. By H. BLUECHER. F. Siemenroth, Berlin. D. 8vo., 800 pp. \$6.25. 1911.
- Theory of the Rotation of the Plane of Polarization. By D. H. BRAUNS. Detroit. Privately printed. 8vo., 21 pp. 1911.
- Physico-Chemical Tables. By JOHN CASTELL-EVANS. 2 Vols. Chas Griffin & Co., London. L. 8vo. \$15.00. 1911.
- The Determination of Nicotin in Nicotin Solutions and Tobacco Extracts. ROBERT M. CHAPIN. U. S. Dept. of Agriculture, Bureau of Animal Industry, Bulletin 133. 1911.
- Chrysotile Asbestos: Its Occurrence, Exploitation, Milling and Uses. FRITZ CIRKEL. Canada Dept. of Mines Publication, No. 69. 1911.
- Complete Guide to Chemical Manipulations. L. P. CLERC. L. Geisler, Paris. 8vo. \$10.00. 1911. (French.)
- Photography in Natural Colors on Autochrome Plates. By V. CRÉMIER. Gauthier-Villars, Paris. 16mo., 111 pp. \$6.00. (French.)
- The Chemistry and Testing of Cement. By CECIL H. DESCH. London. 267 pp. 1911.
- Modern Methods of Water Purification. By DON AND CHISHOLM. E. Arnold, London. 8vo., 384 pp. \$4.00. 1911.
- A Class-Book of Chemistry. By G. C. DONINGTON. The Macmillan Co. 12mo. \$9.00. 1911.
- A Text-book on Gas, Oil and Air Engines. 5th Ed. By BRYAN DONKIN. C. Griffin, London. 8vo., 664 pp. \$6.25. 1911.
- Handbook of Photography. By J. M. EDER. W. Knapp-Halle. L. 8vo., 329 pp. \$3.50. 1911. (German.)
- Applied Thermodynamics. By WM. D. ENNIS. D. Van Nostrand Co. 8vo., 446 pp. \$4.50. 1911.
- Insulating Substances and the Methods of Insulation used in the Electrical Industry. By J. ESCARD. Gauthier-Villars, Paris. 8vo., 314 pp. \$2.25. 1911. (French.)
- An Introduction to Bacteriological and Enzyme Chemistry. By GILBERT J. FOWLER. E. Arnold, London. 1911.
- Guide to the Examination of the Raw Materials, Products and By-products of the Sugar Industry. By R. FRUEHLING. Brunswick. L. 8vo., 535 pp. \$4.00. 1911. (German.)
- Microscopical Examination of Foods and Drugs. By HENRY G. GREENISH. 2nd Ed. P. Blakiston's Son & Co. 8vo., 386 pp. \$3.00. 1911.
- Alcoholic Fermentation. By ARTHUR HARDEN. D. Van Nostrand Co. 8vo., 138 pp. \$1.25. 1911.
- Practical Physiological Chemistry. 3rd Ed. By P. B. HAWK. 8vo., 440 pp. \$2.50. 1911.
- A Concise History of Chemistry. By F. P. HILDITCH. D. Van Nostrand Co. 8vo., 273 pp. \$1.25. 1911.
- Text-book for the Teaching of Practical Chemistry to Medical Men. By F. HOFMEISTER. Brunswick. 160 pp., 8vo. \$1.25. 1911. (German.)
- Chemistry and Toxicology. By JAMES M. HOLLAND. 2d Ed. W. B. Saunders Co. 8vo., 655 pp. \$3.00. 1911.
- A Text-book of Gas Manufacture for Students. By JOHN HORNBY. 6th Ed. The Macmillan Co. 8vo. \$2.50. 1911.
- Wyoming Forage Plants and their Chemical Composition. By HENRY G. KNIGHT. Wyoming Experiment Station, Bulletin 4, 1911.
- Researches on Aluminium. By W. E. KOHN-ABREST. Ch. Beranger, Paris. 8vo., 91 pp. \$1.25. 1911.

- The Behavior of Cast and Wrought Iron Pipes in Water, Salt Solutions and Acids. By O. KROEHNKE. R. Oldenbourg, Munich. 8vo., 122 pp. \$1.25. 1911. (German.)
- Mineralogy of France and Its Colonies; Physical and Chemical Description. By A. LACROIX. Baudry & Co., Paris. 4 vols., 3265 pp. 1893-1910. (French.)
- Wheat Investigations; Milling, Baking and Chemical Tests. By LADD & BAILEY. *N. Dak. Agric. Expt. Station, Bulletin* 89.
- Practical Treatise on Adulterations and Misbrandings. By LE PORTEVIN. Paris. \$1.00. 1911. (French.)
- The Relations between Color and Constitution of Organic Compounds. By H. LEY. Leipzig. L. 8vo., 246 pp. \$2.00. 1911. (German.)
- The Manufacture of Sulfuric Acid and Alkali, with the Collateral Branches. By GEORGE LUNGE. 3rd Ed. Vol. III. Ammonia-soda, Various Processes of Alkali Making and the Chlorin Industry. Guernsey and Jackson, London. 8vo., 744 pp. \$7.50. 1911.
- Ostwald's Handbook of Physico-Chemical Measurements. 3rd Ed. By LUTHER AND DRUCKER. W. Engelmann, Leipzig. L. 8vo., 573 pp. \$3.25. 1911. (German.)
- Practical Guide to Iron and Steel Works Analyses. By WALTER MACFARLANE. Longmans, Green & Co. \$1.25. 1911.
- The Chemistry of Synthetic Drugs. By PERCY MAY. Longmans, Green & Co. 8vo., 229 pp. \$2.25. 1911.
- Literature of Sulfite-cellulose Spent Liquors. By MAX MUELLER. Carl Hofmann, Berlin. 114 pp. \$1.50. 1911. (German.)
- N. Y. State Water Supply Commission; 6th Annual Report, Albany, 1911.
- Introduction to the Study of Organic Chemistry. By J. P. OSSIPOW. Charkow. 8vo., 294 pp. \$1.50. 1911. (Russian.)
- Text-book of General Chemistry. By W. OSTWALD. (In 2 vols.) Vol. II, Part I. Chemical Energy. Leipzig. 8vo., 1104 pp. \$9.25. 1911. (German.)
- Practice of Copper Smelting. By EDWARD D. PETERS. McGraw-Hill Book Co. 8vo., 693 pp. \$5.00. 1911.
- Modern Chemistry. By WM. RAMSAY. Gauthier-Villars, Paris. 2 vols. 16mo., 438 pp. \$1.50. 1909-1911. (French.)
- Report of the Second International Congress for the Prevention of the Adulteration of Foods and Drugs. Geneva. 8vo. \$3.00. 1911. (French.)
- Coal-dust Explosions. By GEORGE S. RICE. *Bureau of Mines, Miners' Circular* No. 3. 1911.
- The Estimation of Total Solids in Milk by the Use of Formulas. By R. H. SHAW, AND C. H. ECKLES. *U. S. Dept. of Agriculture, Bureau of Animal Industry, Bulletin* 134, 1911.
- The Sulfur Bleaching of Commercial Oats and Barley. By LE ROY M. SMITH. *U. S. Dept. of Agriculture, Bureau of Plant Industry, Circular* 74.
- Shellfish Contamination from Sewage-polluted Waters and from other Sources. By GEORGE W. STILES. *U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin* 136. 1911.
- Theoretical and Practical Treatise on the Resistance of the Materials Used in Concrete and Re-enforced Concrete. By N. DE TEDESCO, AND A. MAUREL. Ch. Beranger, Paris. 8vo., 656 pp. \$5.00. 1911. (French.)
- The Status of the Question of Indicators in Volumetric Analysis. By A. THIEL. Stuttgart. L. 8vo., 116 pp. \$1.00. 1911. (German.)
- Chemical Control in Sugar Refineries. By C. TOWRY. Gauthier-Villars, Paris. 16mo., 175 pp. \$0.60. 1910. (French.)
- Qualitative Chemical Analysis of Inorganic Substances. By OLIN F. TOWER. 2nd Ed. P. Blakiston's Son & Co. 8vo., \$1.00. 1911.
- The Use of Rubber, Guttapercha and Celluloid in Dentistry. By H. VIGANO. Berlin. 8vo., 71 pp. \$0.50. 1911. (German.)
- Plant Products; Chemical Constituents and Composition of Plants; Raw Material and Products. By C. WEHMER. Jena. L. 8vo., 937 pp. \$9.00. 1911. (German.)
- Industrial Alcohol; Sources and Manufacture. By H. W. WILEY. *U. S. Dept. of Agriculture, Farmers' Bulletin*, No. 429. 1911.
- Nitrocellulose Industry. By EDWARD C. WORDEN. 2 vols. D. Van Nostrand Co. L. 8vo., 1239 pp. \$10.00. 1911.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

- Buying and Testing Paper Pulp. ANONYMOUS. *Paper*, Vol. III, No. 4, pp. 9-11.
- The Industry of Brewing. By A. C. CHAPMAN. *Journal Society of Chemical Industry*, Vol. XXX, No. 8, pp. 463-469.
- The Conservation of Iron. ALLERTON S. CUSHMAN. *Industrial World*, Vol. XLV, No. 18, pp. 4-18. 1911.
- Germicides and Antiseptics. WILLIAM DREYFUS. *Am. Drug*, Vol. LVIII, No. 7, pp. 23-24.
- Effect of Bleaching Powder upon Bacterial Life in Water. JOSEPH W. ELLMS. *Engineering Record*, Vol. 63, No. 17, pp. 471-473.
- The Refining of Iron and Steel in Induction Type Furnaces. C. F. ELWELL. *Proc. Am. Inst. Elec. Eng.*, Vol. XXX, No. 4, pp. 621-630.
- Technico-Chemical Researches on Kichxia Rubber. FRANK & MARCKWALD. *Gummi Zeitung*, Vol. XXV, No. 24. (German.)
- Castor-oil Products in the Textile Industry. J. GAERTH. *Seifenfabrikant*, Vol. XXXI, No. 15, pp. 358-360. (German.)
- The Manufacture of Thiosulfate. E. SCHUETZ. *Zeitschrift fuer angewandte Chemie*, Vol. XXIV, No. 16. 1911. (German.)
- The Determination of Total Fatty Acids in Oils, Fats and Soaps. P. SIMMICH. *Zeitschrift fuer Untersuchung der Nahrungs- und Genussmittel*, Vol. XXI, No. 1. (German.)
- The Rate of Alcoholic Fermentation. ARTHUR SLATOR. *Journal of the Institute of Brewing*, Vol. XVII, No. 2, pp. 147-159. 1911.
- The Determination of the Iodin Number of Fats and Oils by means of the Bromin Thermal Test. C. STIEPEL. *Seifenfabrikant*, Vol. XXXI, No. 15, pp. 349-352. (German.)
- The Identification of Rape Oil: Its Separation when Mixed with Olive or other Edible Oils. TORTELLI AND FORTINI. *Gazetta chimica italiana*, XLI, April, 1911, pp. 173-182.
- The Yeast Cell. HAROLD WAGER. *Journal of the Institute of Brewing*, Vol. XVII, No. 1, pp. 2-22. 1911.
- Improvements in Cotton Bleaching. WALTER S. WILLIAMS. *Metallurgical and Chemical Industry*, Vol. IX, No. 5, pp. 247-250.
- The Comparative Efficiency of Certain Tanning Materials. ROBERT W. GRIFFITH. *Journal American Leather Chemists' Association*, Vol. VI, No. 5, pp. 211-219.

- Origin of the Thermal Waters in the Yellowstone National Park. ARNOLD HAGUE. *Science*, April 14, 1911, p. 553.
- Purchase of Fuel under Specifications. G. CECIL JONES. *Journal of the Institute of Brewing*, Vol. XVII, No. 3, pp. 182-209.
- An Efficient and Rapid Mercury Still. CHAS. F. KNIPP. *Science*, Vol. XXXIII, No. 852, pp. 667-669. 1911.
- Fuel Control in the Boiler House. R. R. LANSDALE. *Journal of the Institute of Brewing*, Vol. XVII, No. 1, pp. 23-24. 1911.
- Electrolytic Corrosion in Re-enforced Concrete. C. E. MAGNUSON AND G. H. SMITH. *Proceedings American Institute of Electrical Engineers*, Vol. XXX, No. 5, pp. 939-963.

- Recent Researches on Starch. C. G. MATTHEWS AND F. E. LOTT. *Journal of the Institute of Brewing*, Vol. XVII, No. 3, pp. 219-271.
- Mercerizing Yarns for Knit Goods Cotton. MERRITT J. MATTHEWS. Vol. 75, No. 5, pp. 192-193.
- An Improvement in the Method of Malt Analysis. JAMES O'SULLIVAN. *Journal of the Institute of Brewing*, Vol. XVIII, No. 1, pp. 35-48. 1911.
- Manufacture of Aerated Waters. WALTER A. RILEY. *Journal of the Institute of Brewing*, Vol. XVII, No. 2, pp. 117-145. 1911.

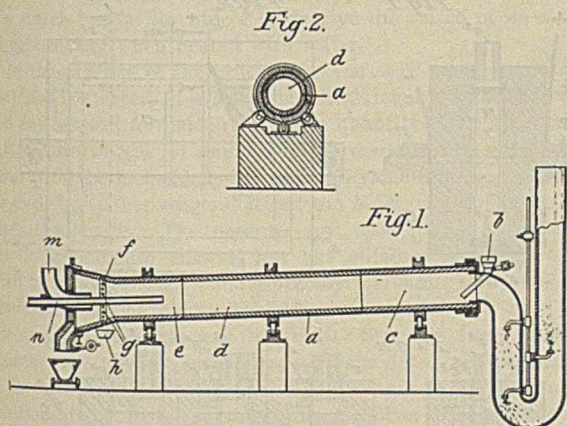
RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

986,271. Process of Refining and Agglomerating Ores and the Like.

This invention relates primarily to the treatment of those ores which can be smelted only with difficulty, first on account of their physical condition and secondly on account of the injurious foreign substances which they contain. To this class belong more particularly the friable iron ores.

According to this invention the revolving furnace, shown in the accompanying illustration, is heated by a water gas flame whereby new results are achieved. By the employment of a water gas flame, not only can all the results heretofore obtained be effected in a simple and certain manner, but it is also possible (owing to the peculiar formation of the flame) to so perform the operations in the furnace that oxidation or reduction and fusion shall take place at will.



In the patentee's apparatus shown in the accompanying illustration, *a* is the revolving drum which is lined with an acid or basic refractory material, and into which the ore is charged as its upper end through the chute *b*. The ore first passes through the drying zone *c* and then enters the oxidizing zone *d*. Here, the sulphur, arsenic, zinc and the like are oxidized and also volatilized, while the residual ore begins to fuse together in lumps and nodules. Any zinc which has not yet been volatilized as zinc oxid passes into the reducing zone *e* where it is volatilized as metallic zinc. Any lead that may be present is also reduced and melted here, and runs off through the annular passage *f* (which is provided with apertures *g*) into molds *h*. The ore passes out from the lower end of the furnace not only in a physical condition adapted for blast-furnace treatment, but also purified, and in a lower stage of oxidation.

For the purpose of keeping the oxidizing and reducing zones effectually separated from each other, the gas and air are pref-

erably admitted wholly or partially at different places. The wide pipe *m* serves for the admission of the water gas which can become ignited at the mouth of this pipe even without any previous admixture of air, while the quantity of air which is necessary for complete combustion or the excess air requisite for oxidation is admitted through the air pipe *n* at a place situated farther back.

By regulating the quantities of gas and air admitted, as well as by the manner in which and the place whereat the gas and air are mixed together, every possible desirable result can be obtained. This adaptability of the furnace constitutes its chief value, since it enables materials to be treated which have no homogeneous or uniform composition.

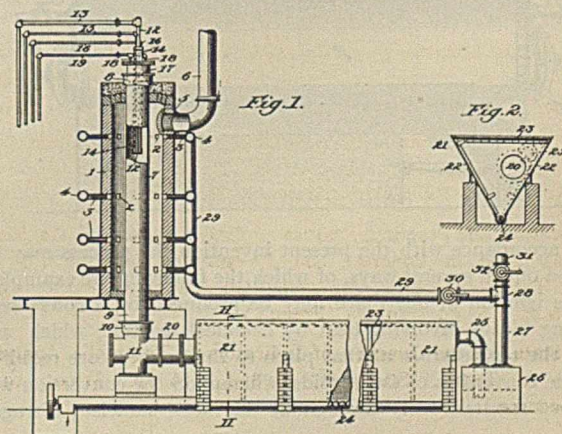
The furnace is to be used in the same manner whether iron ores, copper ores or by-products containing a high percentage of copper are to be treated, the lead, zinc, sulphur, arsenic and antimony being similarly separated. These separated products may be recovered for use according to the special economic conditions in each case. As will be seen by reference to the illustration that the waste gases may be cooled by means of a water spray so the volatile metallic oxides are precipitated in the form of mud and may be removed in that condition.

The inventor is Hugo Dicke, of Frankfort-on-the-Main, Germany, assignor to Jacob Eduard Goldsmid, of Frankfort-on-the-Main, Germany.

986,489. Process of Dissociating Acetylene.

This invention is a process of dissociating acetylene by heat, at approximately atmospheric pressure.

The patentee of this process found that acetylene at practically atmospheric pressures, if suddenly heated to a temperature at or in excess of that corresponding to a dull red heat, dissociates



instantly and quietly into its elements of carbon and hydrogen without the production of any of its polymers, and that the carbon so produced is either deposited in the heating retort, or is carried along with the gaseous hydrogen as a light flocculent powder, easily handled and practically chemically pure. His process of making lampblack from acetylene is based on this discovery.

In using the apparatus illustrated to carry out the process, the retort 7 is heated, preferably by gas introduced through the burners 3, to or above the temperature of dull redness.

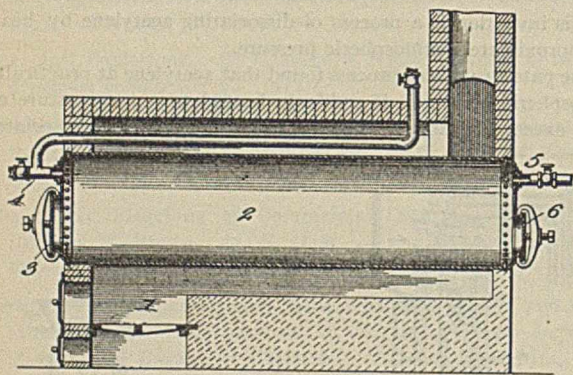
A stream of acetylene, maintained at a temperature below its dissociation point by the water flowing through the jacket 14, is then delivered through pipe 12 into the upper end of the retort. The acetylene, issuing into the retort and suddenly heated to or above the temperature of dull redness, instantly and quietly dissociates, the carbon being set free in the form of lampblack, which largely collects in the retort, while the free hydrogen passes on through the settling chamber 21 and may be returned to the burners 3 to heat the retort. The current of hydrogen may also carry some of the lampblack into the settling chamber. As the retort becomes filled with lampblack, the stream of acetylene is cut off, valve 30 in hydrogen pipe 29 is closed and valve 32 in waste-pipe 31 is opened. An inert gas, preferably at the temperature of the retort, for example hot products of combustion, is then forced into the upper end of the retort through the nozzles 18, blowing the light lampblack out of the retort and into the chamber 21, where it settles, to be removed by the conveyor 24.

The inventor is John M. Morehead, of Chicago, Illinois, assignor to Union Carbide Company, of Chicago.

987,674. Process of Producing Nitrogen Compounds.

This invention relates to a process of producing nitrogen compounds from carbids.

In the production of nitrogen compounds by the reaction of nitrogen with carbids, as for example, the carbids of the alkaline earths, it has been ascertained that it is not necessary for the process that the entire mass of the carbid be brought to the temperature necessary for the reaction by supplying external or intrinsic heat to the entire mass; but that it suffices if this temperature be produced at one place in the mass, when the reaction then continues spontaneously throughout the entire mass. A preliminary condition, however, is that the reaction temperature of from about 800° C to 1100° C. be actually attained at this one place.



In accordance with the present invention the process may be carried out in several ways, of which the following are examples:

The ignition at one place may be produced by a convenient heating means involving heat by chemical reaction, which will raise the temperature at that place to the temperature required for the conversion of the carbids, whereupon the conversion will proceed spontaneously throughout the mass, sufficient nitrogen

being present to effect the conversion. The production of a temperature sufficiently high for the absorption of nitrogen by the carbid at one place or point of the carbid by means of said chemical heating in order to raise the carbid at this one place to the proper ignition temperature may be accomplished: (a) by means of a primer comprising an explosive mass or the like; or (b) by means of substances reacting with carbid with the production of the necessary heat, which substances, if in the solid state such as chlorate of potassium, nitrate of alkali, etc., may be added to the carbid at the place of ignition; while if the substances are gaseous, such as chlorine or oxygen, the same may be added to or employed with the first portions of the nitrogen that are led to the carbid until the ignition has taken place; or (c) the requisite temperature may be produced by substances such as magnesium or aluminium which, when mixed with the carbid at the place of ignition, react with the nitrogen with the production of the desired heat. After the ignition has produced a temperature sufficient to cause a further absorption of the nitrogen, the latter is further supplied, and it will continue to be absorbed with a further development of heat so that the continued supply of nitrogen will cause the absorption to proceed spontaneously throughout the mass.

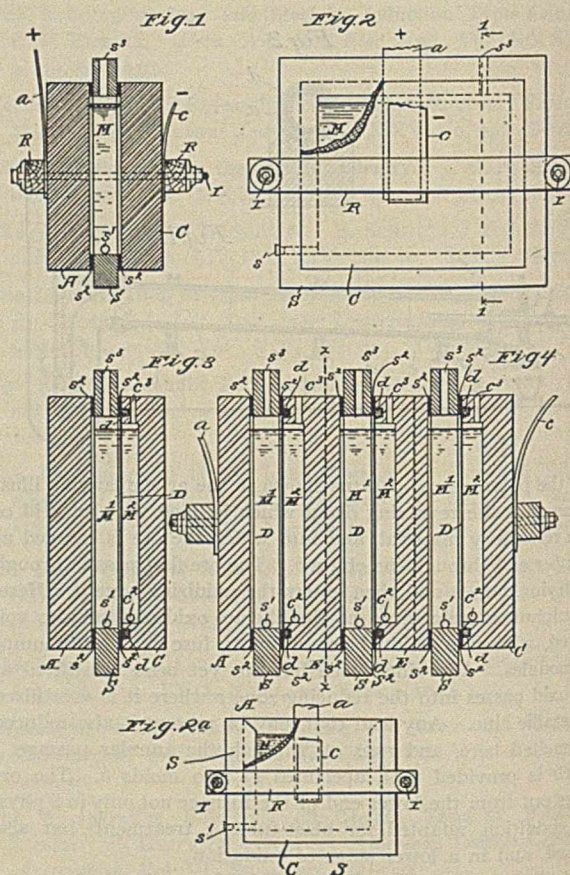
The accompanying illustration shows apparatus in which the process may be practiced.

The inventor is Albert Randolph Frank, of Halensee, near Berlin, Germany; assignor to the Firm of Societa Generale Per la Cianamide, of Rome, Italy.

987,717. Electrolytic Cell.

This invention relates particularly to electrolytic cells for the electrolysis of alkaline chlorids.

By reference to the accompanying illustration, the cell will be seen to comprise a rectangular ring-shaped, or perforated, member, S, which is termed a separator. Upon the opposite



sides of such separator, which is made of suitable insulating material, are clamped blocks or plates, A C, of carbon. These plates, A C, laterally enclose the opening through separator S, thereby forming a cell or chamber, M, for the reception of the electrolyte. Electric current leads, *a c*, are clamped in contact with plates A C respectively by the same clamps, R, which thus hold the latter against separator S, such clamps, R, consisting simply of wooden bars, the ends of which extend beyond the ends of the blocks in question and are joined together by threaded bolts, *r*. Where separator S is of the annular form shown, chamber M will be a closed chamber save for the opening *s*² provided for the introduction of the electrolyte as occasion may arise as well as for escape of gas from the cell and an opening, *s*¹, normally closed, for draining the cell of its contents. If, however, an open cell is desired this result is accomplished by making the separator of U-form instead of a complete annulus or ring. In the use of the cell the chamber M will be charged with the electrolyte, as, for example, a solution of common salt, and an electric current passed through it from A to C. Such plate, A, thus becomes the anode, upon the active face of which chlorine will be liberated while plate C acts as the cathode upon the active face of which hydrogen and caustic soda are liberated. The inventor is Thomas Griswold, Jr., of Midland, Michigan.

982,673. Insoluble Nongelatinizable Starch.

This invention relates to a method of treating starch or starch-containing materials for the purpose of converting it into a hitherto unknown form, which owing to several characteristic properties thereby acquired renders the starch more useful and more valuable for certain purposes as, for instance, in nitrating starch, in manufacturing glucose from starch, etc.

The most characteristic property of starch is its ability of paste-forming or gelatinizing when heated with water above a certain temperature, which varies somewhat for the different kinds of starch. The treatment to which the patentee subjects the starch has for its object to deprive the starch of its ability of gelatinizing when heated with water.

In the practice of the process the starch or starch-containing material is steeped in a solution containing from about five to ten per cent. of formaldehyde and a quantity of an ammonium salt whose content of ammonium is theoretically sufficient to form with the formaldehyde hexamethylenetetramin, although an excess of either reagent, if not too large, will not materially alter the results. The patentee has used in his experiments mostly ammonium chlorid, but has obtained as good results with other ammonium salts, especially inorganic, as for instance ammonium sulphate provided sufficient material was used and the time of reaction was modified. Starches from different sources vary to some extent in their behavior to such a mixture of formaldehyde and ammonium salts, some requiring stronger solutions than others or a longer or shorter time of reaction. The main object of the invention being the production of an

ungelatinizable starch, the quality of starch and the particular ratio of the ingredients is left to the selection of the manufacturer.

The patentee prefers to use an aqueous solution containing from about 5 to 10 per cent. of formaldehyde and from 6 to 11 per cent. of ammonium chlorid to which the starch or starch-containing material is added until a perfectly thin milk is obtained. He preferably uses a ratio, one part of starch to about three or four parts of the solution, but any other convenient ratio may be used without interfering with the results. The whole of the mixture is kept at ordinary temperature, *i. e.*, 20° to 30° C., the ingredients being intimate contact, until a small sample withdrawn from the mass and diluted considerably with water does not show gelatinization on heating, and the starch granules sink to the bottom of the test tube.

When the reaction is completed, the mixture is allowed to settle, the liquid drawn off and the residual starch filtered and washed, until the filtrate does not give any further reaction for the chlorine ion. It can then be dried. The starch thus obtained does not outwardly differ from ordinary starch, but is nevertheless changed into what may properly be called an allotropic form of starch with the properties described above.

The inventor is Bernard Herstein, of Bayonne, N. J.

Improved Process for Coating or Printing with Viscose.

British Patent 15306/09.

Dr. Leon Lilienfeld, Vienna.

Claims (1) a process for coating or printing with viscose either alone with coloring matters or pigments of all kinds, characterized by the fact that the known compounds of viscose with the metals of the magnesium group (zinc compound for example) are dissolved with the assistance of as much alkali as is necessary for replacing the metal of the magnesium group contained in the viscose compound by the metal of the alkali group; (2) method of carrying into practice the process in accordance with Claim 1, characterized by the fact that soaps soluble in water or sulphuric acid or other sulpho fatty acids of their sodium or ammonium salts are added to the printing or coating layers obtained in accordance with Claim 1 in quantities which are not smaller than one-fifth of the proportion of cellulose calculated in air-dry cellulose.

Improvements in the Production of Isoprene.

British Patent 27908/09.

H. Woltereck, London.

Claims the process of producing isoprene from turpentine, the operation of passing the vapors of the same in most intimate contact over heated iron either without or with the admixture of inert gases, such as nitrogen, and at a carefully regulated temperature between 5500 C. and 6000 C. substantially as described.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MAY.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	13 @	15
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.33 3/4 @	2.45
Acetic Acid (28 per cent.).....C.	1.62 1/2 @	1.75
Acetate of Lime (gray).....C.	1.75 @	1.80
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Aniline Oil.....Lb.	11 1/2 @	11 3/4
Benzoic Acid.....Oz.	11 1/4 @	12
Boric Acid, crystals.....Lb.	7 @	7 1/2
Carbon Tetrachloride (in drums).....Lb.	8 1/8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	10 @	11
Citric Acid (domestic).....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.	— @	49 1/2
Dextrine (imported potato).....Lb.	5 1/2 @	7
Dextrine (domestic corn).....C.	2.37 @	2.50 1/2
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	21 3/4 @	22 1/4
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7.17 1/2 @	7.68 3/4
Pyrogallic Acid (bulk).....Lb.	1.00 @	1.05
Paraffine (crude) 120 @ 122 m. p.....Lb.	3 @	3 1/4
Paraffine (refined), domestic 120 @ 122 m. p.....Lb.	4 1/2 @	4 3/4
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1.57 @	1.73
Starch (potato).....Lb.	4 1/4 @	5 1/4
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 7/8 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	29 1/4 @	29 1/2

Inorganic Chemicals.

Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 3/4 @	3
Ammonium Chloride, gray.....Lb.	5 3/4 @	6
Arsenic, white.....Lb.	1.82 1/4 @	2.06 1/4
Ammonium Carbonate, domestic.....Lb.	8 @	8 3/4
Aluminum Sulphate.....Lb.	90 @	1 3/4
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 1/4
Barium Nitrate.....Lb.	5 1/2 @	6 1/2
Borax, crystals in bags.....Lb.	3 1/2 @	4
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.19 3/8 @	1.28 3/4
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 1/4 @	4 1/2
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	90 @	92
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	62 1/2 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 1/2
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Nitric Acid, 42°.....Lb.	4 7/8 @	5 1/4

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 3/4 @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals, f. o. b. works.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 3/4 @	5
Potassium Bichromate, 50°.....Lb.	7 3/8 @	7 1/2
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	66 @	70
Salt Cake (glass-makers).....C.	62 1/2 @	77 1/2
Silver Nitrate.....Oz.	34 1/2 @	37
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 3/8 @	5 1/2
Sodium Bisulphite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent., f. o. b. works.....C.	1.80 @	1.85
Sodium Hyposulphite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	6 1/8 @	7
Sodium Nitrate, 95 per cent., spot...C.	2.10 @	2.12
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 3/4 @	10
Strontium Nitrate.....Lb.	7 3/8 @	7 1/4
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	90 @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 1/2 @	12 1/2
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 1/4
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2
Zinc Dust.....Lb.	6 3/8 @	7

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.10 @	6.15
Cottonseed Oil (crude), f. o. b. mill..Gal.	40 @	40 1/2
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 1/4 @	9 1/2
Lard Oil (prime winter).....Gal.	85 @	91
Linseed Oil (raw, city).....Gal.	91 @	92
Linseed Oil (double-boiled).....Gal.	93 @	95
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Rosin Oil (first run).....Gal.	— @	41 1/2
Spindle Oil, No. 1.....Gal.	14 @	14 1/2
Stearic Acid (double-pressed).....Lb.	9 1/2 @	9 1/2
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	68
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 1/2 @	21
Antimony.....Lb.	9 1/2 @	9 1/2
Bismuth.....Lb.	1.80 @	1.90
Copper (electrolytic).....Lb.	— @	12 1/2
Copper (lake).....Lb.	12 1/8 @	12 1/2
Lead.....Lb.	4.37 1/2 @	4.40
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	42 @	42.50
Silver.....Oz.	— @	53 1/2
Tin.....Lb.	37 3/4 @	43 1/2
Zinc.....Lb.	5.4 @	5.45 1/2