Industrial and Engineering Chemistry

Vol. 20, No. 1

JANUARY 1, 1928

POLITECHNIKI

Our Presidents

THE Council of the Society has been confronted with the difficult problem of choosing from among four outstanding men one to be President of the Society for the year 1928. The election just closed shows Samuel Wilson Parr to have been the choice. Elections as conducted by the American Chemical Society are a model for such organizations. Our local sections suggest names to the Society, but this does not preclude the nomination of others by our membership. The whole Society is privileged to vote in the primary and four candidates receiving the highest number of votes are presented to the Council, now a body of some two hundred and seven men, whose ballots elect. As councilors represent the local sections and the membership at large, we believe our elections obtain for the Society the men desired by the majority. The choice, however, is always difficult to make and no chemist is ever embarrassed because another happens to be chosen.

Samuel W. Parr
Newly Elected President

George D. Rosengarten
Retiring President

We have known President Parr for nearly a quarter of a century; received in a kindly manner when a salesman, those first impressions have endured. Those who have not come under the influence of his genial personality and do not know his hearty laugh would do well to turn back to our American Contemporaries and note page 985 in Volume 17 for 1925.

President Parr has now retired as professor of industrial chemistry at the University of Illinois, though he is still most active in consulting work and in the business of the Standard Calorimeter Company, with which he has long been identified. He is known internationally for his work on the composition, weathering, and spontaneous combustion of coals, calorimetry of fuels, metallurgical chemistry, boiler waters, acid-resisting alloys including platinum substitutes, work upon the potash shales of Illinois, and more recently extensive experiments and semicommercial work on low-temperature carbonization of coals. He is a member of several scientific societies and has been prominent in the work of the American Society for Testing Materials. He did his collegiate work at Illinois, Cornell, Berlin, and Zurich. His home is in Urbana, Ill., and according to the record he was born January 21, 1857.

President Parr has been a loyal member of our Society since 1894 and has served it in nearly all capacities. Active as an individual, he has been identified with local section work and the development of divisions of the Society, notably Industrial and Engineering Chemistry and Gas and Fuel Chemistry. He has served many years upon the Council, has been a member of the Executive Committee, and one of our Directors. He has contributed largely of his time whenever called upon and in whatever capacity. He knows all about coöperation, and we are confident the Society will follow with enthusiasm the leadership which his active administration will supply.

Our out-going President, George D. Rosengarten, has served the Society faithfully and well and is another of those men who hold themselves in readiness to perform such services for the Society as it may demand. He has given us a strong business administration of Society affairs and now, at his own request, returns to the ranks of the privates, from which he may be drafted at any time to bring again to Society affairs a wealth of experience, soundness of judgment, and a devotion to the welfare of American chemistry which will be invaluable.

Nineteen Twenty-Eight

THE phrase "profitless prosperity," coined to describe the business of 1927, has its basis in the steady lowering of commodity prices which today are 15 per cent below those of two years ago. That business has continued in large volume only testifies to the economies instituted, the standardization practiced, the waste eliminated, and the utility made of statistical and scientific data now available in generous measure. Competition may have been a factor in forcing adaptation of such procedures which will be of great value now that encouraging up-turn is noted in several quarters. That business cannot proceed satisfactorily on a profitless prosperity is evident, and we look to 1928 as a year when business will be just as good as we are determined to make it and satisfactory for those who are determined to get it.

When such conditions prevail, the scientist, and particularly the chemist, has his greatest opportunity. When economies in manufacture become vital, the management will do well to make sure of its scientific staff, for in their ability, backed by adequate facilities, is more surely to be found the answer of how to make it for less than in any other quarter. A choice between alternative raw materials cannot be made with safety without scientific advice. In these competitive days a new line of merchandise should not be introduced without assurances as to its adequate supply of sufficiently cheap raw material, its satisfactory service, and a thorough survey of the consuming market.

We expect to see still further developments in the art of advertising and selling, the continued exploitation of color on every hand, and an effort first to create and then to supply popular demand—all on a more scientific basis than has obtained heretofore. Not only will the scientist have his enlarged opportunity in research and production, in control and in management, but in the departments of sales and of purchases with extended demands made upon him in the service departments which today are important, whatever the line of business activity.

Nineteen twenty-eight can be made a good year. Like the cow, its voluntary contributions will be nil and what can be extracted from it will depend upon the man.

Cartel Cogitations

WHILE "conversations are continuing" and preliminary agreements, gradually perfecting the details of the international cartel in chemistry, are being signed in certain cities of Europe, much thought is being given to the new problem in the circles of American chemical industry and the press reflects the views of many who have carefully gone into the possibilities. This new competition, which goes beyond the national phase and bids fair to line the rest of the producing world against the United States in the effort to supply the consuming market, is a threat of disaster, a challenge to brains, a stimulation to greater effort, and a good or a bad thing depending as much upon your point of view and the degree of optimism or pessimism in your make-up as upon any data at present in hand. Excellent and reliable reports of the situation as it is developing come from the Bureau of Foreign and Domestic Commerce and individual observers on the ground have tried to evaluate the several factors.

The size of the international cartel seems overwhelming to some. Others are less concerned with the size than with the leadership under which the negotiations have proceeded. They single out two men who seem qualified by long training and experience as chemists as well as business men to make the cartel a success if such a scheme can be made to realize the purpose of its founders. That such a cartel labors under some disadvantages must be apparent. The possibility of higher prices with the disappearance of competition in certain markets, the weight of overhead, the almost certain internal jealousies, and possible political complications with an organization so large and powerful as to demand the serious attention of government—all have been noted.

There are many diverse opinions as to the most efficient means for strengthening our position, but upon five cardinal points there should be agreement. First, something concrete must be done in earnest and at once to perfect a better organization among the American chemical industry, in which respect even within our own laws we are far behind European organizations. Second, corporations must place upon their directorates a larger number of technically trained men, men who have displayed acumen for the details of business and commerce, but who are thoroughly trained in the science and technology underlying the business with which they are connected. Third, we must go forward vigorously with well-considered conservative programs for industrial research, which always involves adequate support of the fundamental work upon which our applied science rests. The scarcity of thoroughly trained men for research positions would indicate that industry is beginning to realize fully the importance of this third point.

Fourth, the expansion of the service to be rendered by the Bureau of Foreign and Domestic Commerce is of vital importance. We must not depend upon casual information nor upon the reports obtained by men not technically trained. Such information as can be had through legitimate channels deals with complex subjects and requires for its gathering and dissemination the critical discrimination of men technically trained. To secure and hold such men the bureau requires increased funds and to support their work appropriations for assistants and for travel. We must have more data of the utmost reliability and with promptness.

Another cardinal point is again the question of foreign loans, in the making of which we feel sure our bankers look only to the immediate profit of the transaction and not to the ultimate effect upon the American industry, from which this money really comes. Foreign loans involve no risk to the international bankers making them, for they are not loaning their own money and they are not guaranteeing the safety of your money which they loan. Time and again we have pointed out the almost certain effect upon our own industry upon possible interference with our tariff policies and the long-time effect upon American business and prosperity. We have a duty to perform in continually bringing these points before those who have failed to consider the many disturbing factors.

We do not look upon the situation as one to cause alarm, but it does behoove us carefully and calmly to study it, truly evaluate the factors in the equation, and proceed harmoniously upon whatever lines such an analysis may dictate.

Faraday's Idea

NINETY years ago Faraday decided that children should have an opportunity to become interested in science and announced that during Christmas week he would give a series of scientific lectures for them at the Royal Institution in London. So successful were these lectures that such a course has been given in the same institution every Christmas season since Faraday's time, and by the foremost physicists of the English-speaking countries.

Faraday's idea has been perpetuated, but in a more haphazard way in other centers largely, we believe, because it is difficult for many scientific men to speak to children. It requires great skill to know what to present and how to present it so that the school boy or girl carries away a lasting impression of exactly the right kind. A year ago the Franklin Institute decided to inaugurate a similar course of Christmas lectures in Philadelphia, and R. W. Wood of Johns Hopkins gave the lectures. Fortunately, there was in his audience a nine-year old boy who was so impressed that he carried home stories of the wonder-working experiments with radiation which had been demonstrated and described to him. His grandmother sensed at once the value of the intellectual stimulation possible through such lectures and endowed, to the extent of $10,000, this children's course in memory of James Mapes Dodge, her husband and one of the most notable of American inventors.

The first Christmas lectures of the new foundation, three in number, were given by Wilder D. Bancroft on Combustion, Comfort, and Color.

That the impression may be more lasting, the audience is encouraged to keep notebooks and cash prizes are offered for the three best.

We are delighted with these constructive efforts to call the attention of youth to the reality, the service, and the possibilities of science, and believe that the reward will come in increased appreciation for scientific work and in the development of greater numbers of outstanding American scientists.

Election Results

THE election just completed by the Council of the SOCIETY resulted as follows: President, S. W. Parr, of Urbana, Ill.; director from the fourth district, W. D. Bigelow, of Washington, D. C.; from the sixth district, E. C. Franklin, of Stanford University, Calif.; councilors-at-large, H. N. Holmes, of Oberlin, Ohio, Treat B. Johnson, of New Haven, Conn., and Edward Mallinckrodt of St. Louis, Mo. William J. Hale and Joel Hildebrand were tied and according to the Constitution the fourth councilor-at-large must be chosen as between these gentlemen by the Council at its meeting in St. Louis next April.

The Second Session

AMONG your New Year's resolutions, be sure to include in those you intend to keep a determination to participate in the second session of the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY, scheduled for Northwestern University at Evanston, Ill., July 23 to August 18, 1928. You have heard much concerning the success of the first session of the Institute, but unless your information has come from one of those who actually took part in that experiment, it is possible that your picture and ideas are a bit hazy as to what the Institute is and why you should plan to be a part of it.

The Institute is distinctly not a summer school. The fact that arrangements were made for those who desired academic credit for the work done in connection with the Institute, this being desirable in the case of certain teachers seeking promotion, is not to be interpreted as an indication that the Institute of Chemistry competes with any of the regular summer schools, nor that it is organized, planned, or conducted as a summer session.

The Institute is not a symposium and when we shall shortly be able to announce the subjects for general conferences and intensive courses of lectures, it will be seen that if you wish to apply the word "symposium" it will have to be done in a magnified plural. Neither is the Institute just an additional meeting of the AMERICAN CHEMICAL SOCIETY. It is true that you will find many chemists of prominence in attendance, but that is the case these days, no matter what type of scientific meeting or conference you attend. Chemistry is slowly but surely pervading the entire field of science. The Institute is neither organized nor conducted like meetings of the SOCIETY, and this is particularly noticeable in the time available for discussing every topic and for the welcome leisure with which the work is admixed.

Again, the Institute is not a regional meeting. It is not a local section activity. It goes far beyond any of the established regions in drawing its membership and is more extensive also in scope and purpose. While the Institute accomplishes most in the environment of the warm, sympathetic support of the local section nearest its meeting place, it brings no additional responsibility to the local section, requires no local section financing, but offers instead a new opportunity particularly advantageous to those so located that without much effort they can participate in all the interesting features.

The Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY is furthermore not intended to advance the interests of any individuals or of any particular educational institution. The fact that the meeting place does receive favorable press notices is a by-product of the project and incidental to its main purpose. The present plan to choose a new location for each annual meeting gives a larger number of institutions the opportunity to profit from this by-product than if it were held, like other institutes, always in one place. Eventually there might be established an independent center for research, the Institute and a summer colony of chemists modeled after the Marine Biological Laboratory, but that is for the future.

The Institute does, however, definitely plan as a part of its work publicity for chemistry and the accomplishments of chemists. It hopes to contribute much to the recognized constructive effort toward adult education in so far as authentic accounts in the public press may further our persistent, though at times tedious, work of creating so great a body of public opinion favorable to our science as to gain for it sympathy and substantial support.

The Institute, then, is planned as a summer conference on the order of an occupational vacation, varying from a single session to the entire four weeks, depending upon the desires of the individual. Here is a program so arranged that all may be given what they most desire, in so far as it is humanly possible, varying from those wishing a minimum of work with a maximum of rest and diversion to those who want to spend all their waking hours considering the problems of their science. Here is time and place for unlimited discussion, for making more than casual contacts with the fellows of the profession, many of whom have made their names synonymous with chemical achievement. Here is an opportunity to spend a delightful time on the shores of Lake Michigan in a veritable oasis set down in the midst of a great center which offers industry, art, music, and recreation.

Your committee charged with the duty of planning and carrying through the Institute program is in the midst of perfecting details for the 1928 session. These men want your views, and to make it easy, we give you here their names: F. C. Whitmore, chairman, N. E. Gordon, B. S. Hopkins, C. E. K. Mees, C. M. A. Stine, G. L. Wendt, W. R. Whitney, F. W. Willard, and ex officio, C. L. Parsons, H. E. Howe, and S. W. Parr.

Invitations have already been dispatched to prominent foreign chemists whom it is hoped to have present, and ere long you will find in our News Edition the details announced as they are concluded.

Those who are interested in the development of this method for continuing adult education are naturally enthusiastic, for they see the great potentialities of the plan. Industrial leaders caught the spirit of the session of 1927 and have retained their enthusiasm. Members who came long distances were so well pleased that they plan to attend the 1928 session. And our foreign visitors were so favorably impressed that they see in such a plan elements for the improvement of international meetings and congresses. Directors of research laboratories intend to have members of their staffs make the most of the Institute sessions. You will want to give it full consideration in making your plans for the period July 23 to August 18, 1928.

Scientific Sewage Disposal at Milwaukee[1]

Robert Cramer and John Arthur Wilson

SEWERAGE COMMISSION OF THE CITY OF MILWAUKEE, WISCONSIN

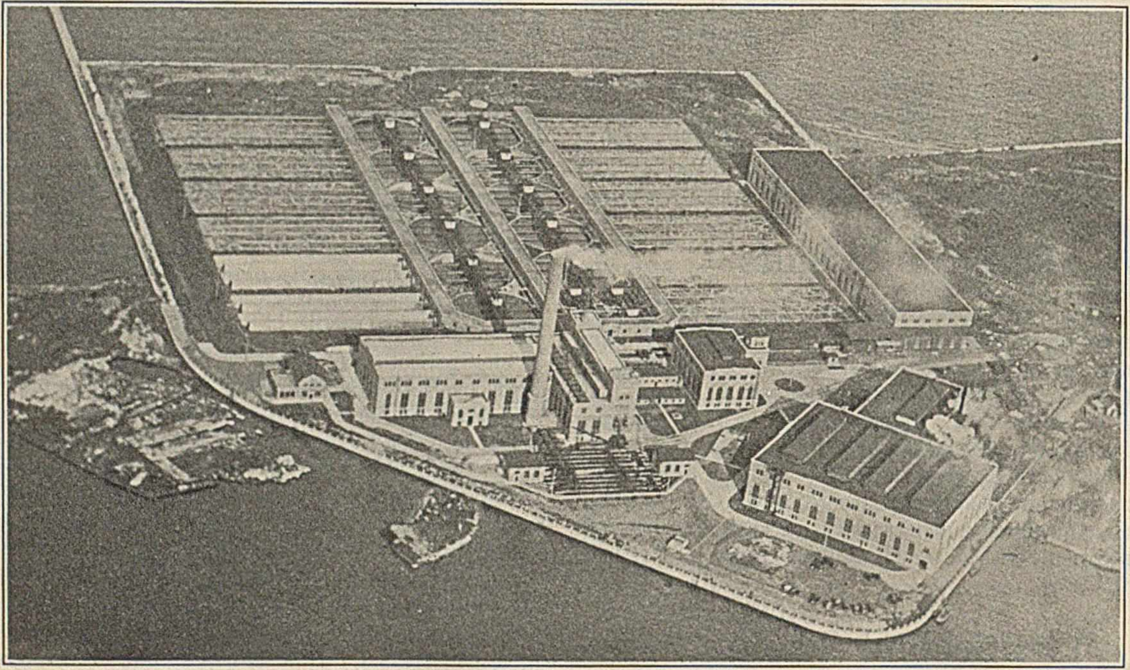

Figure 1—Airplane View of Milwaukee's Sewage Disposal Plant

In the background, from left to right, are aeration tanks, sedimentation tanks, aeration tanks, and fertilizer-storage house. In front of these, from left to right, are the coarse-screen house, power house, experimental plant, and fine-screen house and laboratory. In front of the power house are the grit chambers. To the right of these is the filter house and behind it the drier house.

Probably nowhere else in the world is sewage disposed of so effectively on so large a scale as at Milwaukee. The new activated sludge plant is capable of separating 100,000,000 gallons of sewage per day into practically pure water and a dry powder of high fertilizer value, and with no offense to the surrounding community.

ABOUT fifteen years ago, by a referendum vote of the people of Milwaukee, a commission was created to build a plant that would separate the sewage of the city quantitatively into pure water and dry fertilizer, but no such plant had ever been built previously and all attempts to accomplish the desired result elsewhere had failed. The conditions confronting the commission made research work on a large scale inevitable. The commissioners, after appointment, were not recallable, which freed them from political influence. They were given unlimited taxing power and a complicated problem that had baffled all previous attempts to solve it. Chemical and engineering research was carried out on an unprecedented scale and the result is the present Milwaukee Sewage Disposal Plant, an airplane view of which is shown in Figure 1.

The population of the district served by this plant is about 600,000 and the daily flow of sewage about 100,000,000 gallons. Since the sewage effluent empties into Lake Michigan, which is also Milwaukee's water supply, a high degree of purification is essential. The water-sewage cycle begins with the pumping of the water supply from the lake. In serving the various sanitary and industrial purposes the water becomes polluted with waste materials, which it conveys to the disposal plant, acting as a vehicle for carrying all these wastes to one designated point. It is the purpose of the plant to remove these materials from the water, sending it back to the lake essentially as pure as when it was received.

The scope of this paper is limited to a brief description of the plant and its operation and of some of the chemical principles involved.

Removal of Coarse Material

The sewage is carried to the disposal plant at Jones Island by a system of intercepting sewers terminating in four siphons under the harbor entrance, 75 feet below water level, the two carrying high-level sewage having effective diameters of 72 inches and 48 inches and the two carrying low-level sewage diameters of 54 and 42 inches. The high-level sewage, about 80 per cent of the total, flows out by gravity, while the low-level sewage must be pumped.

All the sewage passes first through coarse bar screens (Figure 2), which remove very large materials. The spaces between the bars are 2 inches in the low-level cage screens and $3^{11}/_{16}$ inches in the high-level rack screens. The coarsely screened sewage then flows through grit chambers (Figure 3), where the velocity of flow is reduced to 1 foot per second, permitting the heavier materials to settle out. These grit chambers consist of eight open concrete channels, each 8 feet wide, 8 feet deep, and 95 feet long and capable of isolation from the rest for the purpose of draining and cleaning, which is done by means of a clamshell bucket operated from a gantry crane.

The sewage then passes through the fine screens, consisting of eight revolving drums, each 8 feet in diameter by 8 feet long and covered with manganese bronze plates $^{3}/_{16}$ inch thick having 27.5 per cent of their surface slotted with

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[1] Received November 14, 1927.

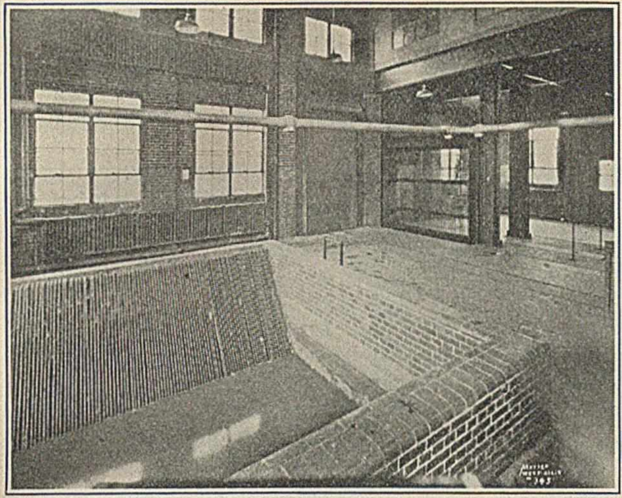

Figure 2—Coarse Screens
To the left are the high-level rack screens and to the right one of the low-level cage screens which has been drawn up to be cleaned.

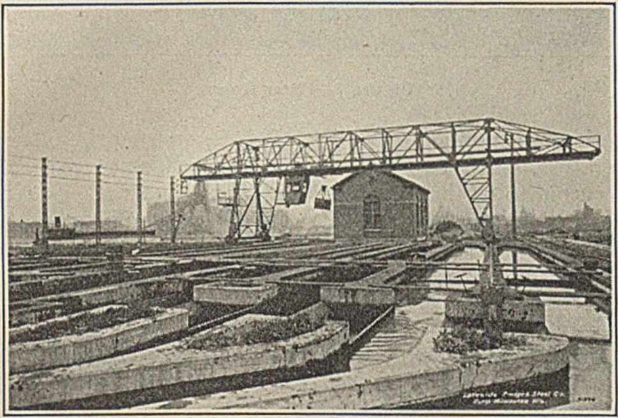

Figure 3—Grit Chambers

openings $^3/_{32}$ by 2 inches. Each screen is equipped with eight brushes for removing the screenings. The peripheral drum speed is from 8 to 12 feet per minute and the brush travel 60 feet per minute. The capacity of the eight screens is 371,000,000 gallons daily with a 12-inch loss of head, or 150,000,000 gallons with an 8-inch loss.

The suspended matter contained in 100,000,000 gallons of Milwaukee sewage is about 130 tons of dry material. Less than 10 per cent of this is removed by the screens and the grit chamber. The really difficult task is to remove the more than 90 per cent remaining which is chiefly present in a fine state of subdivision. This is accomplished by the operation known as the activated-sludge process.

Removal of Finely Divided Material

The screened sewage is passed first into a mixing channel 14 feet wide and 11 feet deep, whose bottom is fitted with porous plates through which air is forced to keep the liquor above thoroughly agitated. At this point activated sludge returned from the system, to be described presently, is mixed with the sewage and the mixed liquor then flows on into the aeration tanks through feed channels, the rate of flow being controlled by sluice gates.

The aeration tanks consist of twenty-four rectangular concrete tanks, each having two parallel compartments 236 feet long and 22 feet wide, with 15 feet effective depth. In concrete containers resting on the bottom of each tank there are 2514 porous plates, each 1 foot square. The general arrangement is shown in the empty tank in Figure 4. Air compressed to 10 pounds per square inch is supplied to each container to be diffused through the porous plate and allowed to bubble up through the mixed sewage and sludge as the mixture passes through the aeration tanks.

The flow is so regulated that it takes about 6 hours for the mixed liquor to travel through the aeration tanks, during which time 1.5 cubic feet of air have been bubbled through it for each gallon of raw sewage entering the system. From the aeration tanks the mixed liquor flows into large sedimentation tanks, of which there is one for each two aeration tanks. An empty sedimentation tank is shown in Figure 5. Each is a concrete tank 98 feet in diameter at the bottom, with octagonal top and with an effective depth of 15 feet. The mixed liquor enters the tank continuously. The sludge settles to the bottom, carrying with it practically all of the finely divided material originally present in the sewage, while the clear water is decanted off. Practically pure water overflows into the effluent troughs at the top of each tank, while the settled sludge is continuously being removed from the bottom by means of hydrostatic head. In Figure 5 the scrapers resting on the bottom of the tank move so as to force the sludge to the center. The clear effluent falls from the troughs into two concrete conduits which empty into the lake. The sludge drawn off contains from 1 to 2 per cent of solid matter. About 90 per cent of it is pumped back to the mixing channel to be mixed with incoming screened sewage and 10 per cent is pumped to the filter house to be converted into dry fertilizer. The screened sewage contains

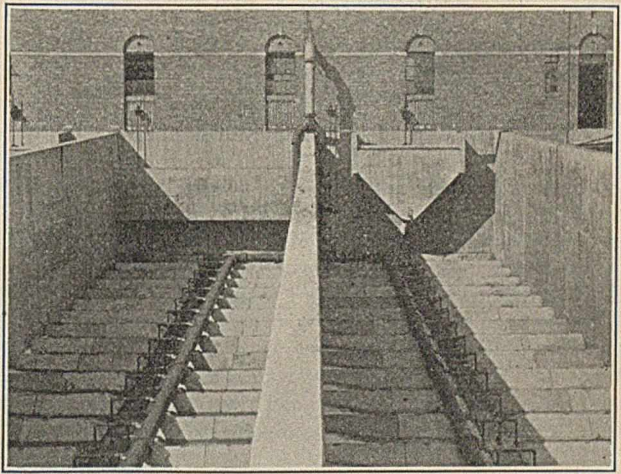

Figure 4—Ends of an Aeration Tank, Showing Method of Placing Porous Plates

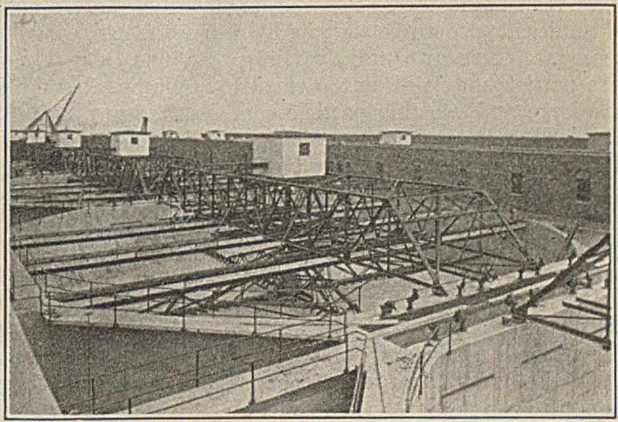

Figure 5—A Sedimentation Tank, Showing Overflow Weirs and Dorr Thickening Mechanism

about 300 parts per million of suspended solids and this is increased to about 3000 parts by the introduction of sludge, before it starts its journey through the aeration tanks.

Mechanism of Aeration

When insoluble materials are suspended in a liquid, the rate at which they will settle depends upon the size of the individual particles. Other things remaining constant, the greater the size of a particle the greater will be its rate of settling. Tiny particles present in sewage that will not settle at all can be made to settle rapidly by causing them to unite with each other to form relatively large particles.

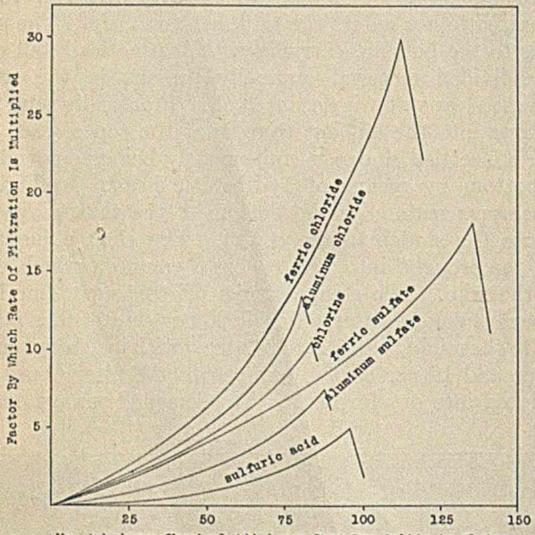

Figure 6—Effect of Adding Different Chemicals upon the Rate of Filtration of Activated Sludge

Much of the finely divided matter of sewage originally consisted of animal or vegetable tissues presenting a relatively coarse structure. But, through putrefaction and other chemical changes, these tissues have broken down into particles which will not settle out from water upon standing. When oxygen is bubbled through neutral sewage, these tiny particles unite with each other, tending to form coarse particles analogous to the original tissues. If the bubbling is continued for several days, the particles become large enough to settle out quickly upon standing.

If some of this settled sludge is now added to another portion of raw sewage and oxygen is bubbled through it, the tiny particles of the sewage, including the bacteria, tend to combine with the larger particles of the sludge rather than with each other. But the large particles are already of sufficient size to settle rapidly when the bubbling has ceased. Where two tiny particles combine, the double-size particle may still be too small to settle out, but where one large and one tiny particle combine, the resulting particle will settle at least as quickly as the original large one. This explains why it is desirable to mix sludge already capable of settling rapidly, and which is called "activated sludge," with the incoming raw sewage before aerating it. The time required to bring the sewage to the point where purification can be effected by settling is thus reduced from days to hours.

It is generally thought that bacteria, or other living organisms, are essential to the building of activated sludge, but experiments conducted at the Milwaukee plant indicate otherwise. With increasing time of aeration of the mixed liquor the particles of sludge are so increased in size that filtration becomes increasingly rapid. The time required to filter 500 cc. of sludge diluted to contain exactly 1 per cent of insoluble matter on a standard Büchner funnel is thus a measure of the extent to which the sludge has been built up in the aeration tanks. This test and previous experiments have been described by Wilson, Copeland, and Heisig.[2] The building of sludge is sensitive to changes in pH value, having optimum action at pH = 7.4. It is favored by rise of temperature, at least up to 25° C., and oxygen is necessary. It occurred to us that, if the action is one of oxidation not involving living organisms, it should be favored by mixing chlorine with the air in aerating. All the sewage passing through one experimental aeration tank for one month was aerated with a mixture of air and chlorine equal to 300 pounds per million gallons of sewage. The result was a sludge that filtered three times as quickly as sludge formed with air alone and, furthermore, the effluent from the chlorine-treated mixed liquor was sterile. This would seem to prove that the action is not a biological, but a chemical one, involving oxidation.

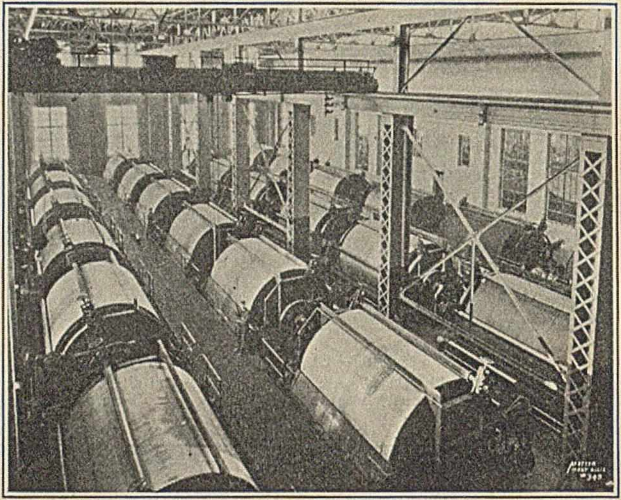

Figure 7—Filter Room

Possibly the action of aeration may be likened to the building of tissues in the animal body. The food is broken down in the animal's digestive tract into more finely divided materials, which pass into the blood streams. In the presence of oxygen, entering by way of the lungs and blood streams,

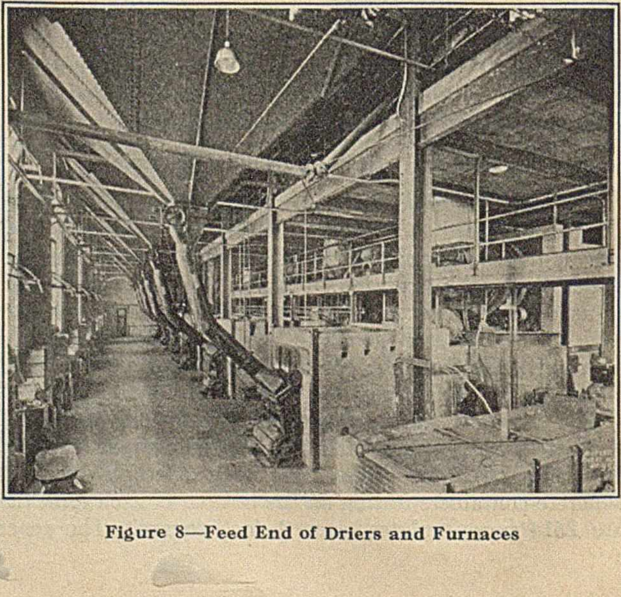

Figure 8—Feed End of Driers and Furnaces

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[2] *Ind. Eng. Chem.*, (*a*) **13**, 406 (1921); (*b*) **14**, 128 (1922); (*c*) **15**, 956 (1923).

these finely divided materials are rebuilt into tissues. If the pH value of the blood shifts much from 7.4, tissue building ceases. Similarly, in the aeration tanks, the building of sludge is stopped by shifts in pH value from 7.4 or by stoppage of the oxygen supply.

Degree of Purification

The screened sewage contains an average of about 300 parts per million of suspended matter and the plant effluent about 15 parts, a reduction of 95 per cent. The average bacterial count of the sewage is 3,000,000 per cubic centimeter and that of the plant effluent about 30,000, a reduction of 99 per cent. The biochemical oxygen demand of the sewage is about 300 and that of the plant effluent about 3. The stability of the plant effluent is well in excess of 120 hours. These are average values obtained during 1927; they may be improved as the research work progresses, but they represent a high degree of purification as they are. Typical samples of sewage sludge mixed liquor and plant effluent are shown in Figure 11. The plant effluent is almost as clear as distilled water.

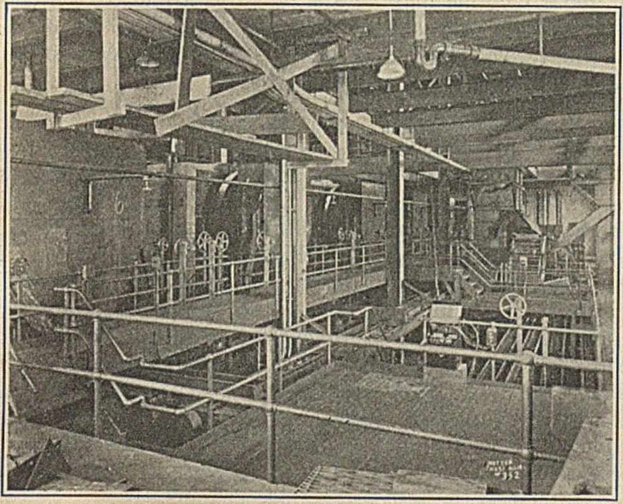

Figure 9—Outlet End of Driers

The Sludge Problem

The most difficult problem encountered in the work at Milwaukee was that of finding a practical method of reducing the waste sludge, containing about 99 per cent water, to a dry powder. Before one day's production could be dried economically by the application of heat, it was necessary to remove from it more than 2,000,000 gallons of water. Filtration was the only practical means known for doing this, and yet the sludge could not be filtered without previous chemical treatment, being of such nature that it would quickly clog the filter cloth, rendering it impervious to water, even under considerable pressure.

The solution of the sludge problem, as worked out by Wilson, Copeland, and Heisig[2] has already been described. They developed a method for measuring the rate of filtration of sludge and gave the arbitrary value 100 to sludge in such condition that it could just be filtered satisfactorily in the big plant. A relative filtering efficiency of 200 meant that only half as long a time was required to filter a given amount as of sludge with a relative filtering efficiency of 100. The building of sludge in the aeration tanks is a function of temperature. In February, when the temperature of the sewage falls to about 7° C., the sludge is built up in the aeration tanks to a degree sufficient to permit continuous purification of the effluent, but not to a degree sufficient to permit satisfactory filtering of the sludge. The relative filtering efficiency of this sludge is usually only about 5, making it necessary to increase its rate of filtration by about 2000 per cent to make filtration practicable. In September, when the sewage is warmest, about 22° C., the relative filtering condition of the sludge is about 100.

Activated sludge is amphoteric, having an isoelectric point at pH = 3.4. By adding sulfuric acid to bring the pH value from 7.4 to 3.4 the sludge is made to lose much of its attraction for water and it tends to coagulate. At the same time its relative filtering efficiency is multiplied by 5, regardless of the initial value. But this is not enough to make February sludge filterable practically. When aluminum sulfate is added and the aluminum compound of sludge brought to its isoelectric point, pH = 4.4, by the addition of acid, the relative filtering efficiency is multiplied by 7.5, still not enough. But when sludge so treated is heated to 80° C., the relative filtering efficiency of the original sludge is multiplied by 40, making filtration easy and practicable at any time of year.

The big plant was built with the idea that the sludge in winter was to be treated with alum, acid, and heat, but when operations were started it was found that the complicated heat exchanger could not be used because it acted like a colloid mill in dispersing the sludge, doing more harm than good. Winter was approaching and some method of treating the sludge to make it filterable had to be found. Research was conducted under high pressure and the conditioning power of a large number of chemicals was tested, without regard to their cost. It was found that the halides of trivalent metals have an enormous effect upon the relative filtering efficiency. Adding enough ferric chloride alone to reduce the pH value to 3.4 causes the sludge to filter at thirty times its normal rate. Ferric chloride is now used to condition winter sludge for filtering. Since it must be used only in winter, its cost is not prohibitive. The most recent quotation on anhydrous ferric chloride made to us was 3 cents per pound, making a cost of about 5 dollars to condition sludge yielding one ton of dry fertilizer selling at 15 dollars.

Figure 6 shows the effect of a number of different conditioning agents upon the relative filtering efficiency of the sludge. The points of maximum occur at the isoelectric point of the sludge, pH = 3.4, or at pH = 4.4 for the aluminum compound of sludge. All these materials hydrolyze, yielding free acid, which lowers the pH value.

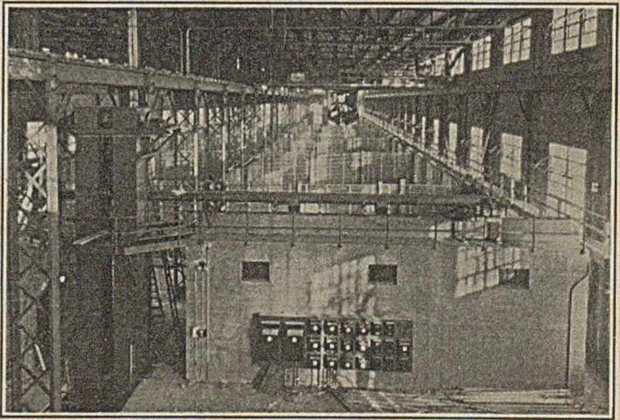

Figure 10—Interior of Storage House

Where it is necessary to multiply the relative filtering efficiency of the sludge by 5 or less, sulfuric acid is the cheapest conditioning agent; for greater values ferric chloride is cheapest. The effect of sulfuric acid is apparently to reduce the attraction of sludge for water by bringing it to the isoelectric condition. The action of chlorine is twofold: it reacts with water yielding hydrochloric acid and nascent oxygen and we get, not only the pH effect, but also an oxidizing action supplementing the action started in the aeration tanks. The aluminum sulfate also has a twofold effect—alteration of pH value and a tanning action. The aluminum compound of sludge at its isoelectric point apparently has a lesser attraction for water than raw sludge at its isoelectric point. The ferric sulfate has a threefold effect—alteration of pH value, tanning action, and oxidizing action.

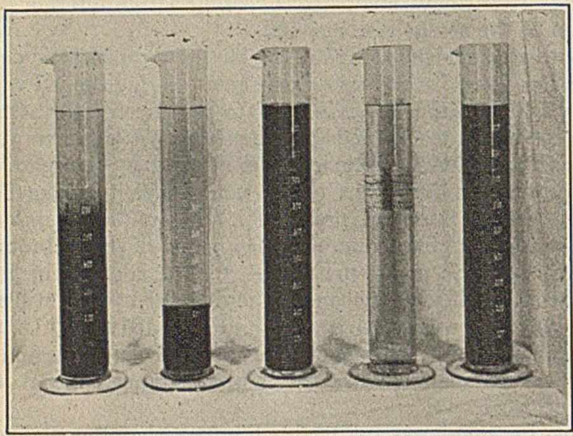

Figure 11—Samples of Raw Sewage, Sludge Mixed Liquor and Plant Effluent

The peculiar difference in action between the sulfates and chlorides is deserving of very careful study. In general, chlorides have a tendency to disperse protein matter and sulfates to prevent dispersion, as shown by Thomas and Foster[3] and by Thomas and Kelly.[4] This might lead one to believe that chlorides should have a lesser conditioning power for sludge than sulfates, which is the reverse of the findings. The chlorides form addition compounds with the proteins by means of the secondary valency forces holding the protein units together. But Gustavson[5] has recently shown that pretreatment of collagen with chlorides causes it to fix more chromium in chrome tanning, while collagen treated with sulfates fixes less chromium than untreated collagen under the same conditions. Apparently the liberated secondary valency forces permit a greater degree of combination with the metal ion. This will also explain why the chloride salts of metal tanning agents are more effective in conditioning activated sludge than the sulfates. They cause an increasing degree of fixation of metal ion with a corresponding decreasing attraction of the sludge for water. A similar observation was made with chromic sulfate and chromic chloride. Nickel sulfate, on the other hand, which is not a tanning agent, proved to be a slightly better conditioning agent for sludge than nickel chloride. The supreme position held by ferric chloride may be attributed to a fourfold action—alteration of pH value, oxidizing action, liberation of the secondary valency forces of the sludge by means of the chloride ion, and a tanning action.

Dewatering the Sludge

The waste activated sludge from the clarifiers flows first into a 42,000-gallon chemical treatment tank, where it is treated with the amount of sulfuric acid or of ferric chloride to give the filter effluent a pH value of 3.4. The tank is equipped with diffuser plates and baffles to permit thorough mixing. The sludge passes through the tank to the filters continuously and a control chemist regulates the flow of chemicals into the tank according to the pH readings of the filter effluent. The treated sludge is delivered to a series of twenty-four Oliver continuous vacuum filters, each of which is 11.5 feet in diameter and 14 feet long, with 495 square feet of effective filtering surface. (Figure 7) The effluent is returned to the screened sewage channel.

The sludge cake from the filters is dropped onto a moving belt and conveyed to a battery of six Atlas direct-indirect-heat continuous rotary driers, each 7 feet in diameter by 60 feet long, enclosed in brick settings. Because of the tendency for the sludge to ball up and dry irregularly, an equal quantity of previously dried sludge is mixed with the sludge cake from the filters as it enters the driers. This lowers the moisture content sufficiently to prevent balling. The feed end of the drier is shown in Figure 8 and the outlet end in Figure 9. As the drum revolves, the hot gases from the furnace, mixed with large volumes of outside air, circulate around and into the drum through numerous air valves attached to the drum shell. About 45 minutes are allowed for the sludge to pass through the driers, during which time the moisture content is reduced from 82 per cent, as it leaves the filters, to about 3 per cent, as it emerges from the lower end of the driers.

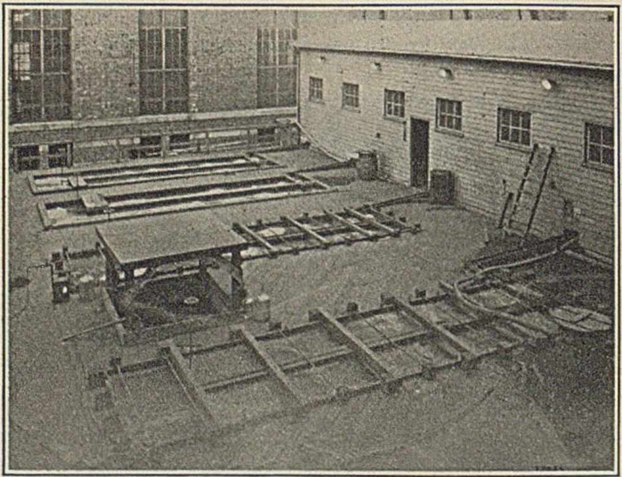

Figure 12—Four Aeration Tanks in Experimental Plant

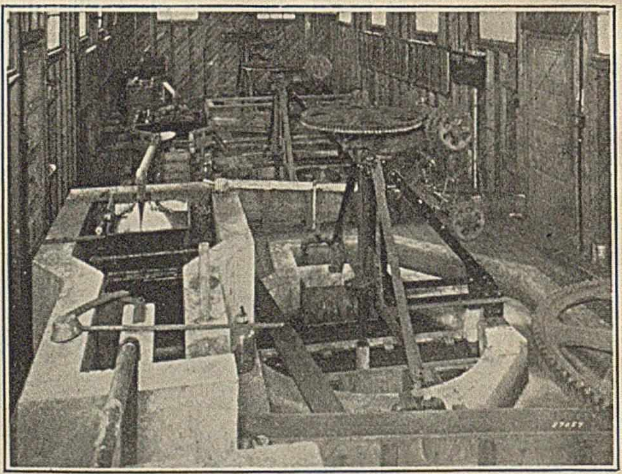

Figure 13—Sedimentation Tanks in Experimental Plant

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[3] *Ind. Eng. Chem.*, **17**, 1162 (1925).

[4] *Ibid.*, **19**, 477 (1927).

[5] *J. Am. Leather Chem. Assocn.*, **21**, 366 (1926).

The temperature of the driers at the inletting end is kept at 1000° C. and at the outlet, 500° C.

The dried material is screened and the coarser portions are then passed through a pulverator. The very fine portions are returned for mixing with the incoming wet sludge from the filters. The remainder is conveyed to a storage house with a capacity of 18,000 tons, or the normal production for about 4 to 5 months. The interior of the storage house is shown in Figure 10. The sludge has a very high fertilizer value and is much in demand. It is known as Milorganite (Milwaukee organic nitrogen). It will be described by Victor H. Kadish in a subsequent paper.

Research and Economy

Because of the large amount of research work required to make this plant possible, it is natural that it should contain well-appointed research laboratories. It is too much to expect that a big plant working on previously untried principles should operate at the highest efficiency as soon as completed. Our knowledge of the best conditions required for aeration, settling, and filtering is still incomplete. The plant is now working very satisfactorily, but it is believed that very great savings are going to result from research work now in progress. The plant, without the sewage, cost about ten million dollars and it costs about one million dollars per year to operate. The return from the sale of fertilizer is about one-half million dollars per year and it is hoped to reduce the cost of operation by one-half, making the actual cost of operation nil, exclusive of capital charges.

This is not a wild dream. The research department possesses a battery of four experimental systems, each one five-thousandth the size of the entire big plant. The four systems operate independently and each has its own aeration tanks, settling tanks, chemical treatment tanks, and filters. (Figures 12 and 13) Here it is possible to study the effect of variable factors, by operating all four systems exactly alike except for the variation of a single factor. The results to date indicate that the air in the aeration tanks need be supplied only in such quantity as may be necessary to keep the water saturated with oxygen and to keep the sludge sufficiently well agitated. With constancy of oxygen concentration, the action proceeds in direct proportion to the product of the concentration of polluting material and the exposed surface of the activated sludge, bacteria playing no part as such. The types of pumps used have an important bearing upon the filtering condition of the sludge delivered and the method of inletting the mixed liquor into the clarifiers has much to do with the purity of the effluent and with the capacity of the entire system. If the results of operation of the small plants can be duplicated in the big plant, we shall need only one-half of the aeration tanks and clarifiers to handle all of the sewage. The savings, including the possible saving in cost of chemical treatment, would be more than half the present net cost of operation, and the research work is only in its early stages.

Milorganite—A New Fertilizer Material[1]

Victor H. Kadish

SEWERAGE COMMISSION OF THE CITY OF MILWAUKEE, WISCONSIN

FOR the first time in the history of sanitation plant food from sewage and trade wastes is being converted into a valuable and commercially marketable fertilizer material. This is now being accomplished on a large scale at Milwaukee's Activated Sludge Sewage Disposal Plant. The product is being marketed under the trade name "Milorganite," which was chosen as the result of a nation-wide contest among fertilizer people. This name ties up the material with Milwaukee and emphasizes its most valuable ingredient —organic nitrogen.

Nature and Composition

Milorganite is an organic product, uniform chemically and physically, and free from bacteria and weed seeds of all kinds. In appearance it looks not unlike dried coffee grounds. It is finely and evenly ground—95 per cent or more passing a 10-mesh sieve and being retained on a 48-mesh sieve—and contains 5 per cent or less moisture.

A composite sample representing 145 carloads shipped between February 1 and September 1, 1927, showed the following analysis:

	Per cent
Moisture	4.08
Total nitrogen	5.42
Equivalent to ammonia	6.58
Water-soluble organic nitrogen	0.30
Water-insoluble organic nitrogen	5.12
Nitrogen insoluble in neutral permanganate	0.71
Availability of water-insoluble organic nitrogen by neutral permanganate method	86.13
Active nitrogen by alkaline permanganate method	3.22
Availability of water-insoluble organic nitrogen by alkaline permanganate method	62.89
Total phosphoric acid	3.08
Insoluble phosphoric acid	0.65
Available phosphoric acid	2.43

This analysis, representing approximately 5000 tons, shows that the insoluble organic nitrogen is in a highly available form. While nitrogen is the most valuable constituent of Milorganite, it also contains some available phosphoric acid which is just as available as the phosphoric acid in acid phosphate.

The finished product runs very uniform chemically day in and out, despite variations in the raw material, because the many tanks, conduits, channels, etc., comprise a huge reservoir containing 1500 to 2000 tons of dry solids, of which approximately only 5 per cent are withdrawn daily. In other words, the suspended solids removed constitute a very small percentage of the quantity on hand and are balanced against the incoming solids in the raw sewage.

Investigations into Fertilizing Value

It was early recognized that the ultimate economic success of the project depended upon the successful marketing of the dried product. In order to determine the fertilizing value of Milorganite compared with other materials in common use, the Sewerage Commission in 1923 established a fellowship in the College of Agriculture, University of Wisconsin, with Mr. O. J. Noer as Fellow under the direction of Prof. E. Truog, of the Department of Soils. For nearly four years intensive research was conducted in the laboratory, greenhouse, and field.

Analyses in the laboratory and pot-culture experiments showed conclusively that the nitrogen in Milorganite was readily available and compared favorably with such standard organic materials as dried blood, tankage, fish scrap, and cottonseed meal.

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[1] Received November 25, 1927.

During a period of three years in excess of one hundred plots were established in Wisconsin on a variety of crops such as corn, potatoes, tobacco, vegetables, small grains, etc., in which Milorganite as a source of nitrogen was compared with other materials. For this purpose ten mixtures of similar analysis were prepared at a middle-western fertilizer plant under actual manufacturing conditions, which obviated the possible criticism that experimental mixtures were not comparable with commercial mixtures. The results secured in the field bore out the preliminary work in the laboratory and greenhouse; in fact, in some instances mixtures containing Milorganite produced greater yields and better quality than those mixtures in which nitrogen was supplied from other sources.

Early indications pointed to Milorganite as being an ideal material for turf fertilization. Consequently, liberal samples were furnished to many golf clubs in all parts of the country for use on greens and fairways. Results were uniformly gratifying and demands for the material for this purpose came in long before production got under way.

Production and Marketing Results

During 1926 production was intermittent during the first half of the year, and up to July 1 only 500 tons were produced. From July 1 to December 31, inclusive, production was approximately 5000 tons, or 27 tons daily average. Shipments for the year amounted to 2200 tons, of which about 80 per cent went to fertilizer manufacturers and the remaining 20 per cent to special markets such as golf clubs and florists.

For the period January 1 to November 15, 1927, production was 16,600 tons (daily average 50 tons). During the same period shipments were 19,700 tons, of which 3000 tons went to special markets and the remainder to fertilizer manufacturers. Orders on hand for delivery up to May 1 amount to 13,000 tons, which will absorb the estimated production to that date. The average return has been about $15.00 per ton f. o. b. Milwaukee. While the price fluctuates with market conditions, the average return over a period of years should not fall below this figure. In the event of future operating economies the return from sales of Milorganite should offset a portion of the cost of purifying the sewage.

At the present time, with an average of 80,000,000 gallons of sewage treated daily, the monthly production of Milorganite is about 2500 tons. For the year 1928 it is estimated the output will run between 30,000 and 35,000 tons. The successful marketing of Milorganite is no longer problematical and every ton produced should be readily placed.

Synthesis of Methane from Water Gas[1,2]

Frank W. Hightower and Alfred H. White

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

This paper presents the results of a study of the conversion of mixtures of CO_2, CO, and H_2, to CH_4 and other products at temperatures of 280–370° C. while at atmospheric pressure and in presence of a nickel catalyst. The results are in general agreement with other investigators in showing the formation of large proportions of methane from gases containing CO, H_2, CO_2, and H_2O within fairly wide limits of composition.

The decomposition of CO according to the equation

$$2CO = C + CO_2$$

appeared to a small degree at 300–370° C., but was somewhat erratic in quantity. It is suggested that the decomposition may be autocatalytic since the decomposition appeared to be less with new catalysts.

The path of the reaction as between the three equations usually written

$$CO + 3H_2 = CH_4 + H_2O \qquad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (2)$$

$$2CO + 2H_2 = CH_4 + CO_2 \qquad (3)$$

depends upon a number of conditions. Reaction (2) appears to be uncomplicated. The question as to whether (1) or (3) dominates is largely a function of the water vapor present. Water vapor represses (1) to a marked extent. If conditions are arranged so that the water vapor is removed at intervals during the conversion, reaction (1) predominates.

The equilibrium constants obtained from this experimental work are compared with those calculated from published data on the reactions.

$$CO + H_2O = CO_2 + H_2$$

$$C + 2H_2 = CH_4$$

$$2CO = C + CO_2$$

The most probable values calculated in this way for $\log_e K$ of the combined reactions vary from 19.4 to 22.24 at 350° C. The highest value we have obtained experimentally is 19.6 and the experimental results are in general below the theoretical.

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ALL efforts to synthesize methane from carbon monoxide or carbon dioxide and hydrogen reacting in the gas phase failed until Sabatier and Senderens[1,*] took up this problem in 1896 in the course of studies of the catalytic effects of finely divided metals on gas reactions. They soon determined that, the conditions of preparation being equal, catalysts of nickel had a more pronounced effect than catalysts of other metals. The possibilities of industrial utilization of such hydrocarbon syntheses were recognized and numerous records in the patent literature attest to attempts to carry out the synthesis of methane on an industrial scale. As this provides a method of converting a non-combustible gas (CO_2), as well as a gas of low-heating value (CO), into a hydrocarbon gas of high-heating value, the processes were naturally first applied to the various forms of artificial consumers' gas, such as illuminating gas and water gas.

Within a few years of the publication of Sabatier and Senderens' first work[1] other investigators had turned from the commercial applications of the synthesis to the chemical principles underlying the reactions. Attempts were made to follow the course of the reactions, determine the conditions for optimum production of methane, and formulate the en-

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[1] Presented before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] This paper forms a part of the dissertation submitted by Mr. Hightower in partial fulfilment of the requirements for the Ph.D. degree at the University of Michigan.

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

ergy relationships involved. At intervals since about 1910 further work along these lines has been reported. The investigations of Sabatier and Senderens;[1-4] of Mayer with Altmayer,[5,7,10] with Henseling[6] and with Jacoby;[8,9] of Jochum;[11] of Armstrong and Hilditch;[12,13] of Haslam and Forrest;[14] and of Neumann and Jacob[16] may be cited as of particular interest. The equations usually written for the synthesis of methane are as follows:

$$CO + 3H_2 = CH_4 + H_2O \qquad (1)$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (2)$$
$$2CO + 2H_2 = CH_4 + CO_2 \qquad (3)$$

Some of these investigations are of interest mainly from the industrial application; a second class includes direct measurements of equilibrium at a definite temperature in one of the reactions noted above; and a third group contains studies of equilibria in reactions other than those cited above, but furnishing data which permit the calculation of equilibrium constants for one or more of these reactions. Investigations of the second and third groups should provide valuable checks upon the trustworthiness of the experimental data secured. Mayer, with Altmayer and Jacoby,[5,7-9] published a series of researches upon the equilibria in the reactions

$$2H_2 + C = CH_4 \qquad (4)$$
$$2CO = CO_2 + C \qquad (5)$$

Cantelo[17] also has recently published data on the equilibrium of (4). Equilibrium data for the water-gas reaction

$$CO_2 + H_2 = CO + H_2O \qquad (6)$$

is also available. From these equilibria the equilibrium for the three methane-synthesis reactions may be calculated. Direct measurements of the equilibrium constants for reactions (1) and (2) have been published only by Neumann and Jacob.[16] Other published measurements of equilibrium constants and studies of catalytic synthesis of methane will be mentioned in the sections to follow.

Apparatus

The apparatus for the experimental work consisted of a Pyrex glass tube containing the catalyst supported in an electric furnace. The temperature of the catalyst was obtained by thermocouples inserted in the tube and the temperature of the furnace was controlled by an electrical controller. The apparatus for circulating the gas has been described in a previous paper.†

In the first apparatus the tube was vertical and the gas passed upward through a layer of broken porous porcelain 4 inches (10 cm.) long placed within the heated furnace. In the second apparatus the tube was horizontal and the gas on entering passed through a 17-inch (43-cm.) length of packed tube, 12 inches (30 cm.) of this being inside the furnace. A perforated porcelain plate separated the catalyst from the gas entrance section of the tube. The catalyst section was 6 inches (15 cm.) long, with a volume of 75 cc. The hot junctions of the thermocouples were situated on the axis of the tube in the middle of the catalyst section. The exit section was packed with broken unglazed porcelain. The three thermocouples, insulated with Usalite sheathing, were led out the exit tube. The thermocouple wires were separately threaded through a rubber stopper fitted to the opening of this tube and the glass-to-rubber joint was covered with a viscous glue-wax coating as described below. The resulting seal gave no evidence of leakage at any time. The gas exit was connected to the water-collection bulb and lines leading to the circulation pump.

Catalysts

All catalysts used in this work consisted of nickel supported on unglazed porcelain. Pieces of unglazed porous plate screened between 10 and 14 mesh were soaked in a concentrated water solution of high-grade nickel nitrate. The percentage of metallic nickel in the finished catalyst varied between 1.3 and 4.9 per cent. The water was driven off from the catalyst by heating at 95–100° C. and the nitrate was decomposed according to one of the following methods:

(A) The porcelain-nickel nitrate product was decomposed by heating in a current of hydrogen, the temperature being maintained at about 200° C. for 2 hours, then raised gradually to 350° C., and finally held at 400–410° C. for 5 hours. At the end of this period the catalyst was allowed to cool in a current of hydrogen. The catalyst was found to be active, and no further reduction of the nickel was sought.

(B) The nickel nitrate–porcelain material was heated in a current of air for 6 hours, the temperature being raised gradually to 460° C., then allowed to cool in air. When at room temperature the air was swept out by hydrogen and the nickel oxide–porcelain material was heated in a current of hydrogen. A temperature of 200–250° C. was maintained for 4 hours. The reduced catalyst was allowed to cool in hydrogen.

The catalysts prepared by both these methods were active and no definite distinction can be made between them.

Preparation of Gases

The carbon dioxide and hydrogen were taken from commercial cylinders without purification. Carbon monoxide was prepared by dropping formic acid (85 per cent solution) into concentrated sulfuric acid heated to between 95° and 120° C. according to the method of Rupp.[19] The gas was passed through a short scrubbing tube containing 20 per cent sodium hydroxide solution to remove acid spray. No attempt was made to remove completely the small amount of carbon dioxide in the gas. The gases were in all cases thoroughly mixed and the samples for analysis were taken immediately before the commencement of the test.

Gas Analysis

The gases were analyzed by ordinary absorption methods for carbon dioxide, unsaturated hydrocarbons, oxygen, and carbon monoxide; and hydrogen and methane were determined by explosion, and nitrogen was estimated by difference. In some cases the copper combustion method was used for determination of hydrogen and methane, but the values were all checked against determinations by the explosion method. The copper oxide–combustion method was found to give reliable values for methane only when the gas analyzed contained less than about 5 per cent CH_4. The gas burets were filled with mercury. Analyses by the absorption method are accurate to within about 0.2 per cent. The compositions of methane, hydrogen, and nitrogen may be about 2 per cent in error.

The quantity of water vapor in the initial gases was calculated from the temperature of the water saturator and that in the product gases was calculated from the differences in weight of the calcium chloride tubes.

Experimental Procedure

The experiments were carried out in two distinct groups, those with the single pass and those with multi-passes. All of them were carried out at substantially atmospheric pressure. A pressure of 5 to 20 mm. above atmospheric was maintained throughout the system in all runs, to avoid the possibility of drawing air into the system. The effect of such a pressure increase, less than 0.03 atmosphere, upon the course of the reactions would be too slight to be noted. All reported gas volumes are computed from the observed data to a pres-

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† *Ind. Eng. Chem.*, **20**, 99 (1928).

sure of 760 mm. and a temperature of 0° C. Water is calculated as vapor under these conditions. In the single-pass tests several liters of the gases were passed through the system, the initial and final water content and the initial and final gas compositions being determined. In the multipass series several liters of gas were also used and the temperature of the furnace was held constant throughout all the passes, as was also the temperature of the water saturator at the inlet. The gases cooled to atmospheric temperature between each pass and therefore the water vapor formed in each pass was removed. The effect of this difference in procedure will be discussed later.

Certain expressions employed in reporting the results of the experiments should be defined. The "H_2:CO ratio" refers to the relative volume proportions of hydrogen and carbon monoxide in the synthetic blue water gas used, the "initial" gas. The term "conversion ratio" is used to indicate the extent to which carbon monoxide and carbon dioxide of the initial gas were reduced to methane. The value of the conversion ratio for each test was set equal to the fraction

$$\frac{\text{Volume of } CH_4 \text{ in product } - \text{ volume of initial } CH_4}{\text{Sum of volumes of initial CO and } CO_2}$$

The rate of flow of a gas through a catalyst is expressed in terms of "space velocity." This commonly adopted unit may be defined as: unit volume of gas, measured at the catalyst exit, passing through unit apparent volume of catalyst in one hour.

Conversion as a Function of Temperature

The study of the effect of temperature upon conversion of blue water gas components to methane was restricted to the range 280° to 377° C. Methane is formed from carbon monoxide and hydrogen at temperatures above and below this range, but the higher yields are obtained from catalytic reduction within the specified limits.

Table I—Effect of Temperature on Conversion of Hydrogen and Carbon Monoxide to Methane

Run	Temperature	Space Velocity	Initial H_2:CO Ratio	Loss in Gaseous Carbon	Conversion Ratio	CH_4 in Product
	° C.			Per cent		Per cent
70-A	285	24.0	1.35	0	0.12	6.1
69-B	293	25.7	1.63	0	0.37	22.3
71-A	300	24.9	1.35	8.9	0.55	55.0
68-A	342	30.0	1.33	19.0	0.60	63.1
67-A	350	30.0	1.33	3.0	0.73	72.1
76-C	352	12.4	1.26	14.3	0.62	65.6
56-B	355	14.4	1.34	9.5	0.65	57.5
56-D	365	15.9	1.34	12.9	0.62	56.3
75-A	377	19.3	1.53	1.1	0.49	52.8

The effect of increasing temperature is shown in Table I. The gas used was synthetic blue water gas prepared in the laboratory as already described, with a ratio of H_2 to CO varying from 1.26 to 1.63. The space velocity varied from 12.4 to 30.0, giving a time of contact of from 2 to 5 minutes. There is no deposition of carbon below 300° C. and above that temperature variable amounts are formed. It will be noted in Table I that minimum amounts of free carbon are formed in tests 67-A and 75-A. The catalyst in 67-A had been used previously but had been given a new reduction in hydrogen just before this test. The catalyst of 75-A was used for the first time. This smaller amount of carbon deposited when a fresh catalyst was used makes it probable that the deposition of carbon is autocatalytic. The results are plotted graphically in Figure 1, on which all the conversion values of Table I are represented. The points which are distinctly below the curve, 68-A and 76-C, are those which show large deposition of carbon, 19.0 and 14.3 per cent, respectively.

The ratio of CH_4 formed to initial CO_2 and CO, as given in Table I, shows a maximum conversion ratio of 0.73 in test 67-A at 350° C. In this test the volume of the initial gas was 750 cc. with 0.5 per cent CO_2 and 39.3 per cent CO, giving a total volume of CO_2 and CO of 299 cc. It contained no CH_4. The product gas measured 306 cc. and contained 72.1 per cent of CH_4, giving a volume of 220 cc. The conversion ratio was therefore 0.73. It has been noted that the catalyst was freshly reduced before this test and that this may account for the small amount of free carbon formed and the higher conversion to CH_4. These results do not necessarily show equilibrium conditions, although the time of contact is relatively long. They are merely the results obtained under the conditions of our tests. They confirm in general the work of Neumann and Jacob, who state that there is no carbon deposition below 303° C. but that carbon deposition takes place in increasing amounts at higher temperatures; but the fact that in test 75-A only 1.1 per cent of the carbon gas was decomposed to form carbon when using a fresh catalyst at 375° C. indicates that caution should be used in generalizing.

Recirculation Tests

The question as to which of the two reactions, (1) and (3), was the primary one under the conditions studied could be answered, in part at least, by a technic which removed the water from the reaction. It was not possible to do this completely, but an apparatus was arranged which attained this end in considerable measure.

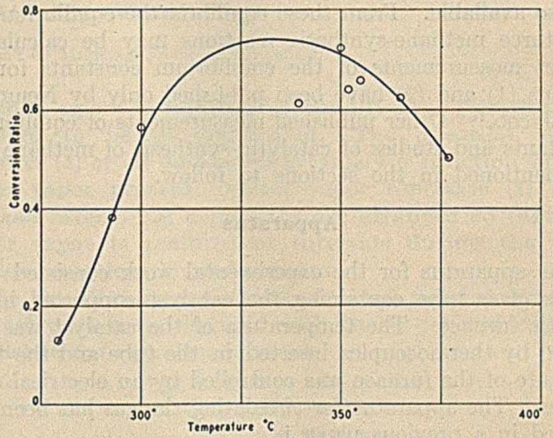

Figure 1—Conversion to Methane as a Function of Temperature

The initial gas was recirculated rather rapidly through the catalyst tube and allowed to cool to room temperature after each pass through the catalyst. Thus it entered the catalyst each time saturated with water at room temperature. The change in volume was measured and samples were withdrawn for analysis at intervals during the recirculation process. Two series of runs of this sort were made, No. 87 at 302° C. with 30 passes and No. 88 at 350° C. with 110 passes. The catalyst was not disturbed during these two series. Since the reaction took place in a glass tube, it was possible to make a visual examination of the catalyst after each series. At the end of series 87 there was a brown discoloration at the exit of the catalyst tube and a mirror-like deposit on the glass at the beginning of the heated section of the inlet end. The catalyst had changed in color at the inlet end from its normal gray to the white of the porcelain support. At the end of test 88 these phenomena were more noticeable. When the catalyst was removed, the deposition of carbon was evident and it was shown that the mirror consisted of nickel.

Table II—Effect of Recirculation of Gas over Catalyst: Series 87 at 302° C.

Gas Component	Number of Passes over Catalyst when Sampled				
	0	3	15	20	30
	%	%	%	%	%
CO_2	0.9	1.5	3.3	5.7	4.3
CO	43.2	44.0	45.3	46.1	47.0
CH_4	0.0	3.6	12.3	17.2	24.5
H_2	53.3	47.8	36.2	29.2	21.1
N_2	2.6	2.7	2.5	1.8	2.0
Ratio H_2:CO	1.23	1.11	0.89	0.56	0.45
Conversion ratio		0.07	0.20	0.24	0.30
Volume, cc.	5560	5075	4050	3476	3014

Test 87 was made with a synthetic water gas with 53.3 per cent H_2 and 43.2 per cent CO at a temperature of 302° C. The gas was circulated 30 times over the catalyst with a space velocity of about 400 at each pass. Volumes were measured and analyses made at five different periods. The data are presented in Table II. The striking thing about the gas composition at the various stages is that CO_2 remains small and the CO, which starts at 43.2 per cent, increases to even higher percentages, while the CH_4 rises from 0 to 24.5 per cent. The carbon balance shows a formation of free carbon amounting at the end of the 30 passes to 6.9 per cent of the initial gaseous carbon present, which is equivalent to 0.23 per cent per pass. The apparent path of the carbon which has changed its form may be calculated as follows:

		Initial CO_2 + CO
		Per cent
$2CO = C + CO_2$	(5)	13.8
$CO + 3H_2 = CH_4 + H_2O$	(1)	26.1
$CO_2 + 4H_2 = CH_4 + 2\ H_2O$	(2)	3.6
		43.5

Test 88 was made in a way similar to 87 at a higher temperature, 350° C., and with a total of 110 passes. The data are presented in Table III. As in test 87, the percentage of CO_2 remains low and the CO varies little from its initial value of 48.6. The apparent path of the reactions may be calculated as follows:

Equation	Initial CO_2 + CO
	Per cent
(5)	28.0
(1)	16.3
(2)	8.0
	52.3

Table III—Effect of Recirculation of Gas over Catalyst: Series 88 at 350° C.

Gas Component	Number of Passes over Catalyst when Sampled						
	0	1	5	30	50	78	110
	%	%	%	%	%	%	%
CO_2	1.3	2.0	3.1	5.7	7.7	7.8	8.9
CO	48.6	49.3	47.0	49.3	48.3	47.9	45.8
CH_4	0.0	3.5	8.1	19.1	22.0	28.9	30.8
H_2	46.5	42.5	34.8	22.1	16.2	9.3	7.2
N_2	3.6	2.7	6.5	3.7	5.7	5.9	6.5
Ratio H_2:CO	0.96	0.86	0.74	0.47	0.34	0.19	0.16
Conversion ratio		0.03	0.14	0.24	0.25	0.30	0.29
Volume, cc.	5740	5496	4850	3610	3270	2980	2785

The errors in gas analysis are too great to follow the reactions quantitatively from one pass to another, but calculations show that the path of the reactions stays fairly constant through the series and is unaffected by the changing ratio of H_2 to CO. The dominant reaction is (1), with (5) furnishing the CO_2 for (2). The dissociation of CO is apparently uninfluenced by the relative proportions of H_2 to CO. The percentage of CH_4 does not rise above 31 per cent and at the end of the run in Table III is changing very slowly and apparently reaching a steady state. The composition of the initial gas was manifestly incorrect to obtain high values of CH_4. Since the reaction is dominantly

$$CO + 3H_2 = CH_4 + H_2O \qquad (1)$$

it is evident that the initial gas should have had three molecules of H_2 to one of CO instead of having approximately one molecule of each, if the maximum conversion was to be obtained.

Influence of Water Vapor

The results of the tests where the water vapor was removed at the end of each short contact have been discussed under the head of Recirculation Tests. The following discussion deals with tests in which the gas stayed in contact with the catalyst for a longer time and the water vapor formed in the reaction remained throughout the single slow pass. Tests 101, 102, and 103-A were all made from synthetic blue water gas at 350° C. and at space velocities of about 16. Comparison of the initial and final gas compositions is given in Table IV. The outstanding difference between these figures and those of Tables II and III is in the percentage of CO. Whereas in Tables II and III this was almost the same in the initial gas as in the final gas, the percentage of CO in the gases of Table IV drops to less than 3 per cent in every case. The CO_2 in Tables II and III does not increase above 7 per cent in the final gases, but in Table IV it rises to high figures. The presence of so much water vapor, as might have been expected, has inhibited the reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (2)$$

so that the dominant reaction becomes

$$2CO + 2H_2 = CH_4 + CO_2 \qquad (3)$$

Neumann and Jacob found very small amounts of CO_2 formed even at 450° C. while Haslam and Forrest found large amounts of CO_2 at temperatures even below 300° C. This difference is due partly to the fact that Neumann and Jacob always had more than 3 molecules of hydrogen for each molecule of carbon monoxide in their gas, while Haslam and Forrest worked with a gas containing only 1.5 molecules of H_2 for each molecule of CO. Our results confirm those of Haslam and Forrest when working under their conditions.

Table IV—Changes in Composition of Gases on Single Slow Pass (Temperature, 350° C.)

Gas Component	Test 101		Test 102		Test 103-A	
	Initial	Final	Initial	Final	Initial	Final
	%	%	%	%	%	%
H_2O[a]	2.7	32.8	7.5	28.2	2.8	9.5
CO_2	1.9	17.3	2.1	20.2	0.4	39.4
CO	32.3	2.7	33.2	2.1	48.4	2.6
CH_4	0	33.2	0	28.9	0	39.7
H_2	56.6	7.6	50.1	11.7	45.6	4.5
N_2	6.5	5.6	7.0	8.9	2.6	3.7
Total volume, cc.	1945	1236	2264	1422	3140	1709
Space velocity	16.8		14.8		16.1	

[a] Calculated as vapor at atmospheric temperature.

Reaction between Carbon Dioxide and Hydrogen

The behavior of a mixture of CO_2 and H_2 was tested in two runs—104 and 105—at 350° C. The gas compositions are given in Table V. Carbon monoxide was absent from the initial gas and is reported in such small amount in the final gas that it may be an error of analysis. The reaction proceeds without complication according to reaction (2). This confirms the work of Sabatier, Mayer and Henseling, and Neumann and Jacob.

Table V—Changes in Composition of Gases Consisting Mainly of CO_2 and H_2 on Single Slow Pass over Nickel Catalyst at 350° C.

Gas Component	Test 104		Test 105	
	Initial	Final	Initial	Final
	%	%	%	%
H_2O	3.0	47.5	8.4	44.3
CO_2	18.8	4.4	21.5	11.1
CO	0	0.1	0	0.2
CH_4	0	25.9	0	20.3
H_2	76.4	19.7	68.7	22.1
N_2	1.4	2.1	1.6	1.8
Volume, cc.	3100	1941		

Path of the Reactions

It has been stated that the path of reaction (2) seems attended with no side reaction. It is otherwise, however, with the reactions which cause the formation of CH_4 from CO. The reaction (3) may be derived by addition of equations (6) and (1). So also an equation can be written involving the formation of CH_4 from CO and H_2O

$$4CO + 2H_2O = 3CO_2 + CH_4$$

This in turn may be built up from (3) and (6).

The heats of reactions and the free energies at 20° C. indicate the strong tendency of all these reactions to go to the right. It is thus impossible to calculate the exact path of the reaction, and in the discussions here the equations (1), (2), and (3) have been used because they have been generally accepted in the literature.

Calculation of Data on Equilibria

For those runs in which determinations of the CH_4, CO_2, CO, H_2, and H_2O in the product gases were obtained, the partial pressures of these components could be calculated and used in computing the value of equilibrium constants for the reactions involved in methane formation. Without attempting to differentiate between the three equations (1), (2), and (3), or to specify the part each played in reaching the final equilibrium, an equation containing all five of the reactants may be used. The sum of equations (1) and (2) gives such a relationship

$$CO + CO_2 + 7H_2 = 2CH_4 + 3H_2O \qquad (7)$$

The equilibrium constant for equation (7), stated in terms of the partial pressures of the components, is

$$K_7 = \frac{(pCH_4)^2\,(pH_2O)^3}{(pCO)(pCO_2)(pH_2)^7} = K_1 \times K_2$$

Table VI gives values of $\log_e K_p$ calculated from the data of a number of runs, according to equation (7). It may be assumed that the highest values of K_p, or its function $\log_e K_p$, represent the nearest approach to equilibrium conditions in the experiments; that is, reaction will not go beyond equilibrium.

Table VI—Experimental Determination of Equilibrium Constant for Reaction (7)
(Temperature, 350° C.)

Run	Space Velocity	$\log_e K_p$
101	16.8	17.9
102	14.8	14.2
103-A	16.1	19.6
103-B	21.0	17.9
104	17.5	16.4

The only published experimental data on K_p for reactions (1) to (3) at lower temperatures is contained in the work of Neumann and Jacob.[16] Their research presented data on equations (1) and (2) over a temperature range of about 800 degrees, from 300° to 1050° C. Their experimentally determined values for the equilibrium constant of reaction (1) were in agreement with the calculated values in the range 860° to 1050° C.; for lower temperatures no values of K_p were published and a recalculation of their results indicates that they did not reach equilibrium at the lower temperatures. Neumann and Jacob appear to have assumed that H_2O was produced from CO and H_2 under their conditions of experiment in amount equal to the CH_4 produced. This assumption was necessary in deriving the partial pressures for K_1 from their data, but it is certainly not warranted in a study of methane formation from blue water gas.

Various combinations of equations (4), (5), and (6) may be added or subtracted to give the equations for the methane-forming reactions (1), (2), and (3). Their equilibrium constants (K_p) may be similarly combined and from such calculations the values of K_p for (1), (2), and (3) may be obtained. For instance, addition of reactions (4), (5), and (6) yields reaction (1).

$$\begin{array}{lr} C + 2H_2 = CH_4 & (4) \\ 2CO = CO_2 + C & (5) \\ CO_2 + H_2 = CO + H_2O & (6) \\ \hline CO + 3H_2 = CH_4 + H_2O & (1) \end{array}$$

Therefore the product of K_4, K_5, and K_6 is equal to K_1. Similarly, reaction (2) is equal to the sum of reactions (1) and (6) and the product of K_1 and K_6 is equal to K_2. K_7 can then be expressed in terms of K_4, K_5, and K_6 instead of K_1 and K_2.

$$K_7 = K_1 \times K_2 = K_4 \cdot K_5 \cdot K_6 \times K_4 \cdot K_5 \cdot K_6^2$$
$$= K_4^2 \cdot K_5^2 \cdot K_6^3$$

The published experimental data on the equilibrium constants for equations (4), (5), and (6) have been used to compute the theoretical values of the equilibrium constant for equation (7) at the temperatures of the experiments reported here. Table VII presents this material. The references cited in this table contain equations suggested by the different workers to represent their data; these equations were used in computing the values of $\log_e K$ at the temperatures indicated for the reactions.

Table VII—Comparison of Equilibrium Constants $\log_e K_p$ for 623° K.

Source of Data	Reaction (4) $K_p = \frac{(pCH_4)}{(pH_2)^2}$	Reaction (5) $K_p = \frac{pCO_2}{(pCO)^2}$	Reaction (6) $K_p = \frac{(pCO)(pH_2O)}{(pCO_2)(pH_2)}$
Lewis and Randall[26] equation	+4.64	+12.18	−3.27
Saunders[27] equation	+4.97	+12.30	
Mayer and Altmayer[5,7] equation	+5.20		
Mayer and Altmayer[7] data	+5.23[a]		
Cantelo[17] equation	+2.50		
Mayer and Jacoby[9] equation		+12.11[b]	
Mayer and Jacoby[9] data		+12.15[c]	
Neumann and Jacob[16] equation		+ 5.64[d]	−2.81[e]
Mayer and Altmayer[10] equation			−3.40
Eastman and Evans[29] data			−2.45[f]
Haber and Richardt[31] equation			−3.40
Engels[32] equation			−3.12
Hahn[33] equation			−3.33

[a] Determined graphically from Mayer and Altmeyer's tabulation of partial pressures.

[b] Using 7.92 for "I" in equation ($C/2 + CO_2/2 = CO$) and multiplying entire $\log_e$ quation by 2.

[c] Estimated graphically from plot of Mayer and Jacoby's data, tabulated by them to 500° C.

[d] Using 8.75 for "I" in equation ($C + CO_2 = 2CO$).

[e] Values given for K at 786–1086° K. plotted and curve extrapolated to 575° K.

[f] Values of K plotted from data given and curve extrapolated to 575° K.

The values of $\log_e K_4$, $\log_e K_5$, and $\log_e K_6$ for the desired temperature are used in the expression

$$2 \log_e K_4 + 2 \log_e K_5 + 3 \log_e K_6 = \log_e K_7$$

Equilibrium constants so computed, for temperatures of 302° and 350° C., are listed in Table VIII. It will be seen that the value of $\log_e K_7$ obtained by use of Mayer and Jacoby's[9] data on reaction (5), Cantelo's[17] on reaction (4), and Haber's[30] on reaction (6) yields the value of 19.37 for $\log_e K_7$ at 350° C. Use of the values determined indirectly by Eastman and Evans[29] in place of Haber's data gives $\log_e K_7$ at 350° C. = 22.24.

Table VIII—Comparison of Values of Equilibrium Constant for $\log_e K_p$ for Reaction (7)
(Temperature, 623° K.)

Run	$\log_e K_p$		Investigator		
	Exptl.	Calcd.	Reaction (4)	Reaction (5)	Reaction (6)
101	17.97	19.02	Cantelo	Mayer	Eastman
103-A	19.6	19.37	Cantelo	Average[b]	Haber
103-B	17.9	22.24[a]	Cantelo	Average[b]	Eastman
104	16.4	23.43	Lewis	Lewis	Lewis
		27.72	Mayer	Saunders	Eastman

[a] Most recent data.

[b] Average of values from Saunders, Lewis, and Randall, and Mayer and Jacoby.

The minimum amount of hydrogen to react stoichiometrically is a volume equal to the carbon monoxide and four times as great as the carbon dioxide. Any larger proportion of hydrogen up to three times the volume of the carbon monoxide and four times the hydrogen should be taken care of by equation (7).

The highest value for the equilibrium constant obtained in our work was 19.6 in run 103-A, obtained with a new catalyst at a space velocity of 16 and with a gas composed of almost equal volumes of CO and H_2. In this test there was a decomposition of CO to form CO_2 and C, which amounted to 8.6 per cent of the total carbon present. If this decomposition took place before the gas traversed the catalyst, it would have no influence on the value of the equilibrium constant. However, it is probable that this thermal decomposition of CO took place while the gas was traversing the catalyst and therefore some of the CO_2 formed did not have time to react with the H_2 before leaving the catalyst. This would cause the equilibrium constant as determined experimentally to be lower than the theoretical.

Working with an entirely different initial gas, CO_2 and H_2, the equilibrium constant calculated in the same manner from the data of test 104 gives a value for the constant of 16.4. It is therefore believed that our results fall somewhat short of the calculated equilibrium conditions. However, in view of the varied possibilities of the reactions, it will be very difficult consistently to reach a result which may be definitely stated to represent equilibrium conditions.

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Bromocresol Green as an Indicator in the Manufacture of Grain-Curd Casein[1]

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TO PRODUCE a grain-curd casein acceptable for technical uses the hydrogen-ion concentration must be carefully controlled. Methyl red was recommended as an indicator for this purpose by Clark and his co-workers in 1920. Unfortunately this indicator is not stable, and the standard tubes must be replaced very frequently to avoid serious errors. Bromocresol green has been suggested for this purpose, as it is stable and, for theoretical reasons, might be expected to exhibit less protein error than methyl red.

In a number of experiments fresh skim milk was treated with dilute hydrochloric acid according to the method of grain-curd casein manufacture developed in this laboratory.[2] The change in hydrogen-ion concentration near the end point was followed potentiometrically and colorimetrically with bromocresol green. As care is required in matching the delicate bluish greens of the indicator, standard tubes were made up for every 0.1 pH (4.5, 4.6, 4.7, etc.), and 10 drops of the indicator (0.5 per cent solution) were used in each 10-cc. sample of the whey.

The results of a typical experiment of the series are given in Table I and Figure 1.

Table I

Cc. HCl per liter skim milk	38	41	42	43	44	45	46	47
pH—potentiometrically	4.64	4.38	4.29	4.22	4.14	4.07	4.01	3.93
pH—bromocresol green	4.8	4.7	4.7−	4.7−	4.6+	4.5+	4.5+	4.5

Comparison of this curve with that of methyl red published with the original method shows clearly that in hydrochloric acid whey the protein error of the bromocresol green is about the same as that of methyl red. The color observed at the end point desired (an actual pH of 4.1) matches that of a 4.6 standard bromocresol green tube. The advantage of using bromocresol green lies in the stability of the color standard tubes, which can be kept for months without change if protected from contamination. Whether the gradations of bluish green produced by this indicator are as easily matched by the individual worker as are the pink shades of methyl red is a question which can be settled only by trial.

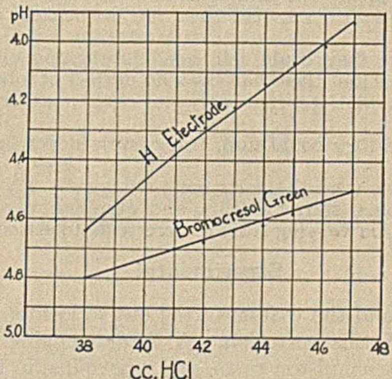

Figure 1

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[1] Received October 31, 1927.

[2] Clark, Zoller, Dahlberg, and Weimar, *Ind. Eng. Chem.*, **12**, 1163 (1920).

Effect of Sulfur in Gasoline on Wrist-Pin Corrosion in Automobiles[1]

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Experiments were made during the winter of 1922-23 by Mr. Kreis, of the Continental Motor Company, and the writer using a Jordan engine fitted with new wrist pins, pistons, and rings for each experiment. The engine was run one hour and allowed to stand idle one hour. All work was done when the temperature was below freezing, though not very cold.

Each test represented from 60 to 75 hours' running time. Results showed that (1) when using a gasoline of 0.040 per cent sulfur there was no corrosion of wrist pins, etc., and that the water condensed in the crankcase contained no free acid; but did contain some ferrous sulfate; (2) when using a gasoline of 0.151 per cent sulfur the corrosion was very appreciable and the water in the crankcase contained free sulfuric acid in small quantities; (3) when using a gasoline of 0.458 per cent sulfur the corrosion was very serious and the crankcase water quite acid.

For several years prior to 1923 complaints of severe corrosion of various parts of automobile engines were occasionally made. The users were generally inclined to blame the lubricating oil, but no evidence could be discovered to prove that the oil was at fault. In 1922 the Continental Motors Company made a rather comprehensive survey of their corrosion complaints, which finally resulted in a coöperative study of the problem by that company and the laboratory of the Standard Oil Company of Indiana.

During the winter of 1922–1923 Mr. Kreis, of the Continental Motors Company, and the writer carried out experiments to determine the cause of wrist-pin corrosion which had been previously noted by the Continental Motors Company and other automobile manufacturers. Prior to these experiments the following facts had been noted by the Continental Motors Company:

1—This company and others had had complaints of corrosion to certain parts of motors from time to time, these complaints being mostly of corroded or badly worn wrist pins. They knew the cars had not been used sufficiently to wear the wrist pins seriously, and careful examination showed that the pins seemed to be chemically corroded or etched. An investigation showed that:

2—In all cases the car had been run on benzene or benzene blend.

3—So far as they could tell, good lubricating oil had been used in all cases and there had been no neglect of lubrication.

4—This trouble occurred only in cold weather, never in summer.

5—So far as they could find, trucks were never injured, only automobiles.

6—Wrist pins were the parts most damaged. Pistons, piston rings, crank pins, starter chains, and even pump rods showed signs of corrosion varying from a mere trifle to serious injury.

Experimental

Mr. Kreis and the writer started out to locate, if possible, the source of this corrosion. A Jordan engine was fitted with new pistons, piston rings, and wrist pins; in fact, it was in perfect order in every way. This engine was placed out of doors and run 1 hour and allowed to stand idle 1 hour.

Preliminary Tests—It happened that the first tests, made in November, were performed during a period of relatively warm weather, the temperature being most of the time well above freezing. These tests were on a blend containing benzene and running about 0.151 per cent sulfur. Exceedingly little corrosion occurred. As soon as the weather went below freezing, tests with the same gasoline showed very marked corrosion. After this fact had been established—namely, that marked corrosion occurred only when the temperature was in the neighborhood of 32° F. or lower—all tests were run only under these conditions. However, there was no weather as low as zero during the entire period of tests.

After the preliminary tests the wrist pins and other parts of the engine were carefully examined. A qualitative examination showed that the "rust" from the wrist pins consisted of sulfide, sulfate, and oxide of iron. This seems sufficient to indicate that sulfur was the chief, if not the only, cause of corrosion.

Gasoline Containing 0.151 Per Cent Sulfur—A series of carefully controlled experiments was then conducted to prove or disprove this point. A motor fuel containing 0.151 per cent of sulfur was purchased in the open market. In other respects this motor fuel was normal. It is believed that it contained about 25 per cent of benzene, though this is not certain. The engine was run 1 hour and stopped 1 hour whenever the weather was colder than freezing. Whenever the air temperature rose above freezing the engine was allowed to stand idle until the temperature fell below freezing again. This occurred once or twice during the test. The entire running time was 75 hours and $68^{1}/_{4}$ gallons of gasoline were consumed. Examination of the wrist pins after this test showed that they were somewhat corroded, quite markedly in fact, though the injury could not be called severe. The oil from the crankcase contained much water, which water was a dilute acid solution of iron sulfate. It was acid to litmus, also to methyl orange.

Gasoline Containing 0.040 Per Cent Sulfur—The engine was now refitted with new pistons, piston rings, and wrist pins. A commercial gasoline having about the same boiling point as the sample previously tested, but low in sulfur, was now used. This gasoline contained 0.040 per cent sulfur, was sweet and non-corrosive. The test was continued for 75 hours and the gasoline consumed was $67^{1}/_{4}$ gallons. Weather conditions were considerably colder than in the previous test. The examination of the wrist pins, pistons, etc., showed that there was no perceptible corrosion. The oil from the crank case contained considerable water which was settled out. This water was neutral to methyl orange but did contain some sulfate of iron.

Gasoline Containing 0.458 Per Cent Sulfur—A third test was made using a gasoline specially prepared by pressure-stilling high-sulfur stock. This gasoline had the

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[1] Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

usual boiling points, was absolutely sweet and non-corrosive to a copper strip. It contained 0.458 per cent sulfur. In all other respects it was a normal gasoline. The engine was again fitted with new parts as before and was run 61 hours. Sixty-four gallons of gasoline were consumed, somewhat less than in the previous tests. The corrosion was the worst yet obtained—in fact, it was very serious. The "rust" scraped from the pins as before was found to consist of sulfide, sulfate, and oxide of iron. The oil from the crankcase was so emulsified that there was considerable difficulty in separating the water from the oil. This was finally done, however, and the water gave all reactions for sulfuric acid. It was acid to both litmus and methyl orange. It also contained sulfate of iron.

SEARCH FOR OTHER CORROSIVE ACIDS—Experiments on these three gasolines were checked, with the same results. Also the water from the crankcase and crankcase oil was carefully examined for possible corrosive acids other than sulfuric. No trace of other corrosive acids could be found. This seems to lay the blame squarely on the sulfuric acid, which could have originated from the gasoline only as all the above tests were made using the same lubricating oil, one regularly purchased and used by the Continental Motors Company.

TESTS WITH DIFFERENT LUBRICATING OIL—One experiment was then performed with the same high-sulfur gasoline previously mentioned and under the same conditions except that the lubricating oil was changed. A lubricating oil containing aluminum oleate, purchased in the open market, was used. No corrosion to wrist pins or other parts occurred, though high-sulfur gasoline was used under severe conditions. However, the use of this oil was severely condemned by the practical engineer of the Continental Motors Company because it emulsified badly, becoming so thick that it could hardly be pumped, deposited a large amount of slush or nearly solid sediment, and had a very bad odor after several hours' use.

Mechanism of Wrist-Pin Corrosion

From these facts was deduced and reported the following hypothesis of the mechanism of the corrosion, which seems in accordance with the opinion now generally held by the industry:

1—Sulfur compounds, regardless of their nature, are burned more or less completely to sulfur dioxide in the cylinder of the engine.

2—Some of this sulfur dioxide along with carbon dioxide and water vapor finds its way past the piston rings into the crankcase, but as long as sulfur dioxide is uncombined with water it has no serious action on metals, nor does it tend greatly to oxidize to sulfur trioxide.

3—If the weather is cold and the engine frequently stopped, much of the water vapor which leaks into the crankcase will condense and will absorb the sulfur dioxide, forming a dilute solution of sulfurous acid. This being churned up with the oil in the crankcase and air tends to go over to sulfuric acid. We would expect this reaction to be very rapid and complete in the presence of finely divided metal, which is always present in used crankcase oil.

4—The sulfuric acid thus formed is nearly insoluble in oils, and oils tend to "wet" the surface of metals in preference to aqueous solutions. Therefore, those metal parts on which the oil film is allowed to remain intact will be very little corroded even in the presence of sulfuric acid. This was found to be true. However, in bearings and on cylinder walls there is a continual tendency to rub off or squeeze out the oil more or less completely, particularly on stopping and starting the engine. Where the oil film is thus broken the acid suspended in the oil has a chance to attack the metal directly and does so. Dry sulfur dioxide, or even dry sulfur trioxide, will not corrode iron at ordinary temperature. Thus there is an initial period before sulfuric acid is formed during which there is no corrosion.

The essential reactions involved in all this may be written thus:

(1) During explosion:

$$\text{Sulfur compound} + \text{air in cylinder} \longrightarrow SO_2 + H_2O + CO_2$$

(2) In cool crankcase:

$$SO_2 + O\ (\text{air}) + H_2O\ (\text{condensed vapor}) \longrightarrow H_2SO_4$$

(3) On crank pin where oil film breaks:

$$H_2SO_4 + Fe \longrightarrow FeSO_4 + H_2$$

(4) On crank pin as secondary reactions:

$$FeSO_4 + H_2\ (\text{nascent hydrogen}) \longrightarrow FeS + H_2O$$

also possibly

$$FeSO_4 + 4\ Fe\ (\text{finely divided}) \longrightarrow FeS + 4\ FeO$$

The last compounds are not in aqueous solution, but under conditions of close contact at fairly high temperatures and pressures; which make for the formation of ferrous sulfide and oxide.

These reactions may not adequately represent all the facts, but there is little doubt but that they give us a fair picture of the mechanism of sulfur corrosion under the conditions studied.

Conclusions

1—Excessive sulfur in gasoline does cause serious corrosion of moving parts within the crankcase, especially in cold weather and when frequent stops are made.

2—There is no evidence that such corrosion occurs in warm weather or to any great extent on cars or parts that are kept continuously running during the day and in heated garages at night.

3—There is no evidence to indicate that anything other than sulfur in the gasoline is to blame. Sulfur combined in the lubricant is not to blame except in so far as it may actually be burned in the cylinder.

4—The corrosion is undoubtedly caused in the first place by sulfuric acid, the formation of iron sulfide and oxide being secondary. As all forms of organic sulfur are burned to sulfur dioxide, which is later changed to sulfuric acid, it is quite evident that the original form of sulfur in the fuel is of no importance.

5—The amount of corrosion is disproportionately greater for high-sulfur than for low-sulfur fuel. This may be explained on the following grounds: The crankcase oil contains small amounts of material which will neutralize the sulfuric acid. In the best of conditions crankcase oil, after a few hours' use, always shows some traces of finely divided iron and when used on dirt roads contains some road dust which is usually alkaline, often consisting essentially of carbonate of lime. If the amount of sulfuric acid formed is insufficient to react with finely divided iron and road dust, no injury results to the solid metal parts. Therefore, a certain small amount of sulfur in gasoline is not injurious. When the amount of acid formed in the crankcase becomes greater than that which can be neutralized by the finely divided iron and road dust, corrosion soon begins.

From the tests described herein it is evident that a sulfur content of 0.040 per cent does no harm, that 0.151 per cent sulfur does appreciable harm, and that 0.458 per cent sulfur does very great harm. Just where to draw the line is hard to say. It is probable that conditions were decidedly more severe than are usually met in the actual operation of an automobile. It is also obvious that the condition of the car as regards tightness of piston rings is a material factor, as well as the type of bearings. It would seem, however, from the data given that 0.100 per cent would be a fair dead line. No doubt a lower sulfur content is desirable, but it is probable that this amount would cause no appreciable injury; on the other hand it seems very certain that 0.200 or 0.300 per cent sulfur would cause very serious damage to a car operated intermittently in cold weather. As weather conditions and the way the car is used vary so greatly, no exact figure can be given for the maximum allowable sulfur.

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Sulfur in Gasoline from the Automobile Standpoint[1]

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It has been estimated that if the oil industry could raise the sulfur limit of gasoline from 0.10 per cent to 0.30 per cent, a saving of 50 million dollars per year in refining costs would be possible. It is recognized that the cause of corrosion in automobiles is water formed by the combustion of the fuel, and that the corrosion effect of this water is greatly increased if it is contaminated with acids resulting from the burning of the sulfur in the fuel.

Crankcase ventilation and control of the jacket-water temperatures by thermostats have been recommended to eliminate the condensation of water from the burning of the fuel and thus combat this corrosion. Records of tests and of performance in service in the hands of the public of engines equipped with such devices and operated on fuels of different sulfur content are given. Although the thermostats and ventilators are of very great value in combating corrosion, it is concluded that, inasmuch as a large number of cars are not so equipped, an increase in the sulfur content of motor fuel at the present time is not in accord with the best interests of the automobile industry and the public.

SULFUR in gasoline is a problem with which the oil industry is very familiar, but in the automobile industry it has not always had as much attention as it deserves. About a year ago there was considerable agitation in certain sections of the oil industry to get the government specifications for sulfur in gasoline raised from 0.10 per cent to 0.30 per cent or higher. An editorial in the February, 1927, issue of *Ind. Eng. Chem.* presents both sides of this problem. According to this editorial the problem from the standpoint of the oil industry is very simple. From the standpoint of the automobile industry, however, it is not so simple. With the value of the twenty-two million motor cars now in the United States placed at fifteen billion dollars, the estimated saving to the oil industry of fifty million dollars is only one-third of one per cent of the value of the automobiles in the hands of the public. On the assumption that this saving is passed on to the public when the possible loss in the value of the motor cars from the corrosion caused by high-sulfur gasoline is considered, this estimated saving of one-third of one per cent does not appear so attractive.

As pointed out by Thorne[2]

> A survey of the published information concerning corrosion discloses an almost unanimous agreement that water in the crankcase is responsible. The source of this water, as is generally known, is the water vapor that is formed as one of the products of combustion.***
>
> Although water alone will cause corrosion, the action may be accelerated by the formation of weak sulfurous or sulfuric acid. These acids are produced by the burning of the sulfur that occurs in fuel, thereby yielding sulfur dioxide and trioxide, and their subsequent combination with water.*** It is known,*** that the sulfur content will approach, and frequently exceed, the 0.10 per cent limit provided in government specifications.*** The chemical activity from this and other contaminants would be negligible if effective control of the formation of water were possible.

He then proceeds to recommend crankcase ventilation and control of the jacket-water temperature by means of thermostats or shutters, to decrease the condensation of water during the warming-up period, to prevent the condensation of water during normal running of the engine, and to eliminate from the crankcase any water which may have condensed during the warming-up period.

Engine Tests Using High-Sulfur Gasoline

The engineers of our organization have been working on this problem for several years, and had previously reached the same conclusions. Since laboratory experiments had indicated that crankcase ventilation and control of the jacket-water temperatures would solve this problem, a number of engines were thus equipped for service during the winter of 1923–1924 in a district where the sulfur content of the motor fuel averaged about 0.25 per cent, with some samples frequently containing as much as 0.35 per cent. A discussion of the problem of corrosion from sulfur in motor fuels, together with the results obtained in these tests on these engines, is given elsewhere.[3] For purposes of comparison with other analyses reported in this paper, the results of analyses of oils taken from the crankcase of motors in this test are given in Table I. Samples 1 to 4 are from cars without crankcase ventilators and operated under unfavorable conditions so that water collected in the crankcases. Samples 5 to 9 are from cars with early experimental crankcase ventilators and operated under conditions tending to evaporate the water from the crankcases as fast as it is formed. All samples except 2 and 4 are from the oil as circulated by the pumps. Sample 2 is the sludge from the oil from sample 1 and sample 4 is the sludge from sample 3.

Table I—Analyses of Crankcase Oils

Sample	Water *Per cent*	Total Dilution *Per cent*	Iron Oxide *Per cent*
	NO CRANKCASE VENTILATORS		
1	6	30	1.39
2	8	22	3.57
3	10	47	1.70
4	7	22	2.02
	WITH CRANKCASE VENTILATORS		
5	None	35	0.097
6	None	24	0.239
7	None	30	0.180
8	1.5	22	0.137
9	None	14	0.164

Although the regular production automobiles of the same make as those on which these tests were made had been equipped with thermostats for jacket-water temperature control for a number of years, the jacket-water temperature control alone did not keep the crankcase oil free from water or protect the engines from very bad corrosion troubles with fuels averaging about 0.25 per cent sulfur, but it did protect them to a very great extent with fuels carrying less than 0.10 per cent sulfur.

Service Tests with New Devices

During the next year, 1924–1925, crankcase ventilators were supplied as extra equipment on most of the engines of this particular make known to be destined for service in districts where high-sulfur fuel was common, and when the new models

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[1] Received September 2. Presented before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *J. Soc. Automotive Eng.*, **18**, 35 (1926).

[3] Mougey, *Automotive Industries*, **50**, 956 (1924).

were brought out in 1925 crankcase ventilators as well as jacket-water temperature controls were supplied as standard equipment on all cars, regardless of their destination. Oil filters were also adopted as standard equipment on this car.

During the years 1924–1925 and 1925–1926 hundreds of analyses of crankcase oil samples from this make of car were made. The averages are given in Table II. These samples were taken from privately owned cars by dealers all over the United States from the oil circulated by the pumps. In studying these analyses it is desirable to keep in mind the value of 0.11 per cent reported by Burkhardt[4] as the average iron oxide content of 225 samples of used crankcase oils taken all over the United States from a number of cars of different makes.

Table II—Average Oil Analyses, 500-Mile Samples, from All Parts of United States

(Figures in per cent)

	THERMOSTAT (1924–1925)			THERMOSTAT, CRANKCASE VENTILATOR, AND OIL FILTER (1925–1926)	
	Summer	Fall	Winter	Fall	Winter
Water:					
Maximum in any one sample	None	None	10.5	None	None
Average	None	None	2.5	None	None
Fuel dilution:					
Maximum in any one sample	42.5	35.0	43.0	24.0	27.0
Average	20.0	24.0	27.0	8.5	12.0
Iron oxide:					
Maximum in any one sample	0.16	0.80	1.59	0.16	0.14
Average	0.09	0.12	0.13	0.03	0.03
Silica and silicotes:					
Maximum in any one sample	0.03	0.09	0.07	0.04	0.01
Average	0.02	0.01	0.03	0.006	0.002

The record of complaints in regard to corrosion on these cars was very interesting. There were no complaints in summer, regardless of the sulfur content of the fuel. During winter, in the 1924–1925 series, covering engines with thermostats but without ventilators or oil filters, there were only a very few corrosion complaints that cars operated on fuels with 0.10 per cent or less of sulfur, although water was found in many crankcases, but with fuels with about 0.25 per cent of sulfur the complaints were very numerous, and very bad, especially in the case of cars in intermittent service. In the 1925–1926 series, with thermostats, ventilators, and oil filters, water in the crankcases was eliminated and no corrosion complaints were received, regardless of the sulfur content of the fuel.

Relation between Sulfur Content and Wear on Engine Parts

There was one peculiarity which misled us for a long time. On engines operated in continuous service in moderately heavy duty, or in long runs such as road tests, no water was found in the crankcases mixed with the oil, the fuel dilution was below the average for similar cars in normal private use, the amount of ash or iron oxide in the oil was very low, and the wear on the cylinders and other rubbing surfaces was much below normal. These conditions will exist with fuels containing up to 0.25 per cent of sulfur, and usually on such cars it will be impossible to show any relation between the percentage of sulfur in the fuel and the wear on the rubbing parts.

Table III shows results from four cars on road tests at our laboratory. Car 3 was equipped with an air cleaner and oil filter, but none of the others had any thermostat, ventilator, or other special device of this nature.

These cars were operated on gasoline with a sulfur content less than 0.10 per cent. At the same time another car was given a 40,000-mile test using a motor fuel containing about 0.25 per cent of sulfur. At the end of each 10,000 miles all of the cars with both kinds of fuels were torn down, examined, and measured. No evidences of corrosion of the rubbing surfaces were found and the actual wear of the engine parts was very much less than for similar cars in normal private use, as is seen from Table IV.

Table III—Average of Daily Analyses of Crankcase Oils from Four Six-Cylinder Cars of Different Makes

CAR	WATER	FUEL DILUTION	IRON OXIDE	AV. DISTANCE BETWEEN DRAINING OIL	AV. DISTANCE PER GALLON CONSUMPTION	DATE OF TESTS 1924
	%	%	%	*Miles*	*Miles*	
1	0	12	0.02	700	1810	December to April
2	0	10	0.02	1500	453	December to March
3	0	19	0.01	2500	1470	April to June
4	0	17	0.03	2000	450	March to June

Table IV—Wear of Engine Parts per 1000 Miles

(Figures in inches)

PART	CAR 3 FROM TABLE III[a]	CAR 4 FROM TABLE III[a]	CAR ON 40,000-MILE TEST[b]	AVERAGE FOR LARGE NUMBER OF CARS ON ROAD TEST[a]
Cylinder top:				
Normal to pin	0.0014	0.0002	0.0019	0.0023
Parallel to pin	0.0010	0.0003	0.0017	0.0021
Cylinder bottom:				
Normal to pin	0	0	0.0001	0.0010
Parallel to pin	0	0	0.0001	0.0008
Cast-iron piston below rings:				
Normal to pin	0	0.0020	0.0003	0.0007
Parallel to pin	0.0008	0.0015	0.0005	0.0007
Piston skirt bottom:				
Normal to pin	0.0007	....	0.0003	0.0010
Parallel to pin	0.0009	....	0.0005	0.0010
Connecting-rod bearing	0.0002	....	....	0.0006

[a] Sulfur under 0.10 per cent.
[b] Sulfur approximately 0.25 per cent.

The results in Table III are in accord with those in Table II, indicating that rapid wear, as shown by high percentages of iron oxide in the oil, is connected with the condensation of water rather than with the fuel dilution in the lubricating oil, although it is true that with crankcase ventilators and control of jacket-water temperatures fuel dilution is reduced at the same time that condensed water is eliminated.

Effect of High Fuel Dilutions

Laboratory tests were made to determine whether abnormally high fuel dilutions, in the absence of water, would result in rapid wear. A six-cylinder engine was chosen for this work. The oil filter was removed to make it possible to determine indications of wear by analyzing the oil for its iron oxide or ash content. In some of the tests the crankcase ventilator was allowed to operate in the normal manner, but since it was impossible to hold fuel dilution at a high figure with this device operating on the engine, it was disconnected for the remainder of the tests. The jacket water was controlled at 54.4° C. (130° F.) for the inlet temperature, and the oil temperature was held at a high value to avoid condensation of water and to make the effect of reduction of oil viscosity by high oil temperature as severe as possible.

The data are shown in Table V.

At the end of this series of tests the engine was examined. The connecting-rod bearings were free from cracks or any indications of failure, and the wear was too small to be measured on either the connecting rods or the cylinder walls. These data do not show, however, whether or not excessive wear would have taken place under dusty road conditions, where no air cleaner or oil filter was used and where the oil was allowed to become as thin as it was during these tests. Under these conditions it is possible that the thin oil would not have sufficient body to maintain a lubricating film greater in thickness than the diameter of the abrasive particles present. The higher ash content in the cars covered by

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[4] *J. Soc. Automotive Eng.*, **19**, 657 (1926).

Burkhardt[4] shows that more impurities are present under actual driving conditions for cars in private service.

These results are in accord with the conclusions of Taylor,[5] who says:

> From the results of the tests made, it appears that, with oils generally used for automobile-engine lubrication, whether light or heavy in grade, no increase in the friction nor increase of the bearing temperature for dilution of the oils up to 60 per cent occurs, provided the bearing pressure is not in excess of 286 lbs. per sq. in. Bearing pressure in automobile engines is usually not in excess of this figure. With heavy oil, this bearing pressure may be increased considerably. Many machines are in operation using oil diluted between 25 and 50 per cent, and are experiencing no apparent ill effects from this dilution. The tendency to attribute burned-out bearings and scored cylinders to dilution of the oil does not seem to be justifiable. In general, the results of these tests indicate that dilution of the oil up to 50 per cent has had no bad effect on the engine in so far as increased friction and temperature of the bearing are concerned. This dilution may be injurious from other standpoints, such as loss of power due to leakage past the piston and the like, but any disadvantage is not apparent along the lines that have been investigated in these tests.

Table V—Effect of High Fuel Dilution and Low Viscosity of Oil in Absence of Condensed Water

Oil used	GMC A-50	GMC A-030	GMC A-030 with 50% kerosene		
Specification limits, viscosity of oil used, Saybolt at 37.8° C. (100° F.)	450–575	270–330			
Load, horsepower	36[a]	36[a]	36[a]	41[a]	36[b]
Length of run, hours	10	10	10	10	10
Speed, m. p. h.	50	50	50	55	25
Water in—av. temperature:					
° C.	54.4	54.4	54.4	54.4	54.4
° F.	130	130	130	130	130
Water out—av. temperature:					
° C.	65	65	63.3	61.1	62.2
° F.	149	149	146	142	144
Av. oil temperature:					
° C.	110	101.1	96.1	98.9	66.1
° F.	230	214	205	210	151
Oil consumption, pounds	...	4.95	16.8[c]	22.0	7.9
Ventilator used	Yes	Yes	Yes	No	No
Dilution of oil as put in engine, per cent	None	None	50	50	50
Average dilution of oil during run, per cent	None	None	12	25	34
Per cent ash in oil at end of run	0.08	0.05	0.05	0.025	0.025

[a] Road torque.
[b] Full load.
[c] High oil consumption due to loss of fuel dilution from oil.

Service Results with Thermostat, Ventilator, and Oil Filter

The results obtained with the combination of jacket-water temperature control, ventilator, and oil filter were so remarkable that other makes of cars adopted the same combination. One make of car, which previously had had only oil filters, adopted the other two devices in 1926. One taxicab company operated a fleet of about two hundred of these cars. In the winter of 1925–1926, before the thermostat and ventilator were used, although the fuel averaged less than 0.10 per cent of sulfur, and probably the maximum sulfur in any lot of the fuel was 0.12 per cent, very severe corrosion troubles were experienced on practically the entire lot of these cars. The crankcase oils were badly contaminated with water and iron oxide. The cars were repaired in the spring of 1926, the corroded parts reground or replaced, and thermostats and ventilators installed. This change absolutely prevented corrosion troubles on this fleet in the next winter, 1926–1927. Under unfavorable operating conditions this make of car in private service had been subject to corrosion troubles previous to the winter of 1926–1927, but after the adoption of the ventilator and thermostat in addition to the oil filter not a single complaint on corrosion was received from the entire year's production, regardless of the fact that many of these cars were operated on fuel with a sulfur content of approximately 0.25 per cent.

Effect of Temperature

Although by the use of thermostats and crankcase ventilators water and corrosion may be eliminated under ordinary service conditions, and under steady running conditions on moderately heavy loads no water will condense, even without thermostats and crankcase ventilators, the condition of intermittent operation on light loads should be considered. These devices depend upon temperature, and in winter, at least for the first few minutes of operation, the necessary temperature is not available.

To throw some light on the limiting values possible under these conditions, tests were made in our cold room. A six-cylinder engine was used, but to stimulate conditions with a perfect circulating thermostat the radiator was disconnected and the jacket-water inlet and outlet were connected with a short rubber hose. A series of short runs was made in which the cooling liquid, consisting of a mixture of glycerol and water, was brought from the cold-room temperature of −23.3° C. (−10° F.) up to 100° C. (212° F.), when the engine was stopped, allowed to cool to the temperature of the cold room, and the run repeated. Warm air was supplied to the carburetor with an electric heater. Owing to this heat the choke was not required and was not used in starting or in running. The engine speed was 1250 r. p. m. and the power developed was 7.5 horsepower (equivalent to road torque at about 25 miles per hour.) After 70 minutes of actual running, consisting of fourteen runs of 5 minutes each, the water in the crankcase was 3.0 per cent, the fuel dilution was 36 per cent, and the highest temperature reached by the oil in the crankcase was −6.7° C. (20° F.).

Four- and Six-Cylinder Engines

Four-cylinder engines appear to be less subject to these corrosion troubles than those with six or eight cylinders, because of their greater breather action. However, there are many records of bad corrosion troubles with four-cylinder engines even when operated on fuels with less than 0.10 per cent of sulfur under conditions favorable to corrosion.

These devices for combating corrosion are too new to be incorporated in all makes of motors, and in some of the lower priced automobiles they may be considered as desirable accessories rather than as devices which should be furnished by the manufacturer on all models.

The data indicate that the problem of sulfur in motor fuel from the standpoint of the automobile industry may be summed up as follows:

1—It has been estimated that increasing the sulfur in motor fuel from 0.10 per cent to 0.30 per cent might result in a saving of fifty million dollars per year in refining costs.

2—A large portion of the automobiles in the hands of the public would suffer very badly from corrosion if operated in winter in intermittent service on fuel with over 0.10 per cent of sulfur.

3—Thermostats without crankcase ventilators will not entirely eliminate water from crankcases, and will not protect engines from corrosion if operated in winter, in intermittent service, on fuel with approximately 0.25 per cent of sulfur.

4—With both thermostats and ventilators, and preferably with oil filters in addition, cars may be operated in all seasons of the year on almost all kinds of service with fuels carrying up to 0.25 per cent of sulfur, with very little trouble from corrosion.

5—On engines operating continuously on moderately heavy duty, even without thermostats or ventilators, practically no corrosion troubles will be experienced, even with fuels carrying up to 0.25 per cent of sulfur. Conversely, it is probably possible to develop corrosion troubles even on low-sulfur fuels on engines equipped with both thermostats and ventilators, if the service is sufficiently intermittent.

6—The injurious effects of crankcase dilution are due largely to the effects of condensation of water, with the fuel dilution in most cases having only a minor effect.

7—In a few years from now, when practically all the cars in

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[5] *J. Soc. Automotive Eng.*, **18**, 41 (1926).

the hands of the public will probably be provided with devices for combating corrosion and condensation of water, the changed conditions may make it desirable to consider seriously an increase in the sulfur content of the motor fuel.

8—Under present conditions, although the automobile engineers have made great advances in combating corrosion, an increase in the sulfur content of motor fuel is not in accord with the best interests of the automobile industry or the public.

Effect of Temperature on the Hydrolysis of Skin and Hair in Saturated Limewater[1]

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The effect of temperature on the hydrolysis of skin and of hair by saturated limewater is a matter of direct, practical importance to every tanner. In unhairing as ordinarily carried out skins are placed in saturated limewater and allowed to remain there until the hair slips easily. This process is possible and effective because the keratins of the epidermal system are more rapidly hydrolyzed at a given (alkaline) pH value than is collagen; hence, before any appreciable damage is done to the skin proper, the keratinous Malpighian layer has disintegrated and the hair can be removed.

Increasing temperature has a greater effect on the hydrolysis of skin by saturated limewater than on the hydrolysis of hair. For a 3-day digestion period hair is more hydrolyzed than skin at temperatures below 35° C., and above this temperature skin is more hydrolyzed than hair. The hydrolysis of hair is a nearly linear function of time at any temperature. The hydrolysis of skin proceeds linearly until a certain amount of decomposition has taken place, after which the remaining skin goes to pieces completely in a comparatively short time. The period of rapid destruction is reached in a few hours at 45° C.; in 1 to 2 days at 40° C.; in 4 to 5 days at 35° C.; in 35 to 40 days at 30° C.; and was not reached at 60 days at lower temperatures.

This behavior lends support to the theory that the hydrolysis of collagen consists of the opening up of secondary valence bonds—rapid hydrolysis setting in when the deaggregation has gone so far that the units are soluble at the temperature employed; while that of keratin involves the breaking of a primary valence bond—probably the —S—S— linkage of cystine.

The time required for satisfactory unhairing can be shortened very much by raising the temperature of the lime liquor. This must be done very cautiously, however, for if the temperature is raised too high great and irretrievable damage will be done to the skins. In practice, few tanners dare to do more than maintain their lime liquors at summer temperatures throughout the entire year.

Practical experience seems to show that there is a rather sharply defined limiting temperature, below which it is entirely safe to operate, but which cannot be exceeded even by a few degrees without disastrous consequences. This limiting temperature varies inversely with the time during which the skins are subjected to the action of the lime. Skins subjected to temperatures of 35° or 40° C. for a few minutes or hours are not noticeably damaged, although if left in the lime liquor overnight they may be reduced practically to gelatin. On the other hand, skins left for long periods on cold limes may undergo considerable damage, as is shown by the work of Wilson and Daub.[2]

The object of the work reported in this paper was to study quantitatively the relative action of limewater on skin and on hair at different temperatures. Hair was employed, not because it is appreciably hydrolyzed during ordinary liming, but because it more nearly resembles the keratins of the Malpighian layer than does any other material at our command. While at any one temperature the keratins of the epidermis may be hydrolyzed ten times as fast as hair, the temperature coefficient of the hydrolysis is probably much the same in both cases. The hair was clipped from all-white calfskins, thoroughly washed, dried, and defatted with chloroform. The skin was from the same batch used in hydrolysis studies previously made in this laboratory.[3] After unhairing in the usual way the material was delimed with dilute acid and salt, washed, and dehydrated with alcohol and xylene. The product consists of snow-white, porous cubes, which soak back almost immediately in water, are easily reproducible, and can be stored indefinitely.

Experimental Method

Samples containing exactly 1 gram of collagen or keratin were weighed into small bottles, treated with 100 cc. of saturated calcium hydroxide solution plus an excess of solid lime, and suspended in a thermostat, with occasional shaking. Series were run at 5-degree intervals from 5° to 45° C. Samples were removed at appropriate intervals, which were naturally longer in the case of the samples digested at the lower temperatures. The undigested skin or hair was filtered off and dissolved nitrogen determined in an aliquot of the filtrate. The percentage of the total nitrogen in the sample that was dissolved was taken as a measure of the hydrolysis that had occurred at the temperature and in the time in question.

Discussion of Results

The data obtained by this method are presented in the accompanying tables and charts.

It is plain from these results that temperature has a vastly greater effect on the hydrolysis of skin than on that of hair. This is best shown by the data presented in Figure 3, where per cent of hydrolysis in 3 days is plotted as a function of temperature for hair and for skin. At 5° C. the hydrolysis is negligible for both materials. In the case of hair the quantity hydrolyzed increases almost uniformly for each 5-degree increase in temperature. The quantities dissolved in 3 days at 10°, 20°, 30°, and 40° C. stand in the

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[1] Presented before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Ind. Eng. Chem.*, **16**, 602 (1924).

[3] Merrill, *Ind. Eng. Chem.*, **16**, 1144 (1924).

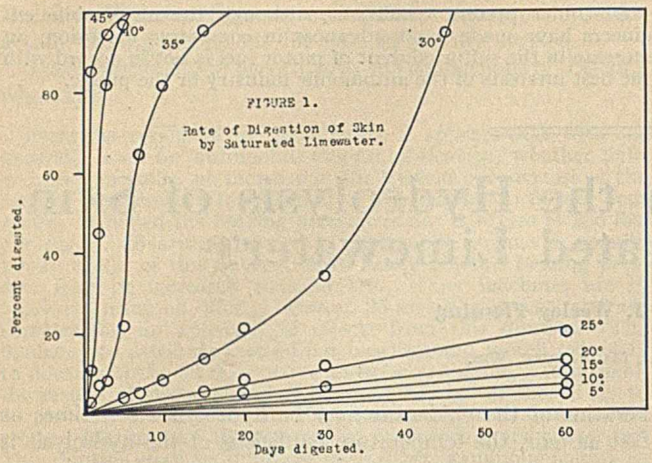
FIGURE 1.

Rate of Digestion of Skin by Saturated Limewater.

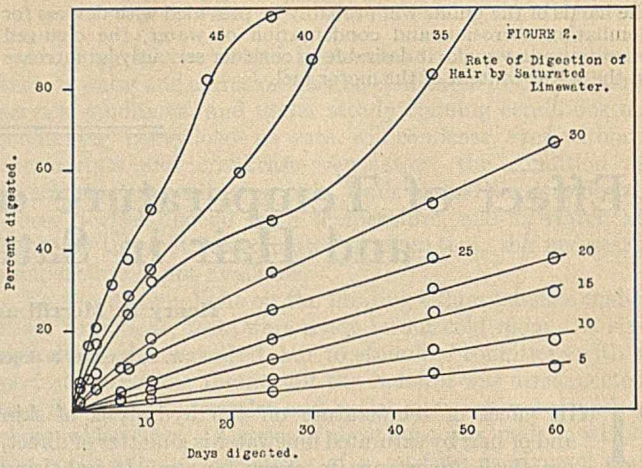
FIGURE 2.

Rate of Digestion of Hair by Saturated Limewater.

Table I—Rate of Hydrolysis of Skin by Saturated Limewater at Different Temperatures

Temperature	2 Hours	6 Hours	1 Day	2 Days	3 Days	5 Days	7 Days	10 Days	15 Days	20 Days	27 Days	30 Days	40 Days	45 Days	60 Days
° C.	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
5			0.94		1.10	1.02	1.57	1.10	1.02		1.97		2.91		4.09
10			1.42			1.10	1.26	1.42	1.34		2.83		4.33		6.53
15			0.79		0.94	1.18	1.65	1.73	2.12		4.33		5.98		9.99
20			1.42		0.47	1.89	2.05	2.05	3.23	4.80		6.14			12.83
25			1.26		1.10	2.12	2.91	3.78	5.27	8.11		11.49			19.68
30			1.26		1.57	3.94	5.01	8.18	13.54	21.01		34.00		94.76	
35			2.68	7.08	8.03	21.96	64.53	81.77	95.57						
40			10.86	44.78	82.01	96.56									
45	2.44	23.69	85.31		94.40	96.54									

Table II—Rate of Hydrolysis of Hair in Saturated Limewater at Different Temperatures

Temperature	2 Hours	8 Hours	1 Day	2 Days	3 Days	5 Days	6 Days	7 Days	10 Days	17 Days	21 Days	25 Days	30 Days	45 Days	60 Days
° C.	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
5			0.94		0.94		1.18		2.20			4.64		9.13	10.86
10					0.83		1.57		2.91			7.95		14.80	17.31
15					1.89		2.75		5.12			12.75		24.08	29.28
20					3.46		4.49		7.79			17.71		30.32	37.30
25			0.94	2.83	7.32	9.05		10.94	14.73			24.95		37.62	(38.33)
30			1.57		5.82		10.86	13.06	17.86			34.16		51.15	66.19
35			2.20		9.84	20.07		24.63	31.95			47.16		83.58	99.43
40			5.98	7.98	16.61	28.73		28.33	34.94		58.87		87.51		
45	1.26	4.93	7.07	16.05	20.78	31.48		37.77	50.08	82.16	97.75				

relation of 2:4:7:15; in other words, the rate of hydrolysis doubles for each 10-degree rise in temperature, which is about the usual temperature coefficient of most reactions. Far otherwise is the case with skin. In 3 days practically no skin at all is dissolved up to 30° C.; in the next 5 degrees the quantity hydrolyzed increases fourfold; at 40° C., 5 degrees higher still, hydrolysis is virtually complete.

Thus it will be seen that (for a 3-day digestion period) hair is more rapidly digested by lime than is skin, below 35° C., and very much less rapidly digested than skin above that temperature. The greatest divergence of the two hydrolysis curves in Figure 3, in the range for more rapid digestion of hair, occurs at about 30° C. This would appear, then, to be the optimum temperature for unhairing, as well as the maximum temperature at which skins can be limed with safety.

The form of the hydrolysis-time curves for hair, given in Figure 2, differs greatly from that of the corresponding curves for skin (Figure 1). The rate of hydrolysis of hair is, in general, greatest at the outset, falling off slowly with time as the quantity of unaltered material decreases. With skin, on the other hand, there is at all temperatures—even at 45° C.—a preliminary passive period during which little apparent change takes place. Following this passive period the hydrolysis of the skin becomes extremely rapid, and goes practically to completion in a very short time. The higher the temperature the shorter is the passive period, and the more rapid the hydrolysis once the latter begins in earnest. At 45° C. rapid hydrolysis sets in after 2 to 4 hours; at 40° C. in 1 day; at 35° C. in 3 to 5 days; at 30° C. after about 30 days; and at 25° C. and under, the stage of rapid hydrolysis is not reached in 60 days.

This difference in the behavior of skin, as contrasted with hair, harmonizes well with what is known of the mechanism of hydrolysis in the two cases. The most widely accepted theory of protein structure assumes that they are composed of comparatively simple polypeptide-like aggregates, which are linked together by secondary valence forces. Hydrolysis may occur either through the disruption of these secondary valence bonds or through the splitting of a primary bond

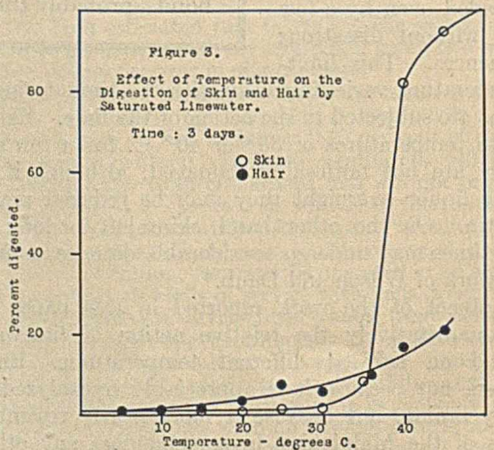
Figure 3.

Effect of Temperature on the Digestion of Skin and Hair by Saturated Limewater.

Time : 3 days.

within the polypeptide complex itself. The work of Bergmann and Stather[4] has shown rather conclusively that the alkaline hydrolysis of hair involves the disruption of the primary —S—S— bond of the cystine; the decomposition of hair by alkali thus takes place as the result of a single reaction, resulting in simple products soluble in the reaction medium at all temperatures. Such a reaction would normally yield a rate curve like those of Figure 2. Skin, however, appears to be hydrolyzed through the disintegration of the secondary valence bonds uniting the primary aggregates of which it is composed. The hydrolysis of skin, therefore, consists of the successive formation of simpler and simpler molecules, the first formed being insoluble in dilute alkali, and some of them at least (for example, gelatin) being much more soluble in the hot than in the cold. Until digestion proceeds so far that the products are freely soluble at the temperature employed, little or no collagen will pass into solution. Once this soluble stage is reached, however, the skin goes to pieces in a very short time.

Looking on the hydrolysis of skin as a stepwise process, which must proceed a considerable distance before any collagen actually passes into solution, we must not be too sure that the skin is unchanged during a brief digestion period at temperatures below 30° C. Indeed, the writers have performed one experiment which proves that skin is considerably altered by liming for 10 days at 5° C., although the amount of collagen dissolved is negligible. Duplicate samples were limed at this temperature for 10 days, the amount dissolved at the end of the period being 1.10 per cent. The samples were then limed at 35° C. for 7 days, side by side with duplicate samples which had not been pretreated. The skin previously limed at 5° C. dissolved to the extent of 73.35 per cent, while only 58.71 per cent of the controls passed into solution, thus proving that even at 5° C. lime exerts a decided hydrolytic action on skin.

[4] *Gerber*, **53**, 9 (1927).

More Effective Dust Fungicides by the Use of Oxidizing Agents with Sulfur[1]

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Against a *Helminthosporium* disease of sugar cane called "eye spot," Bordeaux dust and organic mercury dusts were found ineffective in minimizing infection. Ordinary dusting sulfur gave a slight degree of control.

In a search for more effective fungicides calcium hypochlorite in lime was found to be of no value, which result was later explained by the rapid loss of the chlorine from the hypochlorite mixture in the presence of moisture. A further search for more stable chlorine compounds as fungicides indicates that chloramine T has some promise.

Attempts to increase the fungicidal effect of the sulfur by increasing the frequency of applications showed slightly better results with applications every week than at intervals of 2 weeks, but applications twice a week did not result in further improvements. The degree of control obtained by the weekly applications was not sufficiently satisfactory to be adopted as a plantation practice.

Additions of oxidizing agents such as nitric acid, 0.25 per cent, and in particular potassium permanganate, 1 per cent, to dusting sulfur increased its fungicidal action from 200 to 300 per cent.

Increasing the concentration of potassium permanganate in the dusting sulfur to 5 per cent instead of 1 per cent still further increased its fungicidal activity. A concentration of 10 per cent potassium permanganate in sulfur gave no better results than the 5 per cent concentration.

Under the rainfall conditions in many situations of the Hawaiian Islands the use of these oxidized sulfur preparations as fungicides on cane fields is still not an economic plantation practice. However, these results are presented as a possible improvement which may be utilized by other investigators in combating diseases of other host plants.

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THE problem on which the writers have been working is the control of a disease of sugar cane called "eye spot," caused by the fungus *Helminthosporium sacchari* Butler. This disease is ordinarily a leaf infection with negligible injury, but on readily susceptible cane varieties and under suitable environmental conditions such leaf spots become very numerous, coalesce, and the heavy infection kills the youngest leaves at the growing point of the cane and a top rot results. In the Hawaiian Islands, because the most productive variety is highly susceptible, this disease is on the increase and appreciable losses have resulted.

Sugar cane in Hawaii cannot be commercially sprayed with liquid fungicides because the dense, matted cane growth makes passage through the fields impossible for men or work animals. For this reason attempts have been made to control the disease with dust fungicides which can be applied to the cane from the edges of fields by using power dusting machines mounted on auto trucks or cane cars. These methods have been fairly satisfactory and more recently applications by airplanes have also been successful. However, while the mechanics of placing dust fungicides on the cane were being developed it became apparent that the usual dust fungicides, such as various Bordeaux and sulfur dusts, were but slightly effective, if at all, in the control of the disease. In the first year's work in the winter of 1924-1925, ordinary dusting sulfur, Bordeaux dust, and ordinary hydrated lime were tried, with no appreciable visible differences in degree of infection between the dusted plots and the untreated plots as controls. Ordinary hydrated lime was tried, since in laboratory tests *in vitro* it exhibited a slow fungicidal effect upon the fungous spores;[2] it was also a cheap dust with which to experiment. Subsequently in field tests, however, it was found that in the presence of air and dew on the leaves the calcium hydrate changed to the carbonate fairly rapidly, and experiments in laboratory glassware showed no toxic effect upon the spores by calcium carbonate.

In the summer months of 1925–26 several previously untried fungicidal dusts were used. Calcium hypochlorite

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[1] Received August 31, 1927.

[2] Lee and Martin, *Phytopathology*, **17**, 315 (1927).

at concentrations of 1, 2, 5, 10, and 20 per cent in hydrated lime was tried out in laboratory glassware and under such conditions exhibited effective toxicity to the fungous spores. Proprietary preparations of organic mercury were also effectively toxic in such laboratory experiments *in vitro*. Therefore, in the winter months of 1925–26 such preparations were tried out in field plots with adequate replications and controls.

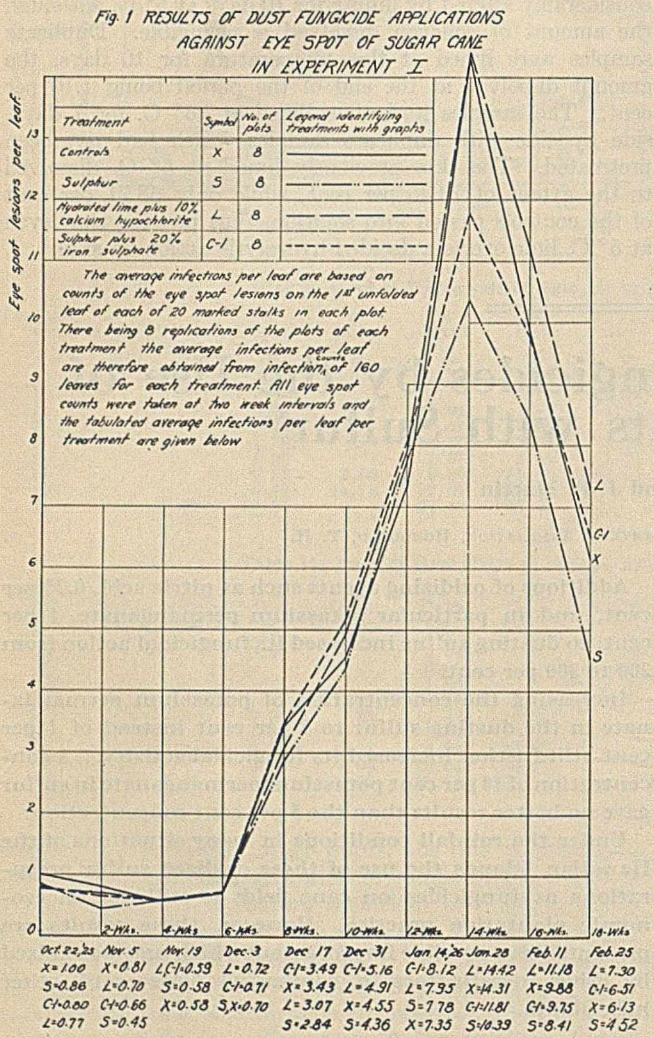

Fig. 1 RESULTS OF DUST FUNGICIDE APPLICATIONS AGAINST EYE SPOT OF SUGAR CANE IN EXPERIMENT I

Treatment	Symbol	No. of plots	Legend identifying treatments with graphs
Controls	X	8	————————
Sulphur	S	8	—··—··—··—
Hydrated lime plus 10% calcium hypochlorite	L	8	— — — —
Sulphur plus 20% iron sulphate	C-1	8	- - - - - - - -

The average infections per leaf are based on counts of the eye spot lesions on the 1st unfolded leaf of each of 20 marked stalks in each plot. There being 8 replications of the plots of each treatment the average infections per leaf are therefore obtained from infection counts of 160 leaves for each treatment. All eye spot counts were taken at two week intervals and the tabulated average infections per leaf per treatment are given below

Method of Measuring Infection in Plots of Different Treatments

Fortunately, the nature of the disease being studied and the character of the host plant have been well suited to measuring quantitatively the degree of infection in the plots under the different treatments with fungicides. Dust-fungicide applications were usually made on plots of 10 rows of cane, each row about 30 feet long; each plot was therefore about $^1/_{28}$ acre in size. All tests had at least 6 replications of each treatment.

In each plot, using an empirical system, 20 stalks of cane were selected and each stalk was marked with a piece of cheap red cloth for future identification. At 2-week intervals the infections were counted on the youngest leaves of each stalk; usually the two youngest unfolded leaves were designated for these infection counts. Thus counts of infections were made from 40 leaves of each plot and if there were eight replications of each plot there would be 320 leaf counts per treatment. The numbers of infections per leaf were then averaged and charted on coördinate paper. By connecting the points representing infections per leaf for each date when counts were made, a graph results indicating clearly the degree of the development of the disease under each treatment. Such graphs are shown in Figures 1, 2, 3, 4, and 5.

Experiment I

The purpose of this test was to learn the effect upon eye spot of dust applications of ordinary sulfur, calcium hypochlorite in a lime carrier, and iron sulfate in a sulfur carrier. The dusts were applied at 2-week intervals, starting October 24, 1925, and ending February 25, 1926, there being nine applications in all for each treatment. The dusts were applied with small hand dusting machines, at the rate of approximately 50 to 60 pounds per acre per application. In these tests and in all other experiments recorded here, the dusts were applied in the early morning when the cane foliage was covered with moisture from dews.

The graphs in Figure 1 show that eye spot started to increase on December 3 and reached the peak of infection on January 28. During the upward curve of eye-spot infection the leaf counts showed the sulfur-treated plots with less disease fairly consistently. At the peak of infection, which is the critical time to reduce loss from top rot, the amount of eye spot in the sulfur-treated plots was 27 per cent less than in the untreated control plots.

There was no significant decrease in eye spot in the plots treated with 10 per cent calcium hypochlorite in lime as a carrier, at any time during the season. As lack of success with the calcium hypochlorite mixture in the field became apparent, laboratory tests were made to determine the persistence of the chlorine of the preparation on the leaf. It was found that in 24 hours in the presence of dew the concentration of chlorine would be reduced to but 2 to 3 per cent of the original concentration. These results made evident the cause for the lack of control in the field by the calcium hypochlorite.[3]

The applications of 20 per cent iron sulfate in sulfur, which were being tried incidentally as a growth stimulant, reduced the eye-spot infections per leaf 17 per cent, as compared with untreated controls; these results presumably may be ascribed to the fungicidal effect of the sulfur used as a carrier. Several dusting preparations containing organic mercury compounds were also tried; the graphs of eye-spot occurrence in plots treated with such preparations are not included in Figure 1. There was no decrease in the disease in the plots treated with such organic mercury preparations.

Although the reduction of the disease resulting from sulfur applications was not sufficient to recommend the practice for plantation usage, it was sufficient to justify continuing the search for more effective fungicides.

Experiment II

The comparative effect upon eye spot of sulfur applications at 2-week intervals, at 1-week intervals, applications twice a week, "300-mesh" sulfur, and sulfur plus creolin was next studied. Since in the previous season the only success in reducing infection was with sulfur, the efforts in the succeeding season were directed towards getting more effective returns from sulfur. Applications of sulfur at different time intervals were tried. Also an attempt was made to obtain a more finely divided sulfur which would pass a 300-mesh screen; the ordinary sulfur previously mentioned had been 200 mesh. It was also found that quantities of liquids up to 1 per cent of the carrier could be added without seriously

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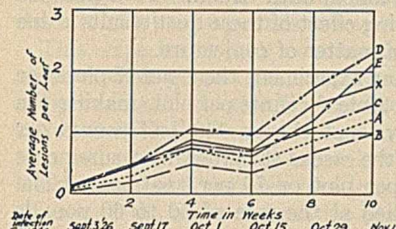
[3] This phase of the problem was very ably carried on by H. W. Kerr and Clyde C. Barnum, then of this laboratory.

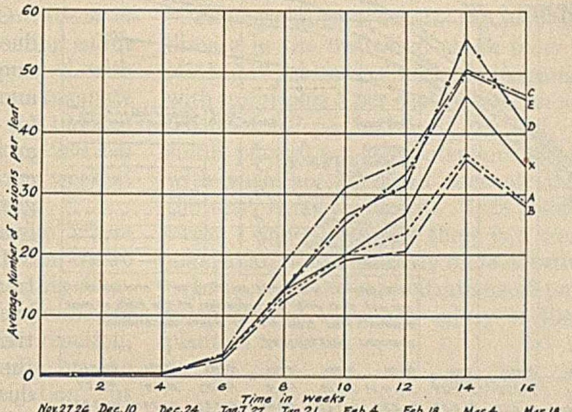
Treatment	Symbol	No. of Plots	Legend identifying treatments with Curves
Sulphur applied at 2 week intervals	A	8	··························
Sulphur applied at 1 week intervals	B	8	— — — — — — — — —
Sulphur applied twice a week	C	8	—·—·—·—·—·—
"300 mesh Sulphur"	D	8	—•—•—•—•—•—
Sulphur Plus 1% Creolin	E	8	—×—×—×—×—×—
Controls	x	8	———————————

The average infections per leaf are based on counts of the eye-spot lesions on the 3rd. youngest leaf on each of 20 marked stalks in each plot. There being 8 replications of the plots of each treatment in the first part of the experiment average infections per leaf were obtained from infection counts from 160 leaves per treatment. In the second part of the experiment there were 7 replications of the plots of each treatment, making 140 leaves upon which infections were counted and averaged giving the results shown in the graph.



Date of infection counts	Sept. 3 '26	Sept. 17	Oct. 1	Oct. 15	Oct. 29	Nov. 12
Tabulated Average infection Per Leaf	D·0.13 C·0.13 E·0.11 X·0.11 A·0.09 B·0.04	C·0.48 E·0.48 D·0.46 X·0.42 A·0.30 B·0.19	D·1.08 X·0.88 C·0.81 A·0.65 E·0.62 B·0.49	D·0.98 X·0.72 C·0.70 E·0.61 A·0.50 B·0.34	D·1.72 X·1.46 E·1.20 C·1.07 A·0.85 B·0.69	D·2.31 E·2.16 X·1.78 C·1.46 A·1.23 B·0.99

Fig. 2: Results of dust fungicide applications against eye-spot of sugar cane in experiment II



Nov. 27 '26	Dec. 10	Dec. 24	Jan. 7 '27	Jan. 21	Feb. 4	Feb. 18	Mar. 4	Mar. 18
C·0.24 E·0.14 X·0.14 A·0.11 D·0.11 B·0.07	C·0.21 A·0.20 E·0.19 X·0.18 D·0.14 B·0.10	A·0.79 E·0.54 D·0.47 X·0.42 C·0.34 B·0.24	C·3.71 E·3.48 D·3.44 A·3.41 X·3.01 B·2.88	C·18.46 D·14.79 X·14.73 E·14.06 A·13.31 B·12.50	C·31.00 D·26.56 E·25.19 A·20.05 X·19.93 B·19.16	C·35.82 E·33.47 D·31.39 X·26.95 A·23.81 B·20.69	D·55.53 C·50.66 E·50.00 X·46.44 A·36.71 B·35.76	C·46.24 E·45.66 D·41.24 X·34.72 A·28.73 B·28.03

impairing the dusting qualities of the mixture. One per cent creolin was therefore added to a sulfur carrier and tried.

These dusts were applied at the rate of 50 to 60 pounds per acre per application. The experiment was started on September 3, but owing to heavy winds which blew down the cane, was discontinued on November 12. It was then started anew in another field and continued through the season of eye-spot infection. In the first location of the test there were 8 replications of the plots of each treatment, with 20 leaf counts per plot or 160 per treatment. In the second location of the test there were 7 replications of the plots of each treatment, with 20 leaf counts per plot or 140 per treatment.

The results (Figure 2) in both locations of this experiment were fairly consistent. At the peak of infection ordinary sulfur applied at intervals of 2 weeks decreased infection 21 per cent as compared with untreated check plots. Sulfur applied at intervals of 1 week decreased infection 23 per cent. In both parts of the experiment sulfur applied twice a week did not reduce infection so well as in the case of longer intervals. Although it might be argued that this is chance, with adequate replications of plots per treatment and duplicated results, the writers are inclined to regard the results as significant, but as to the reason for the lessened effectiveness any statements would be merely conjecture.

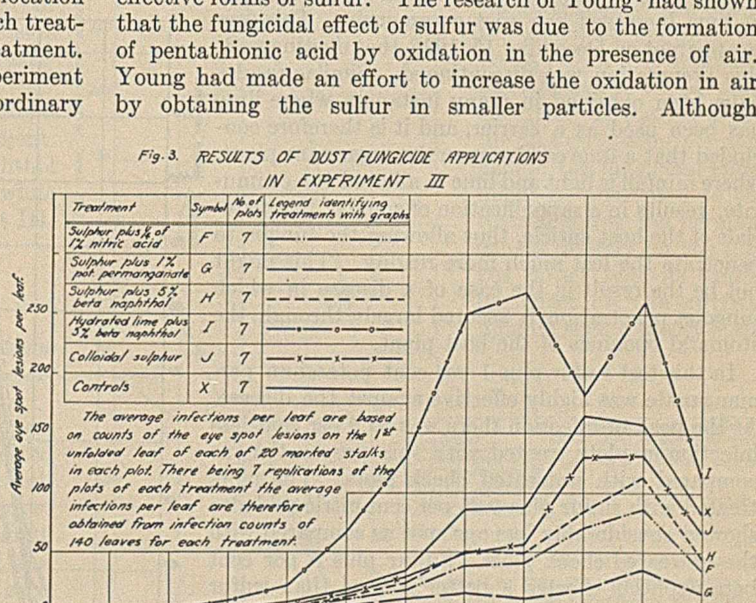
The results with the "300-mesh" sulfur are interesting. In an experiment not reported here arrangements had been made with a mainland firm to supply a grade of sulfur which would pass a 300-mesh screen. While waiting for this material to arrive, the experiment was inaugurated using 200-mesh sulfur on the plots subsequently to be treated with the 300-mesh sulfur when it arrived. With the ordinary 200-mesh sulfur the usual reduction in the amount of infection was secured—that is, from 20 to 27 per cent. On the arrival of the "300-mesh" sulfur it was substituted and applied to the plots treated hitherto with 200-mesh sulfur. The eye-spot curve for the plots so treated immediately showed an upward trend, reached and then passed the curve of eye-spot infection for the untreated check plots. On asking the manufacturers if there was any lime in this "300-mesh" sulfur, they replied that 5 per cent had been added to keep the finely divided sulfur from caking. In the light of the experience of others and their own subsequent knowledge, the writers suspect that 5 per cent lime is sufficient to neutralize the weak polythionic acids formed by the oxidation of sulfur and upon which the fungicidal action is apparently dependent.

The results with the sulfur plus 1 per cent creolin are also significant and show this mixture to be without value, at least in the present problem. The reason for the ineffectiveness of this mixture is also entirely a matter of conjecture at present.

Experiment III

The effect of dust applications of beta-naphthol in lime, compared with beta-naphthol in sulfur, colloidal sulfur, sulfur plus nitric acid, and sulfur plus potassium permanganate was then investigated. In the previous experiment the frequency of the applications of sulfur was the chief variable. In the present experiment efforts were directed towards getting more effective forms of sulfur. The research of Young[4] had shown that the fungicidal effect of sulfur was due to the formation of pentathionic acid by oxidation in the presence of air. Young had made an effort to increase the oxidation in air by obtaining the sulfur in smaller particles. Although Young's results were questioned in England,[5] it was felt in this laboratory that his work should be followed up. It was believed that the natural oxidation of the sulfur in the air might be increased by the addition of oxidizing agents to

Fig. 3. RESULTS OF DUST FUNGICIDE APPLICATIONS IN EXPERIMENT III



Treatment	Symbol	No of plots	Legend identifying treatments with graphs
Sulphur plus ¼ of 1% nitric acid	F	7	—··—··—··—
Sulphur plus 1% pot. permanganate	G	7	—— —— —— ——
Sulphur plus 5% beta naphthol	H	7	- - - - - - - - - - -
Hydrated lime plus 5% beta naphthol	I	7	—o—o—o—
Colloidal sulphur	J	7	—x—x—x—
Controls	X	7	———————

The average infections per leaf are based on counts of the eye spot lesions on the 1st unfolded leaf of each of 20 marked stalks in each plot. There being 7 replications of the plots of each treatment the average infections per leaf are therefore obtained from infection counts of 140 leaves for each treatment.

		2 Wks.	4 Wks.	6 Wks.	8 Wks.	10 Wks.	12 Wks.	14 Wks.	16 Wks.	18 Wks.	20 Wks.	22 Wks.
Dates of infection counts	Oct 20, '26	Nov 3	Nov 17	Dec 1	Dec. 15	Dec 29	Jan 12, '27	Jan 26	Feb 9	Feb 23	Mar 9	Mar 23
Tabulated average infections per leaf.	F·0.29 H·0.27 J·0.27 I·0.23 X·0.23 G·0.19	X·1.24 J·0.69 F·0.56 H·0.54 I·0.50 G·0.42	I·2.17 X·2.22 J·.46 F·1.34 H·1.20 G·0.84	I·8.39 X·2.84 J·2.76 F·2.05 H·2.04 G·1.56	I·23.11* X·7.20 F·5.22 H·5.15 J·5.08 G·3.40	I·67.34 X·17.24 J·15.31 H·13.71 F·10.44 G·4.86	I·129.21 X·34.19 J·29.92 H·26.01 F·19.70 G·11.34	I·249.29 X·86.79 H·51.20 J·49.11 F·39.22 G·17.46	I·267.04 X·86.47 J·56.09 H·50.40 F·43.13 G·12.39	I·181.45 X·165.21 J·129.18 H·83.29 F·70.59 G·17.91	I·263.94 X·157.86 J·131.83 H·112.41 F·86.85 G·36.56	I·110.92 X·83.41 J·67.27 H·47.15 F·37.27 G·15.81

*Necessary to discontinue further applications of this dust because it was so obviously increasing eye spot.

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[4] *Ann. Missouri Botan. Gardens*, **9**, 403 (1922).

[5] *Ann. Appl. Biol.*, **13**, 308 (1926).

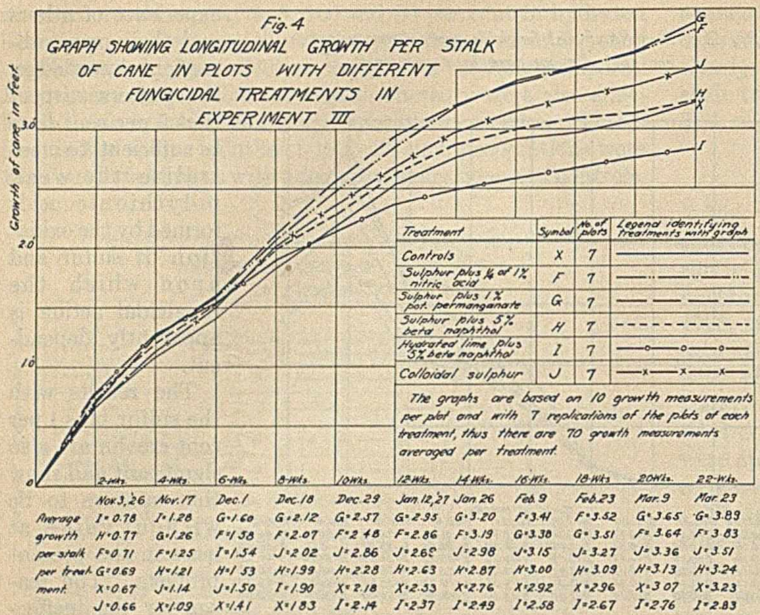
Fig. 4
GRAPH SHOWING LONGITUDINAL GROWTH PER STALK OF CANE IN PLOTS WITH DIFFERENT FUNGICIDAL TREATMENTS IN EXPERIMENT III

the sulfur. Sulfur dusts were therefore prepared, one containing 0.25 per cent nitric acid and another 1 per cent potassium permanganate. Other new dusts tried out were beta-naphthol, 5 per cent in a lime carrier and also in a sulfur carrier, to see if the acid or alkaline reaction of the carrier had any influence on the toxicity of the active fungicidal agent. A more finely divided sulfur preparation sold as a colloidal sulfur was also tried. These dust fungicides were applied in thirteen applications over a period of 22 weeks.

The results (Figure 3) show that beta-naphthol in lime increased eye spot enormously. This was so apparent on December 15, 1926, that dusting with this preparation was discontinued. Similar results have been obtained in many instances where lime has been used as a carrier, and it is therefore concluded that a lime carrier upon the sugar-cane plant, where rainfall is light and lime is allowed to accumulate, results in a saponification of some of the materials of the host cuticle, thus allowing the fungus to penetrate the leaf much more readily. This might not be the result in the case of a disease in which fungous penetration is secured largely through the stomatal openings of the host plant.

In this test sulfur plus 1 per cent potassium permanganate was highly effective against the disease. At the peak of infection there was 89.9 per cent less infection in plots treated with this preparation as compared with untreated check plots. The plots treated with sulfur plus 0.25 per cent nitric acid also showed considerably less eye spot as compared with the untreated check plots. Sulfur plus 5 per cent beta-naphthol effected a better control than sulfur without such a toxic agent; this result as compared with the result with beta-naphthol in lime corroborates the conception that the reaction of the carrier has a decided effect upon the value of the toxic agent. The colloidal sulfur reduced the disease but not so effectively as the oxidized sulfurs.

Graphs showing results of growth measurements of the cane in the plots under various treatments are shown in Figure 4. All forms of sulfur increased the growth of cane and the oxidized sulfurs increased the growth 8 inches per stalk in 22 weeks. By empirical methods the increased growth may be calculated to sugar yields per acre and would roughly approximate 0.5 ton of sugar per acre, which at usual sugar prices would be a very profitable return on the investment in the dust and cost of application.

One's first thought is that the increased growth is due to disease control. Although disease control is unquestionably a factor, one must conclude there is another factor operating to give the increased growth, for the growth curves in the treated plots showed an upward trend almost a month before the eye-spot curves showed an upward trend. To what the growth-stimulating effect of these dust results is due is also entirely a matter of conjecture.

In the foregoing experiment there were 7 plots per treatment, with 20 leaf counts per plot, making the basis for the eye-spot curves 140 leaf counts per treatment. In the case of the growth measurements there were 10 per plot or 70 per treatment. The dusts were applied at the rate of 50 to 60 pounds per acre per application.

Experiment IV

The effect of dust applications of chloramine T in sulfur as compared with chloramine T in lime, beta-naphthol in lime, beta-naphthol in sulfur, sulfur plus potassium permanganate, and ordinary sulfur was the purpose of the next experiment. Following up the very evident toxic properties of chlorine preparations *in vitro* against the eye-spot fungus, but lack of success in field tests with the unstable hypochlorite mixtures, attention was turned to more stable chlorine compounds. Chloramine T in concentrations of 5 per cent in a hydrated lime carrier and in a sulfur carrier were tried, the

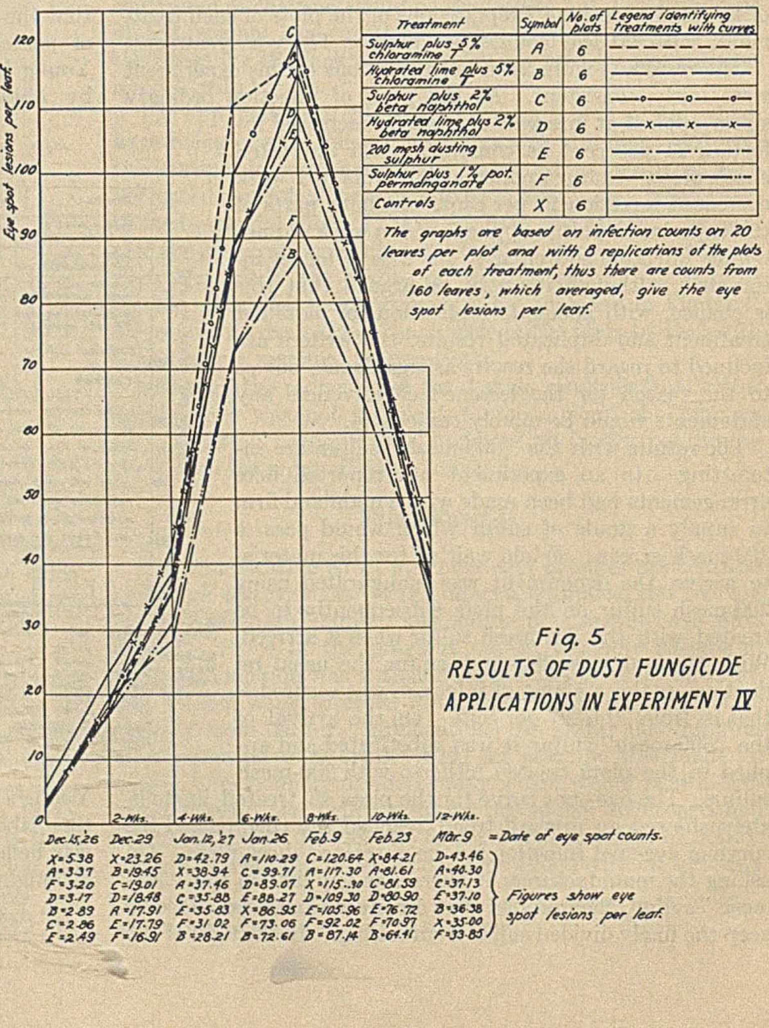
Fig. 5
RESULTS OF DUST FUNGICIDE APPLICATIONS IN EXPERIMENT IV

types of carrier being tested with the idea that the alkaline or acid reaction of the carrier might have some influence on the effectiveness of the chloramine.

In this experiment also beta-naphthol in sulfur was tested against beta-naphthol in a lime carrier, at concentrations of 2 per cent in both cases. Ordinary 200-mesh dusting sulfur was also tried out in this experiment as contrasted with identical sulfur to which 1 per cent potassium permanganate had been added. There were 7 replications of the plots of each treatment with 40 leaf counts per plot, making 280 leaf counts per treatment. The dust was applied every week at the rate of 30 to 40 pounds per acre per application.

This experiment was conducted on a plantation where much more frequent rains occur than at the plantation where Experiments I, II, and III were conducted. At this plantation the soils had an acid reaction whereas the experiments recorded previously were on soils with an alkaline reaction. Whether or not the soil reaction has any bearing on the efficacy of the dusts is a matter of further investigation, but it is at least worthy of record.[6]

The results are shown in the chart in Figure 5.

The lessened efficacy of the dusts on this plantation is apparent if the results recorded in Figure 5 are compared with those recorded in Figure 3. At the peak of infection ordinary sulfur alone gave only an 8 per cent reduction as compared with untreated check plots, while sulfur plus 1 per cent potassium permanganate gave a reduction of 20 per cent. The unexpected result in this test is the reduction of the amount of infection in the plots treated with 5 per cent chloramine T in lime, which amounted to a 24 per cent control of the disease as contrasted with the check plots. This favorable result was obtained under conditions extremely unfavorable for the effectiveness of dust fungicides, and merits further trials with this material. Chloramine T in a sulfur carrier gave no control of the disease which leads to the conclusion that possibly an alkaline carrier is essential for this material.

Neither beta-naphthol in lime nor beta-naphthol in sulfur gave any reduction of the disease in this experiment. Possibly the fact that the concentration of beta-naphthol was but 2 per cent in the sulfur carrier in this test, while it was at a concentration of 5 per cent in Experiment III, may account for this result.

Experiment V

Finally, the effect upon eye spot of dust applications of sulfur with increased concentrations of potassium permanganate was investigated.

The success of sulfur plus 1 per cent potassium permanganate in reducing infection immediately suggested that increased concentrations of the permanganate in sulfur would possibly increase the degree of control. Consequently mixtures of 200-mesh sulfur containing 5 and 10 per cent of potassium permanganate were prepared and tried out in an experiment with six replications of each treatment and six check plots. Twenty leaf counts per plot were made, making 120 leaf counts per treatment. Since the idea of increased concentrations of potassium permanganate arose from the success of the 1 per cent permanganate in sulfur, this experiment was not inaugurated until the middle of the eye-spot season, when infection was nearly at the peak. In all plots at the inception of this experiment eye-spot lesions averaged more than 75 per leaf. The problem in this case therefore was prevention of the disease under conditions of severe sources of infection. The experiment was undertaken on the same plantation as Experiments I, II, and III, where eye-spot occurrence is due more to long periods of dew on the leaves than rainfall.

The results recorded in Figure 6 show that, whereas the disease in the untreated check plots increased from 91 per leaf to 116 per leaf in 6 weeks, in the same period in plots treated with sulfur plus 5 per cent potassium permanganate, infection fell from 101 per leaf to 51 per leaf. The results with the sulfur plus 10 per cent potassium permanganate indicate that with such an increased concentration the effectiveness of the dust is not increased. It is possible that somewhere between 1 and 10 per cent there is a concentration of the permanganate that is slightly more effective than the 5 per cent.

In none of the concentrations of potassium permanganate in sulfur was there any injury to the sugar-cane foliage or plant as a whole.

Discussion

The ability to obtain quantitative determinations of the degree of infection in the case of the disease and host plant under consideration has given an excellent opportunity for a comparison of dust fungicides. In a number of the experiments one making a visual comparison only between plots of different treatments would find it difficult to make a positive statement of the superiority of one treatment over another. The writers have found that often differences of 25 per cent in the degree of infection cannot be determined by the eye, but show up consistently and significantly when an adequate number of infection counts per leaf are made.

Of the new dusts mentioned in the foregoing experiments, those in which the fungicidal action of sulfur has been increased by the addition of oxidizing agents seem to be most effective. In the case of sulfur plus potassium permanganate the fungicidal effect might be attributed to the toxic action of the permanganate directly on the fungus rather than its oxidizing effect on the sulfur. Against such a theory is the

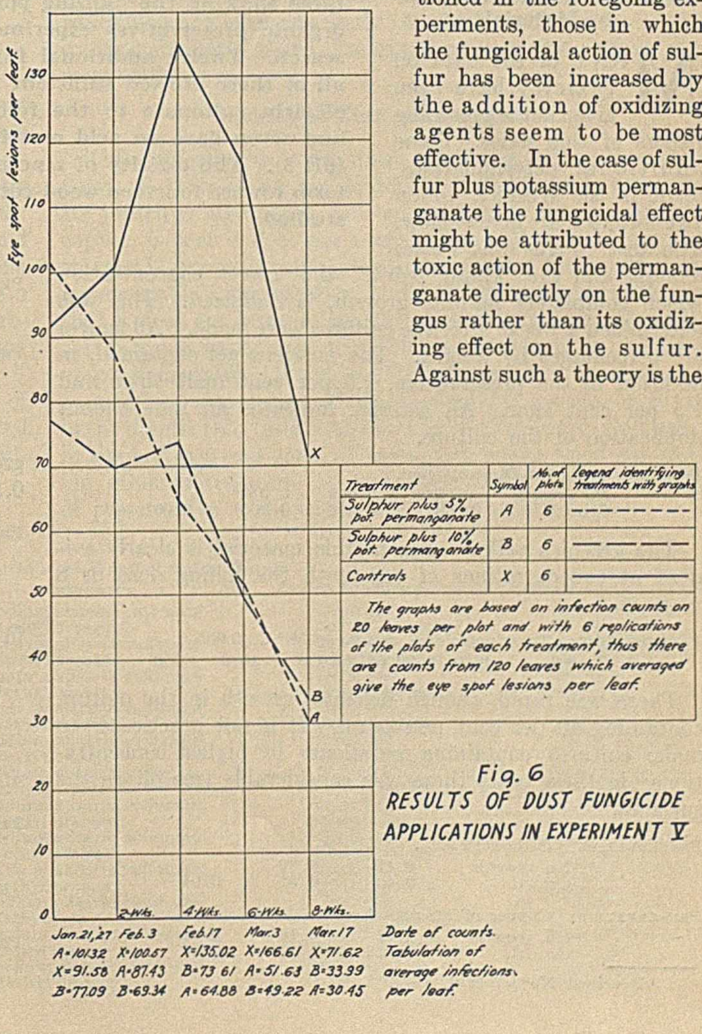

Fig. 6
RESULTS OF DUST FUNGICIDE APPLICATIONS IN EXPERIMENT V

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[6] In this experiment the applications and leaf counts were made by Royden Bryan, assistant in this laboratory, to whom we wish to express credit and appreciation.

fact that nitric acid in sulfur is also effective. Moreover, in more recent experiments other oxidizing agents in sulfur, which have been effective and which in themselves have no fungicidal or germicidal value, have been found. Most conclusive, however, is an experiment in which potassium permanganate in Celite, a non-sulfur carrier with a neutral reaction, has had a very slight effect in reducing the disease. This and experiments with additional oxidizing agents in sulfur will be reported more completely in a subsequent paper.

Sulfur containing oxidizing agents is, of course, to be carefully protected from a source of ignition. At the time of writing more than 30 tons of sulfur plus 1 per cent potassium permanganate have been applied with no difficulties. A few precautions have been taken, as follows: The outlet tube of the motor-driven dusting machines, in which considerable static electricity is sometimes generated by the friction of the passing dust particles, is grounded with a steel chain which is allowed to drag during the operation of the duster. This is a safeguard which should be employed in using all sulfur dusts, whether oxidized or not. The dusts should be kept dry and always stored away from sources of moisture.

The use of a stable chlorine compound, such as chloramine T, holds some promise of being effective under conditions in which the oxidized sulfur mixture would not be advantageous.

Owing to the rainfall conditions in many of the cane-growing localities in the Hawaiian Islands, the use of these fungicide preparations is still not an economic plantation practice. However, with still further improvements the method may become feasible. In the meantime these results indicate that these preparations may be of value for use against other diseases on other host plants, and the writers hope that other investigators will carry further these initial attempts to develop new and more effective fungicidal dusts.

The writers have applied for a patent on the use of oxidizing agents with sulfur as a disinfectant and fungicide; however, any royalties will be employed for the furtherance of research.

Experiments in Wood Preservation[1]

VI—Recent Laboratory Work

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Toxicity data not previously reported are given, also a table showing the "killing points" of the various inorganic preservatives experimented with in this research. Twelve additional fungi have been studied; all of these evolved sufficient acid to convert sodium alizarin sulfonate to the free sulfonic acid (pH 5), and seven gave an acid reaction with methyl orange (pH 3). The toxicity of zinc meta-arsenite in powder form toward fourteen wood-rotting fungi has also been studied.

Toxicity toward *Fomes Annosus* of Various Preservative Materials

Many of the data on toxicity have been given in the preceding papers of this series. Some additional determinations, made in the Western Union Laboratories, are given below. The test fungus was *Fomes annosus* and the "killing point," the lowest concentration which completely inhibits growth, is italicized. This was determined 4 weeks after the cultures were made. All figures are percentages by weight. The nutrient gel contained, in addition to the preservative, 2.5 per cent malt sirup and 1.5 per cent agar. An asterisk indicates an independent duplication of the culture.

PRESERVATIVE: 2,4-Dinitrophenol.

No growth	_0.008_*	0.009	0.010*	
Growth	0.007	0.006	0.005	0.001

The greenish yellow color of this material is clearly evident at concentrations of one-tenth the killing dose or 8 p. p. m.

PRESERVATIVE: Texas petroleum, density at 38° C., 0.905.

Growth	40.0	30.0	20.0	10.0	5.0

There was rapid, though delicate, growth in the culture containing 40 per cent petroleum. It is not practicable to make cultures containing petroleum in higher concentrations; in these cases there was considerable free oil on the surfaces.

PRESERVATIVE: Orthoboric acid.

No growth	_0.15_	0.30	
Growth	0.10	0.08	0.04

PRESERVATIVE: Copper sulfate pentahydrate.

No growth	_0.15_	0.16	0.40
Growth	0.125	0.10*	0.05

Feeble, discolored growth at the 0.125 concentrations, which did not start until the fourth week. Good growth at 0.05.

PRESERVATIVE: Copper fluoride. Precipitated in gel containing copper sulfate by addition of equivalent sodium fluoride.

No growth	_0.08_	0.10*
Growth	0.06	0.02

Very slight growth at 0.06.

PRESERVATIVE: Copper fluoride, powder.

No growth	_0.097_	0.311
Growth	0.05	

PRESERVATIVE: Copper ortho-arsenite, Scheele's green, precipitated in gel.

No growth	_0.04_**	0.05	0.10
Growth	0.03	0.02	0.01

Negligible growth at 0.03, very feeble and discolored growth at 0.02. In powder form, complete inhibition at 0.10 per cent.

PRESERVATIVE: Copper aceto-arsenite, Paris green, powder.

No growth	_0.04_	0.10
Growth	0.03	0.01

The 0.03 culture showed growth of 2 mm. radial increase in 4 weeks.

PRESERVATIVE: Mercuric chloride.

No growth	_0.015_**	0.020*	0.030
Growth	0.010*	0.0075	0.0050

Delicate but healthy growth at 0.010. Vigorous growth at 0.0050.

PRESERVATIVE: Sodium monohydrogen arsenite.

No growth	_0.025_**	0.10	
Growth	0.020**	0.015*	0.010*

Growth sickly and discolored at 0.010.

PRESERVATIVE: Arsenious oxide.

No growth	_0.0150_***	0.0200*	(0.010***)	
Growth	0.0100*	0.0080*	0.0060	0.0050*

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[1] Received November 4, 1927.

Four cultures at 0.010 failed to grow. Growth at 0.005 feeble and brown in color. Corresponding culture with mercuric chloride permitted a white, healthy growth.

In making cultures with arsenious oxide, misleading results are usually obtained by adding the preservative in powder form. Because of the non-wetting properties of the crystals, solution takes place in a very incomplete manner. A solution of arsenious oxide should be prepared by boiling, the undissolved residue filtered out, and a sample of the filtrate analyzed for arsenic content. The solution, properly diluted, may be added to double-strength nutrient.

Table I gives a list of inorganic substances experimented with and their killing points toward *Fomes annosus*. Information in regard to organic preservatives is given in this and the fourth paper[2] of the series.

Table I—Concentration of Preservative Which Totally Inhibits *Fomes annosus*

PRESERVATIVE	FORMULA	"KILLING POINT" *Per Cent of Preservative*
Barium chloride	$BaCl_2$	11.0
Barium carbonate	$BaCO_3$	0.625
Strontium chloride	$SrCl_2$	10.0
Strontium carbonate	$SrCO_3$	3.0
Calcium chloride	$CaCl_2$	8.0
Calcium carbonate	$CaCO_3$	1.50
Zinc chloride	$ZnCl_2$	0.35
Zinc oxychloride	$Zn(OH)Cl$	0.30
Zinc hydroxide	$Zn(OH)_2$	0.30
Zinc meta-arsenite (powder)	$Zn(AsO_2)_2$	0.10
Boric acid	H_3BO_3	0.150
Copper sulfate	$CuSO_4.5H_2O$	0.150
Copper fluoride	CuF_2	0.080
Copper ortho-arsenite	$Cu_3(AsO_3)_2.2H_2O$	0.040
Copper ortho-arsenite (powder)	$Cu_3(AsO_3)_2.2H_2O$	0.10
Copper aceto-arsenite (powder)	$Cu_4(CH_3COO)_2(AsO_2)_6$	0.040
Mercuric chloride	$HgCl_2$	0.015
Sodium carbonate	Na_2CO_3	0.33
Sodium monohydrogen arsenite	Na_2HAsO_3	0.025
Arsenious oxide	As_2O_3	0.015

Further Experiments with Wood-Rotting Fungi

The first paper[3] of this series describes tests with certain wood-rotting fungi which showed that the growth of such organisms is attended by immediate production of acid. These fungi were *Fomes annosus*, *Lentinus lepideus*, *Lenzites sepiaria*, *Polyphorus pilotae*, and *Polyphorus sulphureus*. All cultures reacted acidic to sodium alizarin sulfonate and neutral to methyl orange, indicating that the concentration of the hydrogen ion evolved was pH 5 to pH 4.8. Certain mold fungi—for example, *Rhizopus nigricans*—evolved substances acidic to methyl orange, indicating a concentration of pH 3.

For the purpose of further investigating the reactions of fungi, tests were made with twelve additional species, all of economic importance in the destruction of wood. Cultures were made in quadruplicate by the standard agar-malt sirup formula, one-half being dyed dark red with sodium alizarin sulfonate while the remainder was colored orange-yellow with methyl orange. The dishes of nutrient gel were then inoculated under aseptic conditions with pure cultures of the various fungi listed in Table II. These cultures were obtained from the Forest Products Laboratory, Madison, Wis., through the courtesy of Dr. Audrey Richards.

All the fungi evolved sufficient acid to give a reaction with sodium alizarin sulfonate, indicating acid concentration of approximately pH 5. *Stereum subpileatum* and *Poria subacida* showed faintly acid to methyl orange, corresponding to pH 4. *Poria incrassata*, *Polyphorus betulinus*, *Coniophora cerebella*, *Merulius lachrymans*, and *Daedalia quercina* gave a strong acid reaction with methyl orange, indicating a hydrogen-ion concentration of approximately pH 3.

Merulius lachrymans appeared to produce the most acid; the methyl orange cultures were turned red to a distance of 10 mm. beyond the visible growth of the fungus. This fungus is responsible for large economic losses in the destruction of timber by "dry rot." *Poria incrassata* and *Coniophora cerebella* are also important dry-rot fungi.

Coniophora cerebella, in the methyl orange cultures, first turned the indicator red and then destroyed it. When the fungus had increased to a diameter of 5 cm., it appeared by transmitted light as a white disk 4 cm. in diameter surrounded by a red rim about 1 cm. across, this in turn bordered by a wider orange-yellow band. The white disk represented nutrient in which the methyl orange had been acidified and destroyed, the red portion where it had been acidified but not yet destroyed, and the orange-yellow zone nutrient which had not been attacked. As the boundary lines of the colors were fairly sharp, the appearance of the culture was most striking.

Toxicity of Zinc Meta-Arsenite

This preservative is the most promising, from a practical point of view, of all the materials tested in this research. Its principal advantage, as compared with the arsenites of copper, is that it does not corrode iron and may be used in standard pressure-treating equipment. As compared with water-soluble preservatives, exhaustive tests have shown that it does not increase the electrical conductivity of wood, this being of importance to railroads and telephone and telegraph companies. Wood containing arsenites of zinc and copper has also remained unattacked by insects or fungi in the drastic field tests conducted by the Telegraph Company in the last two and one-half years and, unlike wood containing other water-borne preservatives, has shown little loss of preservative when exposed to the weather.

Table II—Acidic Reactions of Wood-Rotting Fungi

FUNGUS	SOURCE	INDICATOR	ORIGINAL (BASIC) COLOR	FINAL (ACIDIC) COLOR
Polyphorus anceps	White spruce	Sodium alizarin sulfonate	Dark red	Greenish yellow
Polyphorus anceps	White spruce	Methyl orange	Orange-yellow	No change
Polyphorus schweinitzii	Douglas fir	Sodium alizarin sulfonate	Dark red	Greenish yellow
Polyphorus schweinitzii	Douglas fir	Methyl orange	Orange-yellow	No change
Poria incrassata	Southern yellow pine	Sodium alizarin sulfonate	Dark red	Greenish yellow
Poria incrassata	Southern yellow pine	Methyl orange	Orange-yellow	Rose-red
Poria subacida	Balsam fir	Sodium alizarin sulfonate	Dark red	Greenish yellow
Poria subacida	Balsam fir	Methyl orange	Orange-yellow	Orange-red
Stereum subpileatum	White oak	Sodium alizarin sulfonate	Dark red	Greenish yellow
Stereum subpileatum	White oak	Methyl orange	Orange-yellow	Orange-red
Trametes pini	Hemlock	Sodium alizarin sulfonate	Dark red	Greenish yellow
Trametes pini	Hemlock	Methyl orange	Orange-yellow	No change
Polyphorus betulinus	Birch	Sodium alizarin sulfonate	Dark red	Greenish yellow
Polyphorus betulinus	Birch	Methyl orange	Orange-yellow	Rose-red
Polystictus versicolor	Beech	Sodium alizarin sulfonate	Dark red	Greenish yellow
Polystictus versicolor	Beech	Methyl orange	Orange-yellow	No change
Coniophora cerebella		Sodium alizarin sulfonate	Dark red	Greenish yellow
Coniophora cerebella		Methyl orange	Orange-yellow	Rose-red
Merulius lachrymans		Sodium alizarin sulfonate	Dark red	Greenish yellow
Merulius lachrymans		Methyl orange	Orange-yellow	Rose-red
Daedalia quercina	Oak	Sodium alizarin sulfonate	Dark red	Greenish yellow
Daedalia quercina	Oak	Methyl orange	Orange-yellow	Rose-red
Lenzites trabea	Western red cedar	Sodium alizarin sulfonate	Dark red	Greenish yellow
Lenzites trabea	Western red cedar	Methyl orange	Orange-yellow	No change

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[2] *Ind. Eng. Chem.*, **19**, 1231 (1927).

[3] *Ibid.*, **19**, 878 (1927).

The toxicity of zinc meta-arsenite has been studied in the case of *Fomes annosus*, and it was thought desirable to extend these tests to the other fungi which were available. Some of these had not been used for experimental work for several months and it was found that the pure cultures of *Lentinus lepideus*, *Lenzites sepiaria*, and *Polyphorus pilotae* were dead. The others were in good condition, however, and were used in the toxicity tests, the details of which are given in Table III.

The cultures were made with zinc meta-arsenite in powder form dispersed through the gel, as any attempt to precipitate the preservative *in situ* would probably result in the presence of a small quantity of free arsenious oxide in the culture. This method is unfair to the preservative as uniform dispersion of the particles of powder is very difficult to attain. The gel is, of course, non-toxic between the particles.

Wood treated with zinc and copper arsenites shows, after seasoning, a very effective distribution of preservative. Microtome sections of yellow pine containing copper arsenite were stained with dilute potassium ferrocyanide and examined at 1500 diameters magnification. Untreated zones showed no color with the reagent while those parts containing copper were colored pink to mahogany. Photomicrographs showed heavy deposits of preservative in the medullary rays and resin ducts where fungous attack was most severe and lighter uniform deposits in the cells and cell walls. Microscopic studies on wood treated with zinc meta-arsenite indicate a distribution similar to that observed in the case of copper arsenite. We have found no stain which colors the crystals so effectively as ferrocyanide on copper. While the distribution of preservative in the gel is by no means comparable with that actually attained in wood, the tests may be of value if the shortcomings of the method are borne in mind.

Table III shows the effect of powdered zinc meta-arsenite on the various fungi. A (—) indicates no culture of the fungus at the given concentration of preservative. If there could be obtained a distribution of preservative in nutrient gel equal to that in wood treated under commercial conditions, it is believed that all the fungi listed in Table III would be totally inhibited at 0.10 per cent and some of them as low as 0.010 per cent of this preservative. It is interesting to note that the dry-rot fungi which showed sharply acid to methyl orange were also very sensitive to zinc meta-arsenite.

Table III—Toxicity of Powdered Zinc Meta-Arsenite toward Various Fungi

Fungus	Concentration of $Zn(AsO_2)_2$ in Culture and Growth of Fungus				
	0.30%	0.10%	0.06%	0.02%	0.00%
Fomes annosus	—	None	Feeble	Moderate	Good
Polyphorus anceps	None	Feeble	Feeble	Moderate	Good
Polyphorus schweinitzii	—	None	None	Moderate	Good
Poria incrassata	None	None	Feeble	Feeble	Good
Poria subacida	None	Feeble	Feeble	Moderate	Good
Stereum subpileatum	None	Feeble	Moderate	Good	Good
Trametes pini	—	None	None	None	Good
Polyphorus betulinus	—	None	None	Feeble	Good
Polystictus versicolor	—	None	Feeble	Moderate	Good
Coniophora cerebella	—	None	None	None	Good
Merulius lachrymans	—	None	Moderate	Feeble	Good
Daedalia quercina	None	None	Feeble	Feeble	Good
Lenzites trabea	None	Feeble	Moderate	Good	Good
Polyphorus sulphureus	None	Feeble	—	—	—

In a previous paper of this series[4] toxicity tests are described in which wood impregnated with various preservatives is finely ground, mixed with nutrient gel, and inoculated with a fungus. It was found, with sawdust made from treated wood which had been exposed in small pieces to the action of the weather for 10 months, that the zinc meta-arsenite retained its high toxicity while creosoted wood had lost most of its toxicity and zinc chloride–treated wood actually permitted fungous attack.

For example, 20-gram cultures containing 4.51 grams of creosoted wood completely inhibited *Fomes annosus* and 4.49 grams of wood treated with zinc meta-arsenite also prevented growth of the fungus. The creosoted wood had been originally impregnated with 419 kg. per cubic meter (27 pounds per cubic foot) of grade No. 1 creosote while the wood containing zinc meta-arsenite was treated with 10.5 kg. per cubic meter (0.66 pound per cubic foot) of that preservative.

It seemed desirable to test the resistance of the weathered wood containing zinc meta-arsenite against other fungi; therefore additional cultures of this type were prepared. The cultures contained 1.301, 2.784, 4.488, and 6.570 grams of wood with enough agar–malt sirup gel to make the total weight 20 grams. These contained, in the wood, 0.1, 0.2, 0.3, and 0.4 per cent zinc meta-arsenite based on the total weight of the culture. The cultures were next inoculated with the fungi under test.

Table IV lists the fungi and the results of the test. It shows that wood containing zinc meta-arsenite which has been cut into small pieces and exposed to the weather for 10 months has very high resistance to every one of this collection of rot-producing organisms. The wood is not only unattacked itself but is able to prevent fungous growth in the non-toxic nutrient gel with which it is mixed.

Table IV—Toxicity of Wood Impregnated with Zinc Meta-Arsenite toward Fungi

Fungus	Concentration of $Zn(AsO_2)_2$ and Growth of Fungus			
	0.4%	0.2%	0.1%	0.0%
Fomes annosus	None	Feeble	Feeble	Good
Polyphorus anceps	None	Feeble	Feeble	Good
Polyphorus schweinitzii	None	None	None	Good
Poria incrassata	None	Feeble	None	Good
Poria subacida	None	None	Feeble	Good
Stereum subpileatum	None	None	Feeble	Good
Trametes pini	None	None	Feeble	Good
Polyphorus betulinus	None	None	None	Good
Polystictus versicolor	None	Feeble	Feeble	Good
Coniophora cerebella	None	None	Feeble	Good
Merulius lachrymans	None	None	None	Good
Daedalia quercina	None	None	Good	Good
Lenzites trabea	None	Ncne	Feeble	Good
Polyphorus sulphureus	None	None	None	Good

A Cheap and Accurate Metal Scale for Scientific Instruments[1]

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THE writers recently had occasion to alter the scale on a color grader used for honey and sirups. The method adopted was to make a "positive" zinc etching of the desired scale and attach it to the instrument in place of the original. The scheme apparently should have wide application and, although the idea undoubtedly is not new, it does not appear to be generally known.

An ink drawing is made two or three times as large as the desired scale. The drawing is sent to the print shop with instructions as to the *exact size* of the reproduced scale. Instead of the usual reversed etching, a "positive" is made. The characters of the scale stand out in relief, the accuracy is the same as the original drawing, the scale is durable, and the cost is negligible compared with an etching or an engraved scale.

Calendar of Meetings

American Chemical Society—75th Meeting, St. Louis, Mo., April 16 to 20, 1928.

American Electrochemical Society—Hotel Stratfield, Bridgeport, Conn., April 26 to 28, 1928.

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[4] *Ind. Eng. Chem.*, **19**, 1343 (1927).

[1] Received November 21, 1927.

Carbon Monoxide in Two Large Garages[1,2]

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Carbon monoxide was determined continuously in the Government Fuel-Yard Garage, Washington, D. C., during nearly three weeks of January, 1927, and in a large commercial garage in Pittsburgh, Pa., through the greater part of the four succeeding months. A carbon monoxide recorder was used, the records indicating carbon monoxide in parts per ten thousand and fractions thereof. Maximum and average concentrations of carbon monoxide for each of three periods per day and for one hour in each day showing maximum average carbon monoxide were compiled. The maximum indication exceeded 8.9 p. p. t. t., the upper limit of the recorder, on a few occasions, but only momentarily. The average concentration through the hours 7:20 A. M. to 4:30 P. M. at the Government Fuel-Yard Garage in no case exceeded 1 p. p. t. t. The highest average at the commercial garage for the hours 6:00 A. M. to 6:00 P. M. was 1.64 p. p. t. t. The highest average for any one hour was 4.33 p. p. t. t. at the commercial garage; this may cause headache in some persons. The carbon monoxide was not found very injurious, but no very cold weather occurred during the period of the records. In very cold weather when garages are kept more tightly closed to retain heat, worse conditions may occur if operations are otherwise the same.

THE Government Fuel Yards at Washington, D. C., operated by the U. S. Bureau of Mines, maintains a garage for the storage, maintenance, and repair of motor trucks and cars used in distributing coal to the many government buildings. During the cold weather of December, 1926, some employees in the garage suffered from headache attributed to carbon monoxide from motor exhausts. The Bureau of Mines was requested to determine the carbon monoxide in the garage through a period to ascertain the hygienic conditions. Continuous records of the carbon monoxide were then obtained through nearly three weeks of January, 1927.

Records of carbon monoxide were also obtained through most of February to May, 1927, in a large public corporation garage at Pittsburgh, Pa.

The carbon monoxide was recorded as high as 8.9 parts per ten thousand (p. p. t. t.) in the government garage. However, the average concentration through the working hours of a day in no case exceeded 1 p. p. t. t. In the corporation garage the highest average found through a working day (6:00 A. M. to 6:00 P. M.) was 1.64 p. p. t. t. The maximum carbon monoxide exceeded the upper limit of the records, about 8.3 p. p. t. t., but such high concentrations existed only momentarily. The highest average through any one hour was 4.33 p. p. t. t., which may cause headache in some persons. On the whole, the carbon monoxide was not found to be very bad as regards effect upon workmen in the garages.

An investigation of the carbon monoxide in thirty-one public garages in New York City had been made by the New York State Department of Labor starting November, 1923;[3] they report a single analysis from each garage. The results show one garage with 20 p. p. t. t., nine with 15 p. p. t. t., seven, 10 p. p. t. t., seven, 5 p. p. t. t., and seven, no carbon monoxide. These concentrations are mostly much higher than those from the continuous records reported hereafter. The grab samples taken in adverse situations in small garages may account in part for the differences between the two investigations; at any rate, it appears that the results of the former investigation are hardly representative of averages of carbon monoxide in the large garages.

Description of Garages

Government Fuel-Yard Garage—The Government Fuel-Yard Garage is a one-story brick structure of 47.3 by 57.6 meters (155 by 189 feet) plan. The side walls rise 5.2 meters (17 feet) to the roof; the roof rises therefrom to a height of 5.8 meters (19 feet), where it meets the monitor or raised portion running the length of the building and 22.3 meters (73 feet) wide. The height from floor to top center of roof is 8.44 meters (27 feet, 8 inches). There are five large doors for entrance of cars on three sides. Windows are set all along the monitor and may be opened for ventilation; the sides of the building are mostly of large windows in which are small sashes that open outward at the bottom. At the front is an office and an oil room, both of which are completely partitioned off; above these are wash rooms. A small storage room for passenger cars is also separately enclosed, and a boiler room is in a basement at the front. The garage is partitioned with wire screens into storeroom, machine shop, repair shop, and storage spaces. The heating in the garage proper is by steam coils in four unit heaters at the monitor. Electrically driven fans circulate air from the room through the heating coils and discharge it vertically downward. There is no provision for entrance of fresh air other than through windows and doors.

Thirty-three heavy trucks, four light trucks, and several passenger cars and special cars were housed in the garage. Nearly all the cars left the garage and returned between the hours of 7:30 A. M. and 5:00 P. M.

Public Corporation Garage—The garage at Pittsburgh occupies a four-story building 19.9 by 40.6 meters (65.3 by 133 feet) in plan, of brick and reinforced-concrete construction; the stories are 3.9 meters (12.83 feet) high from floor to ceiling. The lower floor is used for storage of about twenty-five passenger cars, and sometimes a few trucks; there is one entrance for cars to this floor from a street at the front of the building. The second floor, on which the carbon monoxide was recorded, is used mostly for storage of trucks, about twenty in number of 1 to 5 tons capacity, mostly the larger; a space at one side is used for washing cars, and one corner is screened off for a tire-repair shop; small repairs are also made on the second floor. There is one entrance for cars to the second floor from a street at the rear on a higher lever than the front street. The third floor has a paint shop, carpenter shop, battery shop, and repair department for trucks. On the fourth floor is a machine shop, blacksmith shop, storeroom, and repair department for light

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[1] Presented before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Published with approval of the Director, U. S. Bureau of Mines.

[3] Ciampolini, *J. Ind. Hyg.*, **6**, 102 (1924).

cars. A stairway and an elevator for cars are included. Large windows are set closely around the building on the front, back, and one side. In each window is a smaller window sash which opens outward at the bottom. This garage stores and maintains the trucks for an important public service corporation, as well as for others. The garage is open 24 hours a day and the trucks come and go at any hour.

Carbon Monoxide Recorder

The carbon monoxide recorder and its characteristics have already been described completely.[4] Some essentials of the recorder follow:

Principle—When carbon monoxide unites chemically with oxygen to form carbon dioxide according to the equation

$$2CO + O_2 = 2CO_2 + 67{,}960 \text{ gram calories per gram molecule of CO}$$

the heat liberated increases the temperature of the gases themselves and the matter in contact with them. The recorder uses this effect as a means of indicating as well as recording the concentration of the carbon monoxide in air. Hopcalite catalyst[5] is employed to promote the union of carbon monoxide and oxygen. Thermocouples generate electric potentials which increase with the temperature, hence with the carbon monoxide, and the effects are recorded by a recording potentiometer calibrated in terms of carbon monoxide.

Mechanism and Structure—Figure 1 is a picture of the carbon monoxide recorder and Figure 2 is a diagram of the essential parts. Arrows point as the gas flows. The motor-driven blower, a, forces the gas through the train or succeeding parts; the excess gas is wasted through a side outlet controlled by a hand-operated valve. The gas passes through the four bottles, b_1, b_2, b_3, b_4, in series; the second and third of these contain sulfuric acid wash to dry the gases and remove hydrocarbons, ammonia, and other gases soluble in or retained by sulfuric acid. The first and fourth bottles serve as traps to prevent passage of acid to other parts of the apparatus. The gases pass next through a canister, c, which contains granular activated charcoal, alkaline granules, and filters of absorbent cotton. These allow the air and carbon monoxide to pass through, but retain all other gaseous impurities or suspensoids which may materially affect the catalyst. Hydrogen, methane, and some carbon dioxide, when present, are not restrained, but these gases (at their low concentrations) have no effect or a negligible one under the conditions of operation.[4] Methane is not oxidized nor does it affect the catalyst at the temperature employed. Hydrogen has an effect so small that it may be disregarded, and carbon dioxide is inert. The parts d, e, and f constitute the flowmeter and accessory parts for adjusting the flow and maintaining a constant rate. The gases pass to the receptacle j, which contains broken, fused calcium chloride to remove any additional water vapor coming from the flowmeter parts. From there the gases pass to the steam bath, k, heated by a gas flame. A reflux condenser, l, stops escape of steam and constitutes a vent which maintains atmospheric pressure in the steam bath so that the steam temperature is as constant as the barometer. The gases pass through coil m in the steam bath, where they are heated to 100° C., then through the cell n, which contains the thermocouples and catalyst to cause the reaction.

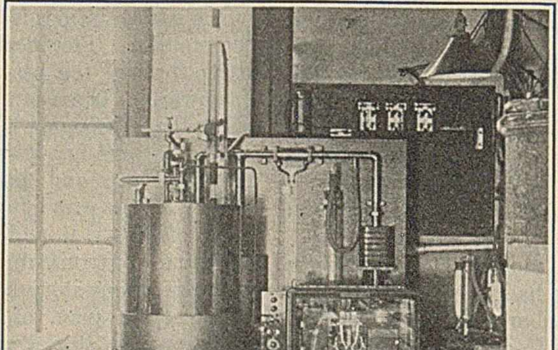

Figure 1—Carbon Monoxide Recorder

Figure 3 shows the cell in detail. Forty-eight pairs of differential couples of silver and constantan or of copper and constantan were used in two cells employed in this investigation. The differential couples were connected in series on mica cards. The cell was filled around to lower junctions to about one-third the depth with granular pumice stone; granular hopcalite catalyst filled the other two-thirds of the cell and surrounded the upper thermo-junctions.

The gases escape from the apparatus through a guard tube, o, Figure 2, containing calcium chloride and activated charcoal to prevent penetration of water vapor and gases to the hopcalite when not in use.

Potentials generated by the thermocouples when carbon monoxide is oxidized, thereby heating the upper thermo-junctions above the temperature of the lower, are transmitted through leads to the recording potentiometer, p, which is calibrated in terms of carbon monoxide as parts per 10,000 parts of air-gas mixture. The calibration was made with synthetic mixtures of carbon monoxide and air of known proportions, passed at a rate (46 liters per minute, more or less) to produce maximum thermo-electric effects.

Carbon Monoxide in the Garages

Government Fuel-Yard Garage—Figure 4 presents a summary of the records of carbon monoxide in the government garage from January 11 to 29, 1927. Each day has been divided into four periods and carbon monoxide is indicated as maximum and average parts per 10,000 through each period per day. The periods are 7:20 to 8:00 A. M. when the trucks were leaving for work, 8:00 A. M. to 3:45 P. M. when occasional trucks arrived or departed, and when motors were sometimes operated while they were undergoing repairs or adjustments; 3:45 to 4:30 P. M. when most trucks returned; and 4:30 to 12:00 midnight when cars rarely came or went and only occasional repair work was done. After midnight and until morning the carbon monoxide was nearly zero and the records are not presented.

The air sampled was led to the carbon monoxide recorder through a hose from seven positions in the garage, mostly at points about man high. The carbon monoxide did not differ much at the different positions either vertical or lateral; most of the variations were due to the number of motors operating at a time, their distance from the inlet to the sampler, and the air currents or ventilation existing at the time.

The maximum indicated carbon monoxide, according to Figure 4, was 8.9 p. p. t. t. or more on January 25. The maximum average during any period was 1.77 parts between 7:20 and 8:00 A. M. of the 15th. The maximum average during any one hour was 2.80 parts from 8:00 to 9:00 A. M. of the 17th. The weather during the entire period of testing was not very cold; on only two days was the official temperature below freezing throughout a day. The minimum official temperature was −13.3° C. (8° F.) on the 27th; the lowest maximum for a day was −2.2° C. (28° F.) on the 16th.

Corporation Garage—Figures 5 to 8 show the carbon monoxide on the second floor of the corporation garage. The second floor has the most carbon monoxide as more machines come and go there, and they are mostly the heavier

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[4] Katz, Reynolds, Frevert, and Bloomfield, U. S. Bur. Mines, *Tech. Paper* **355** (1926); Katz, U. S. Patent 1,578,666 (March 30, 1926); British Patent 249,088 (May 12, 1927).

[5] Lamb, Bray, and Frazer, *Ind. Eng. Chem.*, **12**, 213 (1920); Katz and Bloomfield, U. S. Bur. Mines, *Tech. Paper* **300** (1923); Frazer and Scalione, U. S. Patent 1,345,323 (June 29, 1920).

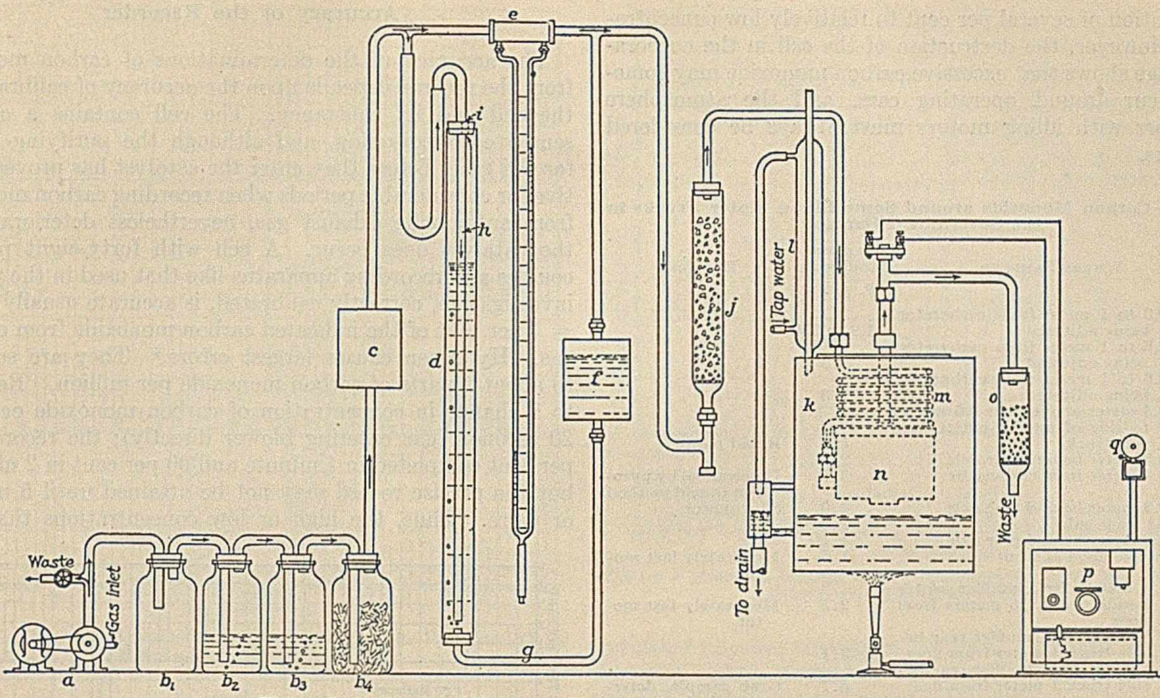

Figure 2—Diagram of Essential Parts of Carbon Monoxide Recorder

and more powerful trucks; motors are also operated there during lesser repairs and adjustments. Samples were drawn from nine positions, eight of them on the lateral half without windows along the wall and from about 25 feet from front wall to 10 feet from the rear wall; the height was about 6 feet. The positions were not very different as regards carbon monoxide. During a few periods where no records are shown interruptions occurred due to failure of recording ink to flow, the record chart becoming jammed, and stopping of the water flow during repairs.

There was no very cold weather during the period covered. The coldest official temperature at Pittsburgh during the February period was −5.6° C. (22° F.) on the 21st, whereas the lowest maximum for a day was −1.1° C. (29° F.) on the same day. The coldest during the periods covered in March was −7.2° C. (19° F.) on the 3rd and the lowest maximum was −3.3° C. (26° F.) on the same day.

On March 6 excessively high temperatures were produced in the cell due to the entrance of some unknown high concentration of carbon monoxide. The silver thermocouple wires (No. 28 B. and S. gage) melted and the cell was destroyed. A new cell was put in on March 22; thereafter two cells were used alternately a week at a time and re-calibrated before each period of use. The circumstances giving rise to the excessive concentration of carbon monoxide that destroyed the cell are not known, but undoubtedly exhaust gas with relatively small admixture of air entered the hose sampler.

Table I—Maximum Average Concentrations of Carbon Monoxide in Corporation Garage during the Daily Periods and Their Respective Maxima

(Figures in parts per ten thousand)

CARBON MONOXIDE	12 to 6 A. M.	6 A. M. to 6 P. M.	6 P. M. to 12 M.	ONE HOUR OF MAXIMUM AVERAGE CO
Maximum average	1.13	1.64	1.80	4.33
Highest indicated during period of maximum average	3.68	4.55	6.08	6.08
Date	3/5/27	3/22/27	2/25/27	10:27 to 11:27 P. M., 2/25/27

The carbon monoxide exceeded 8.3 p. p. t. t., the maximum range of the recorder in the corporation garage, for short periods on only two days—February 18 and 20. Table I shows the maximum average carbon monoxide for each of the three daily periods, the maximum indication during those periods of highest average, and the maximum average for any one hour with the maximum indication during that hour.

Carbon Monoxide around Idling Motors

The carbon monoxide was recorded for short periods at different points about idling trucks in the government garage. Usually repairs or adjustments were being made by mechanics at the time, such as adjusting the carburetor, tightening brake bands, and similar jobs. These cars were away from other cars, walls, or other obstructions to air currents. Table II summarizes the records. The outlets for exhaust gas were about 2 meters ahead of the rear axle.

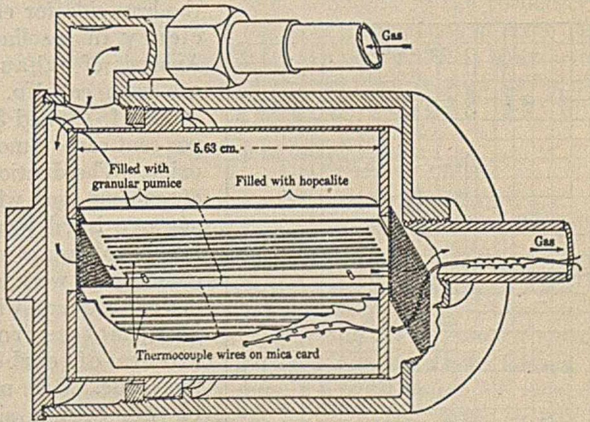

Figure 3—Details of Cell Containing Thermocouples and Catalyst

The maximum concentration of carbon monoxide determined was 7.0 p. p. t. t. at a point 1.2 meters directly behind the muffler of a motor idling at moderate speed. Under a truck behind the rear axle center (2.3 meters from muffler) a concentration of 5.2 p. p. t. t. was found as a maximum. It appears thus that the carbon monoxide in exhaust gas from an idling motor usually is quickly diluted from an initial concentration of several per cent to relatively low concentrations. However, the destruction of the cell in the corporation garage shows that excessive carbon monoxide may sometimes occur around operating cars, and the atmosphere under cars with idling motors must always be considered dangerous.

Table II—Carbon Monoxide around Some Idling Motor Trucks in the Government Garage

Truck No.	Where Sampled	Carbon Monoxide *P. p. t. t.*	Remarks
1	0.6 to 1 meter from carburetor being adjusted	1.9 to 2.4	
2	0.6 to 1 meter from carburetor being adjusted	3.0	
3	0.6 to 1 meter from carburetor being adjusted	1.3	
3	0.3 meter above floor 0.6 meter to side of muffler outlet, beside truck	5.4	Rapid motor
3	0.3 meter behind rear axle	2.2	
4	0.4 meter from carburetor	3.7	Determined by pyrotannic acid method
5	0.3 meter behind rear axle	2.0	Slow motor
5	At front axle	1.2	
5	0.3 meter behind rear axle	4.1	
6	Above hood at front	1.5	Moderately fast motor
7	1.5 meters from muffler center beside truck 1.5 meters from floor	2.5	Moderately fast motor
7	0.6 meter from muffler rear beside truck 1 meter from floor	3.1	
7	0.6 meter from muffler rear beside truck 1 meter from floor	5.7	Grab sample, determined by pyrotannic acid method
8	Beside hood	1.0	
8	1 meter back of muffler beside truck, at right	1.7	Slow motor
8	Undiluted exhaust gas	340.0	Determined by Orsat method
8	1 meters back of muffler beside truck at left	2.5	
8	2.3 meters from muffler behind rear axle center, under truck	4.2 to 5.2	
9	1.5 meters behind truck at right 1.2 meters high	0.7	
9	1.5 meters behind truck, 4.5 meters high	1.2	
9	3.6 meters behind truck, 1.5 meters high	0.7	
10	1.2 meters directly back of muffler	7.0	Moderately fast motor
10	Under rear axle directly back of muffler	5.0	

With carburetors adjusted for rich fuel mixture the carbon monoxide in exhaust gas may be as high as 13.5 per cent. Carburetors were adjusted at the government garage toward the lean side for efficiency in gasoline.[6] Analysis of exhaust gas from car No. 8, Table II, showed 3.4 per cent carbon monoxide. The dilutions of exhaust gas with air are hardly sufficient to insure mechanics who work under or about cars with idling motors from effects of carbon monoxide. One mechanic became sick while so engaged during the tests in the government garage, but the carbon monoxide under the car was not determined at the time. The practice is now forbidden there; motors must be stopped while men work under cars.

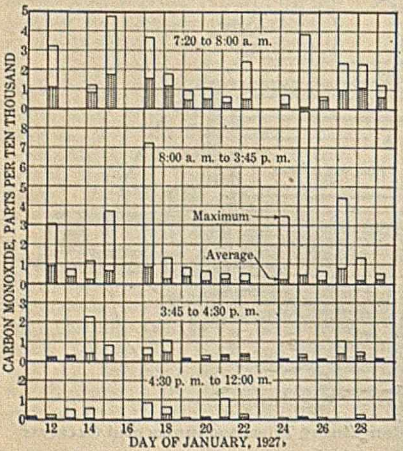

Figure 4—Carbon Monoxide in Government Fuel-Yard Garage, Washington, D. C., January 11 to 29, 1927

Accuracy of the Recorder

The accuracy of the determinations of carbon monoxide from the records depends upon the accuracy of calibration of the cell and its constancy. The cell contains a catalyst sensitive to poisoning, and although the purifying system for the gases before they enter the catalyst has proved effective for considerable periods when recording carbon monoxide from automobile exhaust gas, nevertheless deterioration of the catalyst does occur. A cell with forty-eight pairs of couples and recording apparatus like that used in the present investigation, correctly calibrated, is accurate usually within ± 5 per cent of the indicated carbon monoxide from exhaust gas. Hydrogen causes largest errors.[4] They are sensitive to about 2 parts of carbon monoxide per million. Response to a change in concentration of carbon monoxide occurs in 20 seconds (gas entering blower directly); the record is 70 per cent completed in 1 minute and 90 per cent in 2 minutes, but the precise record may not be attained until 5 minutes or more. Thus, the high or low concentrations that exist only about a minute may not be recorded exactly; the averages taken from the records should, however, be very nearly correct.

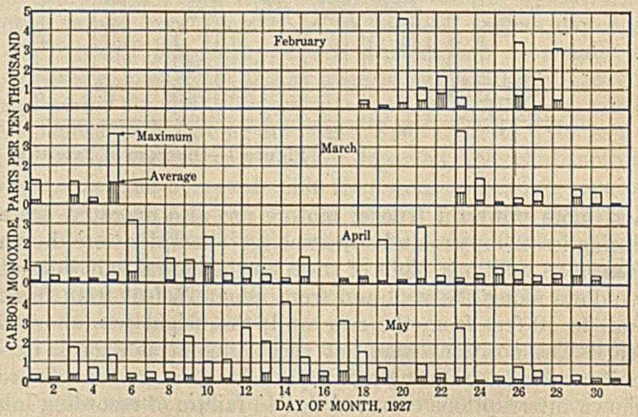

Figure 5—Carbon Monoxide in Commercial Garage Recorded Daily between Midnight and 6:00 A. M.

Different lots of catalyst in cells have not always retained their calibrations with the same permanence. One of the best lasted 5 months without apparent change in a recorder at the Liberty Tunnels at Pittsburgh, and after 9 months' continuous operation was 60 per cent accurate, determined by re-calibration in the laboratory. The carbon monoxide recorder in the government garage started on January 11, and after continuous operation was checked on the 22nd by mixing exhaust gas and air continuously in a large bottle at uniform rates, drawing the supply to the recorder therefrom and determining the CO for check by the pyrotannic acid method.[7] The recorder showed 7.1, 7.4, and 7.4 p. p. t. t. in three trials and the pyrotannic acid method showed 7 ± 1 p. p. t. t. each time. No deterioration is indicated, and the recorder was undoubtedly much more accurate throughout the period of use at the government garage than the pyrotannic acid method.

When recording was resumed in the corporation garage, after the first cell was destroyed, two cells were used alternately beginning March 26, a week at a time and re-calibrated in the laboratory with carbon monoxide precisely diluted with air, between periods of use. The calibrations are given in Table III.

According to Table III, cell No. 7, calibrated before and after five periods of use totaling 42 days, showed decreases in sensitivity after four of the five periods and an increase

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[6] Jones and Fieldner, *U. S. Bur. Mines, Repts. Investigation* 2487 (June, 1923).

[7] Sayers and Yant, *U. S. Bur. Mines, Tech. Paper* 373 (1925).

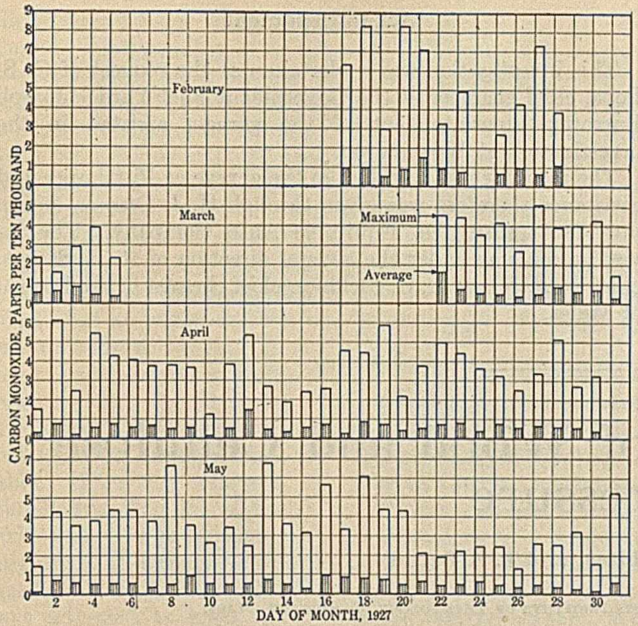

Figure 6—Carbon Monoxide in Commercial Garage Recorded Daily between 6:00 A.M. and 6:00 P.M.

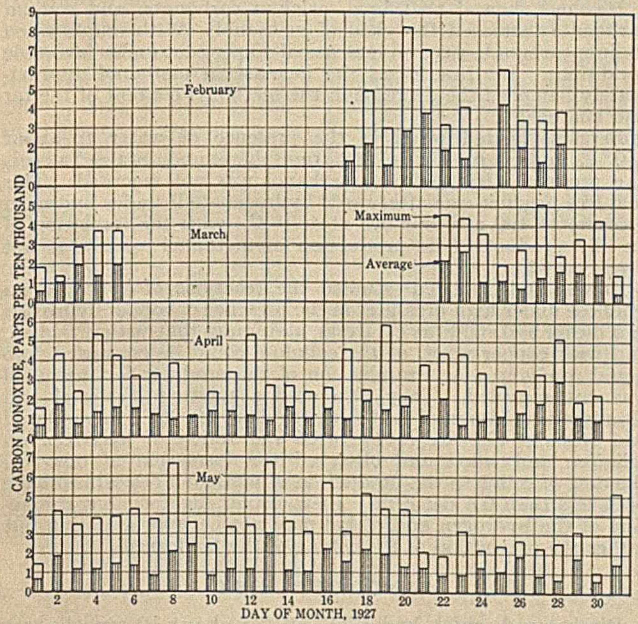

Figure 8—Carbon Monoxide in Commercial Garage during the Hour of Highest Average on Successive Days

after one period. The increase may have been due to changes in articulation of the granules with resultant gas passage through more effective channels in the catalyst. The greatest change was a 16 per cent decrease in potentials after the first week; the changes total 28 per cent decrease in 42 days.

Cell No. 9 was used 28 days; the greatest change was a decrease of 9 per cent in potentials after the first week, an increase of 7 per cent followed; then there were smaller decreases. The total decrease in 28 days was 11 per cent.

The recorder was operated each week at the "best rate" for the cell, which is the rate of gas flow producing maximum potentials, where small changes of flow cause no changes in potentials. The best rates decrease as deterioration of the cells progresses.

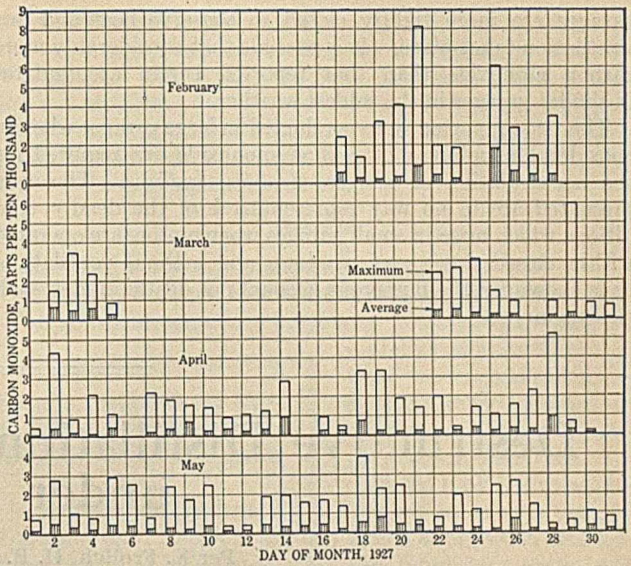

Figure 7—Carbon Monoxide in Commercial Garage Recorded Daily between 6:00 P.M. and Midnight

The changes may have been due only partly to deterioration of the hopcalite catalyst; part may have been caused by loss of catalyst due to attrition of the fragile granules and resultant physical changes in the cells. The cells were firmly but not tightly packed at the start. When they were removed and transported to the laboratory they were handled with ordinary care—carried in a coat pocket or a hand case on trips by automobile or by street car. At the end of the operations the granular materials were loose in the cells.

Table III—Changes in Calibration of Two Cells Used to Record Carbon Monoxide in the Corporation Garage

Cell No.	Week Beginning	Best Flow Rate	Potential per 1 P.p.t.t. per Couple Start	End	Calibration Change Based on Flow Rate during Recording Period	Remarks
		Liters/Min.	Millivolts		Per cent	
7	March 26	38	0.0306	0.0257	−16	
7	April 9	28	0.0267	0.0248	− 7	
7	April 23	28	0.0248	0.0278	+12	
7	May 7	30	0.0278	0.0269	− 3	
7	May 21	26	0.0273	0.0234	−14	To June 1 11 days
9	April 2	49	0.0300	0.0274	− 9	
9	April 16	36	0.0278	0.0298	+ 7	
9	April 30	35	0.0298	0.0284	− 5	
9	May 14	27	0.0286	0.0272	− 4	

Thus the records of carbon monoxide in the corporation garage may have been as much as 16 per cent in error on a few days, but it is doubtful that errors were that large; average errors are undoubtedly less than 8 per cent, or half of the possible extreme error.

Discussion of Results

Four parts of carbon monoxide per 10,000 of air is a maximum that may be endured by persons for one hour without noticeable effects,[8] and 1 p. p. t. t. may be taken as a maximum for continuous exposure for about 7 hours per day without noticeable effects.[9] Only once was 4 p. p. t. t. exceeded as an average for one hour; that was in the corporation garage on February 25. Momentary concentrations above 8 p. p. t. t. were recorded on only 5 days among 105 days on which records were obtained. A cell in the carbon monoxide recorder was ruined one day by an unknown excessively high concentration of carbon monoxide, but on the other hand concentrations were not found in excess of 7.0 p. p. t. t. under or near trucks with idling motors, excluding immediate discharge from the mufflers.

No tests were conducted in coldest winter weather, when

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[8] Henderson, Haggard, Teague, Prince, and Wunderlich, *J. Ind. Hyg.*, **3**, 72, 137 (1921).

[9] Sayers and Yant, unpublished report of Bureau of Mines.

garages are more tightly closed to conserve heat and less ventilation takes place. It is possible that considerably more carbon monoxide than that reported herein accumulates in similar garages in the coldest weather.

The tests reported were conducted in large garages wherein considerable volumes of carbon monoxide are required for the accumulation of dangerous concentrations. The data presented are in no way representative of the deadly conditions which arise in small garages when motors are operated within closed doors and windows and without ventilation, as is shown by the numerous accounts of deaths under such circumstances.

Acknowledgment

This investigation was undertaken at the request of G. S. Pope, chief engineer of the Government Fuel Yard. Joseph Burrows, superintendent of the garage, assisted in the investigation at Washington.

The recorder was installed in the garage at Pittsburgh and assistance therefore was given through H. J. Diemar, superintendent of service, Equitable Auto Company. The investigation was under the general direction of R. R. Sayers, chief surgeon, and A. C. Fieldner, chief chemist of the Bureau of Mines.

Destructive Distillation of Wood and Cellulose under Pressure[1]

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Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

UNTIL recently wood distillation has provided the sole supply of methanol for industry. During the last few years, however, the wood-distillation industry has been threatened with severe competition from the synthetic product, and hence the question has quite naturally arisen as to the possibility of increasing the yield of alcohol in the dry distillation of wood. In an effort to study this problem the present research was undertaken. Birch wood was distilled under pressure alone or in the presence of catalysts. In some cases hydrogen pressure was employed, and in others the autogenous pressure of the gases evolved in the distillation.

An increase in alcohol might result from one or more of the following causes: (1) vigorous reduction of the primary alcoholic groups in cellulose; (2) more complete conversion of the methoxyl in the wood to methanol; (3) combination of the gaseous products of distillation, carbon monoxide and hydrogen, particularly when in the nascent state; and (4) reduction of small amounts of formaldehyde usually formed in the distillation of wood. Of these four possibilities the first one would seem to offer most promise as far as quantity is concerned.

Cellulose in the form of sulfite pulp was used in similar experiments. This served to determine whether cellulose or lignin was the source of the increased yield observed with wood.

Previous Investigations

In his extensive studies of the destructive distillation of wood under atmospheric[2] and reduced[3] pressures, Klason showed that a primary tar was first formed and that this decomposed exothermically at 275° C. The production of methanol was unaffected by reduction of the pressure. Klason was the first to show the production of small amounts of formaldehyde in the distillation. By distillation of cellulose he demonstrated that the alcohol in wood did not come from this component.

Palmer[4] investigated the distillation of wood in the presence of phosphoric acid as a catalyst. Under atmospheric pressure an increase in the yield of methanol and acetic acid was found, but under autogenous pressure of 4 to 7 atmospheres a decrease was observed. Hawley[5] has been unable to confirm Palmer's results.

Hawley[5] showed that lime, calcium carbonate, and sodium carbonate increased the yield of methanol. With maple wood sodium carbonate gave an increase of 40 per cent under favorable conditions. In these cases the increase in methanol approximately balanced the decrease in the methoxyl content of the tar and charcoal.

Bergius[6] heated wood in the presence of water to about 340° C. under a pressure of 200 atmospheres and obtained a coal-like product. His yield of methanol was not recorded. This coal-like product was afterwards hydrogenated[7] under hydrogen pressure of 100 atmospheres at 400° C., with the formation of an oily product. The production of methanol again was not investigated.

Bowen and Shatwell[8] studied the reactions of hydrogen on cellulose under high pressures in the presence of copper hydroxide and nickel hydroxide as catalysts, and found that with nickel all, and with copper most, of the cellulose could be converted into liquid products. An examination of the products for methanol was not recorded. They also used a mixture of nickel and aluminum oxides and obtained similar results. Fierz-David and Hannig[9] likewise investigated the action of hydrogen on cellulose and wood and observed the formation of oils. In the case of cellulose the production of methanol appears to have been less than 0.5 per cent. Fierz-David suggests that the action of the hydrogen and nickel may not be hydrogenation but rather the prevention of the coking of the tar formed.

Experimental Work

Birch wood which had been cut for about 12 months was used in the form of small cubes of approximately $^1/_4$-inch (6-mm.) edge. When catalysts were employed, a known weight of hot, dry wood was placed in a solution of the required salt. Upon saturation the wood was again dried and weighed. Additional catalyst could be added by repeating the process, the total amount of catalyst introduced being estimated either by direct analysis or by difference in weight of the untreated and treated wood. Cellulose was used in the form of sulfite pulp dried at 120° C. before using in uncatalyzed runs. When catalysts were employed the moist pulp was placed directly in the salt solution and dried at 120° C.

A known weight of dry material, or material of which the moisture content was known, was placed in a chrome-vana-

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[1] Received August 13, 1927. Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Z. angew. Chem.*, **25**, 1205 (1909); **27**, 1252 (1910); Hawley, "Wood Distillation," p. 52 (1923).

[3] *J. prakt. Chem.*, [2] **90**, 413 (1914).

[4] *Ind. Eng. Chem.*, **10**, 264 (1918).

[5] *Ind. Eng. Chem.*, **14**, 43 (1922).

[6] *Z. Elektrochem.*, **19**, 858 (1913).

[7] Bergius, Friedländer's "Patentsammlung," XIV.

[8] *Fuel Science Practice*, **5**, 138 (1926).

[9] Fierz-David, *Chemistry & Industry*, **44**, 942–4 (1925); Fierz-David and Hannig, *Helv. Chim. Acta*, **8**, 900 (1925).

dium steel reactor of 5 cm. internal diameter and 45 cm. length, corresponding to a volume of 850 cc. The reactor was supplied with an electric heater and had a thermocouple well extending into its central part in order to permit representative temperature readings. The chamber was supplied with connections at both ends for introduction and removal of gases under pressure. Electrolytic hydrogen was supplied from a storage cylinder of 2 cubic feet (56 liters) capacity under a pressure of about 250 to 300 atmospheres.

In starting a run the heater was turned on and gas admitted to the chamber until the pressure was somewhat less than that at which the run was to be made. In order to secure uniform heating an hour was allowed for each rise of 100° C. By this procedure the exothermic reaction was hardly noticeable. When the temperature had reached 100° C. the exit valve was opened slightly to give the required gas flow, and the inlet valve was adjusted to keep the pressure in the chamber as nearly constant as possible. By employing a flow of gas throughout the run the products were continuously removed from the sphere of action, and it was hoped that by this means the greatest advantage might be obtained from the use of hydrogen, and that none of the methanol formed at low temperatures would be decomposed at higher temperatures. This dynamic method, therefore, represents an improvement on the enclosed, static systems employed by previous investigators. According to Fierz-David[9] the production of liquid products is really due to the prevention of the primary tar from coking. If this is true, the removal of the products as formed should favor the formation of liquids.

Wood and cellulose, either alone or impregnated with catalysts, have been distilled under pressure in an atmosphere of hydrogen, nitrogen, or of the gases evolved in the distillation.

Pressure alone favors the formation of methanol, as evidenced by a doubling of the methanol yield under a hydrogen pressure of 200 atmospheres. The autogenous pressure of the gases evolved in the distillation has a similar effect. With the catalysts studied the yield of methanol is usually decreased at atmospheric pressure and barely improved when higher pressure is employed. Check experiments on cellulose demonstrate that the increased methanol yield is derived from the methoxyl groups and not from the cellulose molecule. With nickel as a catalyst and hydrogen under 200 atmospheres, cellulose is almost completely converted into gaseous and liquid products, the latter consisting of phenols and saturated and unsaturated hydrocarbons. When nitrogen is substituted for hydrogen the cellulose is volatilized to practically the same extent.

Whether this process of decomposition of cellulose and wood to form phenols and hydrocarbons will meet with commercial success would seem to depend to a large extent on the development of suitable equipment for continuous operation.

The liquid products were condensed under pressure and withdrawn from a receiver at intervals, while the exit gas, after passing a water scrubber, was collected in a holder in order to make possible analysis of a composite sample at the end of the experiment. On completion of the run the pressure was allowed to drop slowly, permitting any high-boiling liquids remaining in the chamber to distil over into the receiver. Depending upon the conditions studied, the duration of a run would be from 6 to 10 hours. When the apparatus had cooled, the liquid lines were blown out with gas in order to remove any product remaining in the system.

The gas was analyzed by the ordinary methods, while the liquid products, after topping in a distilling column, were subjected to careful fractionation in a micro-fractionating column developed in this laboratory for analytical purposes. The fractionation separated the products into (1) a constant-boiling mixture of methyl acetate, acetone, and methanol, and (2) pure methanol. Experiments with synthetic samples showed that the constant-boiling mixture contained approximately 15 per cent methanol. Hence, the yield of methanol could be found by adding 15 per cent of the low-boiling fraction to the alcohol fraction. The methyl acetate was determined by saponification with standard caustic soda and the acetone estimated either by difference or, more accurately, by Messinger's method. In cases where a large amount of oil was formed, the methanol could not be determined very accurately by fractionation, and hence the methyl iodide method was used. The acetic acid was determined by titration with standard alkali.

Results

The results are summarized in Table I.

Standard Run at Atmospheric Pressure—Before commencing the experiments employing pressure and catalysts a preliminary distillation of wood was carried out under atmospheric pressure, to serve as a standard of comparison for later runs.

In the table yields are reported in grams per 100 grams of dry wood distilled. The figures for acetic acid and methanol include the potential methanol and acetic acid present in the form of ester. The results agree well with those found by other experimenters, as will be seen from the second horizontal column taken from Hawley's book.[2]

Autogenous Runs—Runs 15, 3, and 16 were made under the pressure of the gases evolved in the reaction.

The low pressure in run 3 was caused by frequent tapping of the liquid products, allowing some of the gas to escape. In runs 15 and 16 the liquid was not withdrawn until the end of the run. The yields of charcoal, acetic acid, and methanol showed a decrease with rise in final temperature. In runs 15 and 3 the alcohol yields were, respectively, 80 and 67 per cent above the standard run (1), but in run 16 the yields were negligible. This decrease indicates the decomposition of the products due to secondary reactions at temperatures above 375° C.

The residue showed lustrous particles resembling coal mixed with charcoal of the same type as in run 1. This is presumably due to the fact that the pressure prevents the volatilization of much of the tar, which therefore is decomposed giving a coke-like substance. In run 16, where the pressure and temperature were high, the quantity of tar in the liquid product was very small. Obviously, the high autogenous pressure in this run was a direct result of the decomposition of the tar into gaseous products. Analysis of the gases indicated the presence of large amounts of hydrocarbons. That hydrocarbons are evolved on heating tar above 400° C. has been shown by Bergström and Wesslen.[10] It will be noticed that in these three runs, as in other pressure experiments, the carbon monoxide–carbon dioxide ratios in the gases were much lower than in runs at atmospheric pressure.

There seem to be several causes to which the observed increase in methanol might be attributed: (*a*) directly to

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[10] "Om Träkolning," p. 180; Hawley, "Wood Distillation," p. 65 (1923).

the effect of pressure during the reaction, (*b*) the combination of carbon monoxide and hydrogen under the influence of pressure, and (*c*) the prevention of the decomposition of methanol under the influence of pressure.

Run under Hydrogen Pressure, No Catalyst—The conditions in run 4 should favor the methanol yield if (*a*), (*b*), or (*c*) above were important factors. Further possibilities of methanol formation were present in this case: (*d*) the direct hydrogenation of the primary alcoholic groups in cellulose, and (*e*) the reduction of formaldehyde and formic acid, although these reactions were not considered probable in the absence of the catalyst.

These results show that the methanol yield was about 105 per cent greater than that obtained in the standard run at atmospheric pressure (run 1). Less ester was produced than in the low-pressure autogenous experiment (run 15). The acetic acid yield was not altered by hydrogen pressure. The constancy of the total acetic acid in runs 1, 15, and 4 suggests that pressure does not alter the yield. The free acetic acid had diminished to 3.87 and 4.18 per cent in runs 15 and 4, but this decrease was balanced by an increase in ester. The stream of hydrogen in run 4 may have reduced the combination of acid and alcohol to ester by lessening their time of contact in the chamber. The charcoal in run 4 was similar in appearance to the autogenous residue. The quantity was somewhat less than in run 16, probably owing to the removal of the tar from the chamber before decomposition took place.

Zinc-Chromium Catalysts—In the runs 2, 5, and 6 the wood was impregnated with a mixture of zinc and chromium nitrate before distillation. Mixtures of the oxides of zinc and chromium have been recommended repeatedly by Patart[11] and Badische Anilin und Soda Fabrik[12] as catalysts for the formation of methanol from carbon monoxide and hydrogen under pressure. The nitrates were chosen since they are readily soluble salts and give the oxides on heating. The proportion of the salts was varied in each experiment, the total amount of catalyst being 3 to 5 grams of metallic oxides per 100 grams of dry wood.

Table I—Distillation Data for Wood and Cellulose

(Basis 100 grams of dry wood or cellulose)

Run	Catalyst	Rate of Gas Flow[a] Liters per hour	Pressure Atmos.	Final Temperature ° C.	Organic Residue Grams	Ratio $CO:CO_2$	Methyl Acetate Grams	Acetic Acid Grams	Methanol Grams
				WOOD—STANDARD RUN AT ATMOSPHERIC PRESSURE					
1	None		1	372	42	0.5	0.125	5.68	1.52
Hawley	None		1	400	38.5	..	..	5.24	1.55
				WOOD—AUTOGENOUS RUNS					
15	None		100	280	50	0.120	2.48	5.88	2.74
3	None		90	372	44	0.087	1.05	4.23	2.54
16	None		300	500	37	0.088	0.0	2.23	0.20
				WOOD UNDER HYDROGEN PRESSURE					
4	None	30	200	483	33.6	0.13	1.84	5.67	3.11
2	Cr-Zn = 4[b]	30	1	378	42.5	0.47	Negl.	5.29	1.14
5	Cr-Zn = 1[b]	30	200	454	26.4	0.09	0.47	1.75	1.97
6	Cr-Zn = 0.5[b]	30	200	440	27.8	0.09	0.89	3.57	1.78
8	Cu-Zn-Al[b]	30	200	423	19	0.07	Negl.	..	0.5
10	Cu-Zn-Al[b]	30	200	450	26	0.064	3.8	11.2	4.77
11	Nickel acetate[c]	30	200	400	20	0.11	2.11	..	3.18
18	Nickel acetate[c]	30	200	500	8	0.11	1.61	..	2.06
7	None	40	10	364	..	0.52	0.20	7.15	1.33
19	Nickel acetate	40	10	500	25	0.18	1.56	..	2.13
13	Sodium carbonate[d]	50	200	525	42	0.20	Negl.	..	2.31
				CELLULOSE UNDER HYDROGEN PRESSURE					
9	None	35	200	402	34	0.45	Negl.		Negl.
12	Zn-Cu-Al acetates[e]	35	200	520	10	0.10	Faint		Faint
14	Nickel acetate[c]	35	200	500	2.3	0.25	..		..

[a] Normal temperature and pressure.
[b] 3 to 5 grams, calculated as oxides.
[c] 7.5 grams, calculated as oxide.
[d] 33 grams.
[e] About 5 grams.

The results under atmospheric pressure (run 2) show a decrease in the yield of alcohol and a slight diminution of acetic acid. The methanol formation was expected to be reduced, since catalysts for the combination of carbon monoxide and hydrogen under high pressure also catalyze the reverse reaction when the pressure is reduced. In run 6 the temperature was kept at 340° C. for some time, since 300° to 400° C. is given as the optimum temperature range for the combination of carbon monoxide and hydrogen in the presence of the catalyst used.[10,11] Nevertheless, the methanol yield was less than that obtained in the corresponding run (4) without catalyst, and there was a marked diminution in the acid formed. The charcoal in runs 5 and 6 showed more signs of destruction of the original form of the wood than in previous experiments. A rather large quantity of tar was formed and this tar was lighter than usual and slightly more oily, separating more readily from the aqueous layer.

Copper-Zinc-Aluminum Catalysts—In run 8 a mixture of the nitrates was employed, but in run 10 this was altered to the equivalent mixture of the acetates. A very violent reaction near the beginning of run 8 caused the use of nitrates to be abandoned. This reaction may have been due to the nitration of cellulose with subsequent decomposition, or to reaction of the nitrates with hydrogen.

In run 8 a low-boiling oil obscured the fractionation curve. Most of this oil reacted with alkali, and a fractionation after hydrolysis showed that the methanol was greatly reduced. The yield of alcohol in run 10 was apparently very high. The acetic acid yield was large on account of hydrolysis of the acetate before decomposition. In later experiments using acetate as catalysts the acetic acid was therefore not estimated. It may be inferred that the high methanol yield is due to the simultaneous decomposition and reduction of acetic acid introduced with the catalyst. Results of other work in this laboratory would tend to exclude this possibility, however.

In both of these experiments there was a large yield of a light mobile tar and a small yield of charcoal. The structure of the wood was not retained by the charcoal. No doubt the wood had been partially converted into oils, a result which confirms the observation made by Bowen and Shatwell[8] and by Fierz-David[9] using copper oxide as a catalyst.

Nickel Catalysts—Nickel acetate as a catalyst with 200 atmospheres of hydrogen was employed in runs 11 and 18. Nickel oxide has been shown by Ipatiew[13] to be a very active hydrogenation catalyst under high pressures. On

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[11] *Tech. Eng. News*, December, 1926.

[12] U. S. Patent 1,558,559 (October 27, 1925).

[13] *Ber.*, **36**, 1990, 2003, 2014, 2016 (1903).

this account it was thought that it might favor the reduction of the cellulose molecule and the formic acid and formaldehyde usually produced.

In run 11 the fractionation curve was obscured by a low-boiling oil. This experiment was then repeated in run 18, the product coming from the receiver below 350° C. being kept separate from the portion produced at higher temperatures. The fraction obtained from run 18 below 350° C. contained about 4 cc. of oil per 100 grams of dry wood; it was topped and fractionated in the usual way. The fractionation curve was fairly smooth and showed that this product contained most of the methanol. The high methanol content of run 11 as compared with run 18 is probably due to an error in fractionation introduced by the low-boiling oil, since no chemical check analysis was made. The amount of alcohol was not large compared with that obtained in the absence of catalyst in run 4.

Both of these runs gave nearly complete conversion of wood into liquid and gaseous products. Run 18 gave 92 per cent conversion, yielding 25 cc. of oil per 100 grams of dry wood. A portion of this oil was dried over sodium sulfate and subjected to a "micro-Engler" distillation. Of the liquid 40 per cent boiled within the range 60° to 225° C., 43 per cent of the distillate being soluble in 60 per cent caustic soda. After treatment with alkali, 26 per cent was dissolved in concentrated sulfuric acid. The remaining 31 per cent was insoluble and presumably consisted of saturated hydrocarbons. This portion had an odor resembling that of gasoline.

RUNS UNDER 10 ATMOSPHERES HYDROGEN PRESSURE—This pressure was of considerable interest since it might eventually be employed commercially.

The results of run 7 without catalyst showed a high acid production, but a poorer yield of methanol than under atmospheric pressure in run 1. In run 19 with nickel acetate as catalyst the methanol yield was about the same as in the corresponding high-pressure run 18. The ester formation was not so great as in run 18, showing the favorable influence of high pressure on ester formation. Messinger's method showed a slightly smaller quantity of acetone than in run 18, 0.221 per cent as against 0.284 per cent. Not much importance is attached to this apparent increase in acetone with increase in pressure, however, since the accuracy of the analysis is greatly affected by small amounts of unsaturated compounds. The $CO:CO_2$ ratio in run 7 was high, 0.52. This was reduced to 0.18 in run 19.

SODIUM CARBONATE AS CATALYST—Hawley[2] has shown that under atmospheric pressure sodium carbonate increases the methanol yield by about 40 per cent under favorable conditions.

The results of run 13 showed only a slight improvement on Hawley's figure for maple under atmospheric pressure in that a 52 per cent increase in methanol was realized. This yield, however, was not so great as that obtained when using hydrogen without a catalyst (run 4). There was little or no methyl acetate present in the liquid product, a result which would be expected in the presence of alkali.

CELLULOSE UNDER HYDROGEN PRESSURE—In order to throw further light on the source of alcohol increase, several experiments (runs 9, 12, and 14) were performed with cellulose (sulfite pulp). With catalysts very definite exothermic reactions were observed. They commenced at 230° to 240° C. and were accompanied by a rise in temperature to 300° C. or above. The corresponding pressure rise was negligible, indicating that there was little evolution of gas. There was practically no flat portion on the fractionation curve in any of these experiments on pulp. Hence it seems that little or none of the alcohol produced in the corresponding experiments on wood (runs 4, 10, and 18) was obtained from cellulose. In runs 12 and 14 with catalysts large amounts of oil were produced, and accordingly the weight of the charcoal obtained was reduced. The use of nickel acetate favored the production of oils more than the mixture of copper, aluminum, and zinc acetates. This is in perfect agreement with the results of runs 10 and 18 on wood. Almost complete volatilization was obtained from nickel acetate, leaving a residue of only 2.3 grams organic residue per 100 grams of dry cellulose.

An experiment was also made with cellulose using zinc chloride as a catalyst. The results showed no indication of alcohol. A much lower temperature of decomposition was observed in agreement with the observations made by Schwalbe,[14] who used a similar catalyst, magnesium chloride.

CELLULOSE UNDER NITROGEN PRESSURE—Fierz-David[9] has suggested that the complete volatilization of cellulose in the presence of hydrogen and a catalyst is not due to hydrogenation. He believes that hydrogen merely acts as an inert gas improving the mechanics of the process. To test this theory cellulose impregnated with nickel acetate was distilled under 200 atmospheres of nitrogen. A considerable quantity of oil was formed, similar to the product of the first stages of the distillation in runs 12 and 14 with cellulose and hydrogen. The amount of charcoal was only slightly greater than in the corresponding run (12) with hydrogen. Thus a conversion of 86 per cent of the cellulose into volatile products was obtained. A small quantity of aqueous liquid was formed, boiling within the methanol range. This liquid was treated with phosphorus diiodide, but no traces of methyl iodide were obtained.

Summary

1—When wood is distilled in a closed system, the effect of autogenous pressure alone is to increase the yield of methanol by somewhere around 65 to 80 per cent depending upon the final temperature reached. These results were obtained with pressures slightly less than 100 atmospheres at temperatures ranging from 280° to 370° C. Further increase in temperature with a corresponding increase in pressure results in the decomposition of the initially formed products, and the methanol yield is poor.

2—Substituting hydrogen for the gases evolved by the destructive distillation of wood results in a somewhat higher increase in methanol yield. The figure 3.11 grams of methanol per 100 grams of dry birch wood, or 105 per cent above the yield at atmospheric pressure, apparently is the highest yield of methanol ever reported. Pressure does not affect the yield of acetic acid.

3—With the catalysts here studied the yield of methanol is usually decreased when atmospheric pressure is employed in the distillation. When combining the effect of catalysts with hydrogen under 200 atmospheres, the methanol yield is barely improved. Only in one case (run 10) was an increase of more than 200 per cent of methanol observed. Since the catalyst was used in the form of acetates, however, this figure should not be stressed, although as already mentioned, the possibility of obtaining methanol from the reduction of acetates seems rather remote.

4—Distilling the wood under a hydrogen pressure of 10 atmospheres results in a slight decrease of the methanol yield. At this pressure nickel does not materially alter the course of the reaction.

5—With nickel as a catalyst and hydrogen under 200 atmospheres more than 90 per cent of the original dry wood is converted into volatile products, resulting in a high yield of an oily product of which 40 per cent boils below 225° C.

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[14] *Papier-Fabr.*, **24**, 157 (1926).

This low-boiling fraction contains about 43 per cent phenolic compounds, 26 per cent unsaturated hydrocarbons, and 31 per cent saturated hydrocarbons. A catalyst containing copper gives a lower yield of oils. In no case is there an appreciable increase in methanol.

6—Experiments with cellulose demonstrate that the increases in methanol yield observed with wood are not due to the cellulose content. With nickel and hydrogen under 200 atmospheres practically all of the cellulose, or 98 per cent, is converted to volatile products, of which a large percentage are liquids of the general type mentioned above under 5.

7—In substituting nitrogen for hydrogen 86 per cent of the cellulose is converted to volatile products in the presence of nickel.

Conclusions

From these data it can be concluded that it is possible to convert the cellulose molecule into volatile products but that no success has been met with in controlling this reaction so as to obtain methanol. When reaction takes place the products are phenols and unsaturated and saturated hydrocarbons. Although high in some cases, there is no reason why the methanol yields observed should not have been derived from the methoxyl in the original wood, since according to Hawley only 70 per cent of this methoxyl is ordinarily recovered as useful products in wood distillation.

The results obtained when distilling cellulose under pressure in an atmosphere of nitrogen bring up the question as to the mechanism of hydrogenation in certain processes. Thus, it is claimed that in the berginization of coal the 5 per cent of hydrogen consumed in the process are converted into gaseous products and do not enter into the liquids.[15]

Whether the decomposition of cellulose and wood to form phenols and hydrocarbons will meet with any commercial success would seem to depend largely upon the development of suitable equipment for continuous operation. The fact that the reaction goes almost quantitatively makes the process compare favorably with the berginization of coal. The effect of the inert nitrogen pressure suggests as a possibility the substitution, for hydrogen, of the gases generated by the reaction itself. The catalyst field has barely been touched upon.

In continuing this investigation the mechanism of reaction will be studied for the dry distillation of cellulose and wood in atmospheres of hydrogen, carbon monoxide, and nitrogen, using different types of catalysts.

Acknowledgment

The writers wish to acknowledge the assistance rendered by E. V. Fasce in the examination of the liquid products.

[15] Tropsch, Lecture delivered at the Institute of Chemistry, State College, Pa., July, 1927.

Effect of Temperature on the Rate of Decomposition of Nitrocellulose[1]

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An improved method of studying the rate of evolution of nitrogen oxides from heated nitrocellulose at various temperatures has been developed.

It is shown that the logarithm of the rate of evolution of nitrogen plotted against temperature gives a straight line. The stability of the nitrocellulose sample examined is largely responsible for the slope of the resulting line. From the determination of the temperature coefficient of the decomposition rate, an idea of the stability of nitrocellulose at lower temperatures is obtained.

Additions of small amounts of various salts change the stability of nitrocellulose, as shown by the change in the temperature coefficient of the decomposition rate. This method is a valuable means of determining the effects various materials will have on stability.

STABILITY tests for nitrocellulose fall into three classes: (1) the so-called "trace tests" in which the time taken to color a very sensitive reagent paper is noted; (2) tests in which the temperature of the nitrocellulose is raised to the point where decomposition is so rapid as to be detected by less sensitive reagents or by the observance of fumes; and (3), the tests which are dependent on the quantitative determination of the products of decomposition. Probably the best known examples of these methods are, respectively, the Abel KI test, the 135° C. or German test, and the Will test. All of these tests are open to criticism. Often the Abel KI test is a measure of the accumulation of nitrogen oxides over a period of time and is not a true indication of the keeping qualities of the nitrocellulose.[2] Furthermore, unless it is carried out under strictly defined conditions, results may be obtained which may lead to erroneous conclusions as the test paper is easily affected by traces of substances present in the atmosphere. The main objection to the German and Will tests is that they are conducted at an elevated temperature and results are not necessarily indications of stability at ordinary temperatures.

Frequently a sample of nitrocellulose may be considered stable by one test but unstable when subjected to another test. This is especially true when two tests, such as the Abel KI and German test, are applied to the sample. It was therefore deemed advisable to establish, if possible, a correlation between the various methods of judging stability. The method described herein is the result of an extensive study on the subject and is offered as a better means of studying relative stabilities of uncolloided nitrocellulose.

This method of testing the stability of nitrocellulose is dependent on the determination of the rate of evolution of nitrogen oxides from heated nitrocellulose at two or more temperatures. The method of measuring the decomposition is a modification of that outlined by Philip,[3] who measured the rate of decomposition of nitrocellulose heated in air at 135° C. by absorbing the nitrogen oxides formed in a potassium iodide solution. In order to adapt the method to lower temperatures the original apparatus and method of

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[1] Received August 16, 1927.

[2] Robertson, *J. Soc. Chem. Ind.*, **29**, 133 (1910).

[3] *Ingeniörs Vetenskaps Akedemeins, Handlingar* **28**.

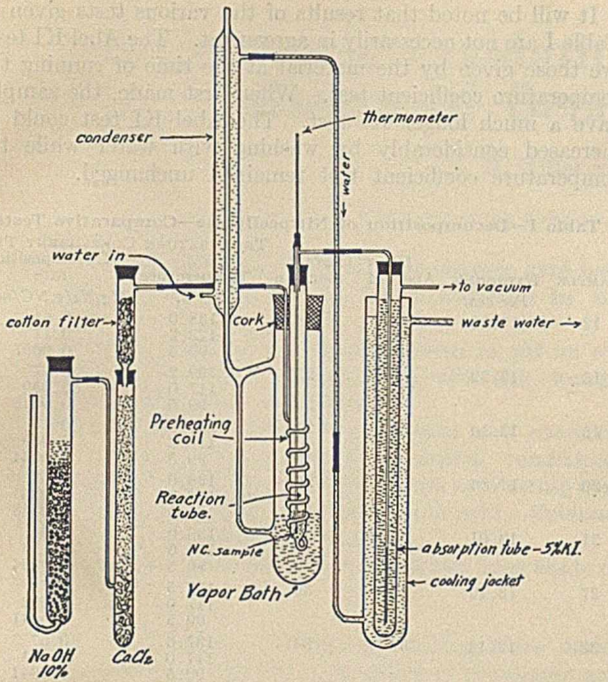

Figure 1—Apparatus for Determining Rate of Evolution of Nitrogen from Nitrocellulose

operation had to be modified considerably because of the lower rate of decomposition.

Apparatus

It was necessary to design an apparatus capable of keeping the temperature of a nitrocellulose sample constant over a long period of time. The device finally chosen was an all-glass vapor bath fitted with a reflux condenser and a side arm to return the condensed liquid to the bottom of the bath. Such an arrangement keeps a constant temperature for a long time, the only variation being the change of boiling point due to barometric variation.

A special form of decomposition tube is used for holding the sample under examination. The preheating coil serves to heat the incoming air to the temperature of the sample. The thermometer used to register the temperature of the sample was graduated to 0.1° C. and the bulb was immersed in the sample during the run.

Figure 1 shows an assembly of the complete apparatus. The air used to sweep out the products of decomposition from the reaction tube was first freed from carbon dioxide and acid gases by passing through a 5 per cent sodium hydroxide solution, dried with calcium chloride, and then filtered through a cotton filter to remove any dust picked up in the calcium chloride drying tube. After leaving the reaction tube, the stream of air was passed through a 5 per cent potassium iodide solution, which absorbed as NO_2 the nitrogen oxides given off by the nitrocellulose. The absorption tube was fitted with a capillary tip to insure good break-up of the air stream containing the NO_2. It was kept cool by a water jacket through which the waste water from the condenser circulated. This cooling was essential, for otherwise considerable iodine was lost by evaporation. With a proper absorption tube, 99 per cent of the NO_2 was absorbed by one tube. The liberated iodine was titrated by the electrometric method described by Foulk and Bawden.[4]

Reagents

Potassium Iodide—A 5 per cent solution was used to absorb the nitrogen oxides liberated by the nitrocellulose. The solution must be neutral, since alkali will react with NO_2 giving low results.

Sodium Thiosulfate—An approximately 0.01 N solution of sodium thiosulfate was used to reduce the liberated iodine. The solution was prepared by dissolving 2.5 grams of $Na_2S_2O_3.5H_2O$ to 1 liter of distilled water freed from oxygen and carbon dioxide by boiling. The strength of the solution was determined by titrating against a known weight of recrystallized iodine dissolved in a potassium iodide solution.

Experimental Procedure

The rates of decomposition of nitrocellulose were determined at three temperatures. Commercial meta-xylene was used for temperatures of 136–140° C., butyl alcohol at 116–118° C., and distilled water at 99–100° C. The main differences in temperature at any given point were due to varying compositions of the xylene and butyl alcohol. When the bath was once charged, the temperature varied only with the barometric pressure. In a few cases butyl acetate was used for temperatures between 120° and 124° C.

The samples of nitrocellulose were first air-dried and then last traces of moisture removed in a vacuum desiccator charged with phosphorus pentoxide. At the higher temperature 2 grams of sample were used, while at the intermediate and lower temperatures 5 grams were taken to shorten the time required to liberate a titratable amount of iodine.

Each sample was allowed to come to bath temperature before the absorption tube was attached. At the lower

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[4] *J. Am. Chem. Soc.*, **48**, 2045 (1926).

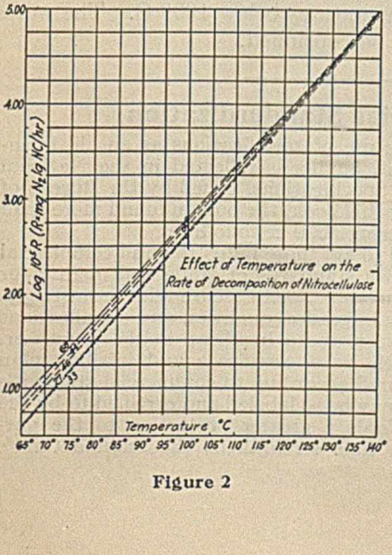

Figure 2

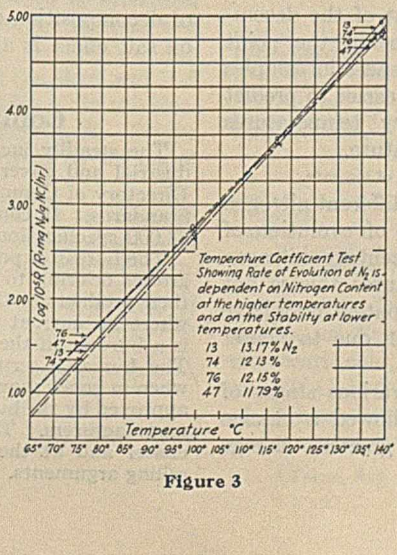

Figure 3

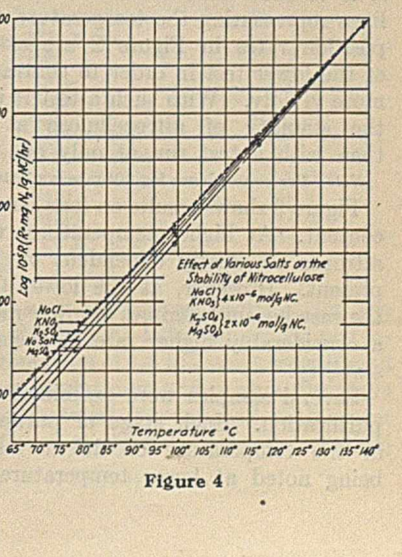

Figure 4

temperature the time required to reach bath temperature was about 15 minutes, but slightly longer periods were necessary for the higher temperatures. In addition, a somewhat longer period was necessary to reach a uniform rate of evolution of nitrogen oxides. This time varied with the temperature. One hour at 100–140° C. was sufficient.

The time of establishing the constant rate of evolution of nitrogen oxides from the nitrocellulose varied from 1 to 2 hours at the higher temperature to 16 to 20 hours at the lower temperature. Titrations were made at intervals of time depending on the temperature of the experiment. (Thirty minutes at 137–140° C., 1 hour at 116–118° C., and 3$^1/_2$ to 4 hours at 99–100° C.)

During the experiment the rate of air passing through the apparatus was not changed. The rate of flow of air showed no influence on the experiments so long as the preheating of air was sufficient or the absorption capacity was satisfactory. However, if the rate of air was changed during the experiment, a slight change in rate of decomposition was noticeable at first, but this soon became normal again. From 4 to 5 liters of air per hour were passed through the apparatus. (This comparatively high rate was probably responsible for the fact that no trouble with condensation of $NO_2 + H_2O$ was noted as in the Will test where the rate of flow of carbon dioxide is only 1 to 1.5 liters per hour.)

Results

A straight line is obtained when the logarithm of the rate of evolution of nitrogen oxides expressed as N_2 is plotted against temperature. This has been made the basis of the new stability test herewith presented. This test is dependent on the temperature coefficient of the decomposition reaction rate and will hence be the temperature coefficient test.

In Table I are given a few of the results representative of tests made on a large number of nitrocellulose samples. Most of the nitrocellulose examined was representative of that used in the manufacture of smokeless powder, although several tests were also made on lower nitration material.

Applications of Test

As a Measure of Stability—The data obtained in the temperature coefficient test can be interpreted much more clearly if the results are shown graphically. Figure 2 shows some of the results of the nitrocellulose samples given in Table I. At higher temperatures there is practically no difference in samples of the same nitration, but as the temperature decreases the samples show greater differences. The lower the temperature at which samples are compared the easier it is to show differences in stability. For this reason the lines representing the temperature coefficient of the decomposition rates in Figure 2 are extended below the point of the lower test in order to contrast differences in samples more vividly. With such a test it is much easier to predict the stability of nitrocellulose at ordinary temperatures than with a test run at only one temperature.

Note—For convenience log 10^5 rate is plotted instead of log rate.

Figure 3 shows results on four samples of different nitrogen content. At higher temperatures the rate of evolution of nitrogen is greatly dependent on the percentage nitrogen present. However, at the lower temperatures this is not the case because samples of lower nitrogen content may have a considerably higher rate of decomposition due to poorer stability.

Several samples were examined during various stages of purification. Each stage of purification showed a change in the temperature coefficient test, the greatest change being noted at lower temperatures.

It will be noted that results of the various tests given in Table I are not necessarily in agreement. The Abel KI tests are those given by the material at the time of running the temperature coefficient test. When first made, the samples gave a much longer KI test. The Abel KI test could be increased considerably by washing with water while the temperature coefficient test remained unchanged.

Table I—Decomposition of Nitrocellulose—Comparative Tests

		Heat Tests		Temperature Coefficient Test	
Sample	Nitrogen	Abel KI	German	Temperature	Decomposition rate
	Per cent			° *C.*	*Mg.N$_2$/g.NC/hour*
12	13.26	5	26	138.0 123.2 99.5	0.61 0.11 0.0057
13	13.22	4	25	139.2 117.0 99.5	0.87 0.050 0.0048
15	13.10	10	24	137.8 118.2 99.5	0.74 0.059 0.0054
20	12.86	5	25	136.0 118.7 99.5	0.53 0.055 0.0048
21	13.01	5	27	136.0 123.6 99.5	0.61 0.118 0.0054
27	13.19	47	30	137.5 117.0 99.5	0.71 0.042 0.0041
33	12.13	38	34	137.6 117.0 99.5	0.67 0.041 0.0041
44	13.07	34	25	138.7 116.2 99.3	0.86 0.051 0.0052
46	13.20	34	27	138.6 116.0 99.0	0.85 0.046 0.0048
68	13.25	29	30	138.5 117.2 99.5	0.83 0.055 0.0060

As a Method of Studying the Effect of Various Materials on Stability—The presence of certain materials in nitrocellulose changed the stability of the sample. The effect of the addition of small amounts of various salts to nitrocellulose was studied. The salt was dissolved in sufficient water to wet the nitrocellulose thoroughly, after which the water was evaporated leaving the salt adsorbed on the fibers.

In Figure 4 are shown results obtained with various salts. The change in the temperature coefficient test by the addition of such small amounts of impurities is a further indication that the temperature coefficient of the decomposition rate is dependent on stability and is therefore a good means of determining stability.

Further Work in Progress

The study is still under investigation and with more precise methods it should be possible to establish the rate of decomposition at temperatures below 100° C. The work on salt effect is also to be continued.

Commercial Standardization

The steadily increasing use of specifications as an aid in industrial and governmental buying is reflected in the National Directory of Commodity Specifications, issued by the Bureau of Standards. In compiling this book, the bureau found more than 27,000 specifications covering 5000 commodities.

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Atmospheric Oxidation of Methyl and Glycol Esters of Beta-Eleostearic Acid[1]

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The methyl and glycol esters of β-eleostearic acid have been prepared, the glycol ester being obtained in fair purity.

An empirical method for determination of pH on oils is given and the data obtained align with the changes of other variables upon oxidation.

Studies have been made of the physical and chemical changes upon oxidation under controlled conditions. These indicate the formation of polymers containing considerable added oxygen and condensed split acid. Evidence of ketol and enol formation is noted.

Comparison of these studies with similar ones made on β-eleostearic acid and its glycerol ester indicates the importance of consistency upon the trend of reaction and on the final product.

A hypothesis is proposed to account for the observed relation between the various esters as evidenced in oxidational trend and in the properties of the reaction polymers. This hypothesis assumes that an important function of the valency of the alcohol is the stability it imparts to the ester, thus determining the tendency to split off β-eleostearic acid, which through condensation and aggregation of its long carbon chains actively influences gel formation.

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A KNOWLEDGE of the changes taking place during atmospheric oxidation of the esters of eleostearic acid with mono- and dihydric alcohols should furnish valuable information relative to the oxidation of tung oil and to its gel formation. With this in mind the general study of the atmospheric oxidation of tung oil, the first part of which consisted of an investigation of the effect of oxidation on tung oil and on α- and β-eleostearic acid and β-eleostearin,[2] has been continued by the preparation of the methyl and the di-acid glycol esters of β-eleostearic acid and their subsequent treatment.

While the polymerization of the methyl ester in an atmosphere of carbon dioxide has been investigated,[3] no systematic study of its oxidation has been made. The same may be said in regard to the glycol ester, and in the latter case the investigators[3,4] make no reference either to the method of preparation or to the purity of the material obtained.

Apparatus

The apparatus is shown in Figure 1. Air, admitted through the reducing valve, *R*, was measured with the meter, *M*, and its volume controlled with the aid of the differential flowmeter, *F*. The air was then conditioned to the desired absolute humidity by bubbling through water and sulfuric acid mixtures of the proper density[5] in the absorption tubes, A_1, A_2. It was blown into the charge through eight holes of 1 mm. diameter which were equally spaced in a circular 1-cm. pipe lying on the bottom of the reaction vessel, *K*, and connected with the inlet pipe, *I*.

The reaction vessel, *K*, a Pyrex jar 22.8 cm. deep and 12.5 cm. inside diameter, was immersed in paraffin oil in the electrically heated, thermostatically controlled bath, *B*. Proper circulation of the oil in the bath was secured by means of the agitator *S* driven 2065 r. p. m.

Mixing of the charge was effected with the agitator S_2, a 6-mm. vertical shaft through which were placed alternately at right angles fifteen pieces of rod 3 mm. in diameter and 5 cm. in length. This agitator revolved at a speed of approximately 1430 r. p. m.

The spent air and fumes were withdrawn through the outlet pipe, 7, inserted in the lid of the reaction vessel. Samples of the charge were withdrawn through the thermometer hole 5.

Materials

TUNG OIL—Two lots of commercial tung oil used in the preparation of the esters had the following constants:

	LOT 1	LOT 2
Specific gravity, 20°/20° C.	0.9390	0.9390
Refractive index at 20° C.	1.5200	1.5189
Acid number	2.91	5.49
Saponification number	194.3	197.8
Iodine number (Hübl)	171.4	173.15
Browne heat test, minutes	11.75	12.25

β-METHYL ELEOSTEARATE—This was prepared by the esterification of α-eleostearic acid (m. p. 46–48° C.) with 98 per cent methanol in the presence of 3.5 per cent dry hydrochloric acid. The mixture was allowed to stand overnight, washed first with dilute sodium bicarbonate solution, then with concentrated calcium chloride solution, dried over calcium chloride, and finally distilled *in vacuo* using an atmosphere of carbon dioxide whenever possible. The distillate was a limpid, colorless oil of low viscosity. Saponification yielded β-eleostearic acid (m. p. 67–68° C.).

The material had the following constants:

	DETERMINED	THEORETICAL[a]
Boiling point, ° C.	171 (6 mm.)	209 (10 mm.)
Iodine number	166	172.8
Saponification number	215	190.5
Oxy acids	3.2	0.0
Acid number	0.0	0.0
Molecular weight	295[b]	294
Refractive index	1.4938 (20° C.)	1.4842 (12° C.)
	ULTIMATE ANALYSIS	
	Per cent	*Per cent*
Carbon	75.7	77.5
Hydrogen	11.78	11.58
Oxygen	12.52	10.89

[a] Morrell, *J. Soc. Chem. Ind.*, **37**, 181T (1918).
[b] Determined in benzene.

β-GLYCOL DIELEOSTEARATE—This was prepared by the method of Ruttan and Roebuck.[6] Ethylene glycol and α-eleostearic acid, in the proportion of 1.5 to 2 mols, were stirred at 180° C. in the presence of platinum and in an atmosphere of carbon dioxide. The material was washed with water and an unsuccessful attempt made to remove the residual

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[1] Presented before the Division of Paint and Varnish Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Paper presented before the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[3] Nagel and Gruss, *Z. angew. Chem.*, **39**, 10 (1926).

[4] Fonrobert and Pallauf, *Chem. Umschau Fette, Oele, Wachse, Harze*, **33**, (*a*) 1, (*b*) 41 (1926).

[5] Wilson, *Ind. Eng. Chem.*, **13**, 326 (1921).

[6] *Trans. Roy. Soc. Can.*, [3] **9**, June, 1915.

acid, which amounted to 8 per cent. The product was a yellowish liquid which on standing yielded a white, semicrystalline solid, apparently an agglomerate of crystals of the ester and oxidized material. The acid liberated on saponification was the beta acid (m. p. 67–68° C.).

The ester thus prepared had the following constants:

	DETERMINED	THEORETICAL
Iodine number	144	173.1
Saponification number	157	191.0
Acid number	16.15	0.0
Molecular weight	556[a]	586
Oxy acids	6.7	0.0
	ULTIMATE ANALYSIS	
	Per cent	*Per cent*
Carbon	75.3	77.8
Hydrogen	12.01	11.28
Oxygen	12.69	10.91

[a] Determined in stearic acid.

Examination of the constants indicates that the material is the di-acid ester containing 8 per cent free eleostearic acid and some oxidized material, but with little or no glycol monoeleostearate present.

Analytical Methods

Standard methods of analysis were used whenever possible, but with these modifications. The iodine number was determined by the Hübl method, dibutyl phthalate being used as a solvent in the case of the glycol ester; the sample was heated in 10 cc. until dissolved. Molecular weight was determined cryoscopically using acetic acid, benzene, and stearic acid, the stearic acid being the most satisfactory. Ostwald pipets were used to measure viscosity. Ketones were estimated by Straches' method.[7] Free methanol was determined by Wright's method,[8] and the combined methanol by splitting the ester with sodium hydroxide, distilling, and analyzing the distillate.[9] The hydroxyl groups were estimated on the basis of increase of weight when acetylated for several days with freshly distilled acetic anhydride at 30° C. in a sealed vessel. In the case of the more insoluble gels solution was first effected in dibutyl phthalate and a correction made for the blank.[10] Since this work has shown that these substances give off little volatile matter upon oxidation, ultimate analysis was used to determine the amount of oxygen absorbed. The active acidities were determined by an empirical pH method. One gram of the material was dissolved in 10 cc. of carbon tetrachloride, shaken in a separatory funnel with 50 cc. distilled water, and the pH obtained colorimetrically.

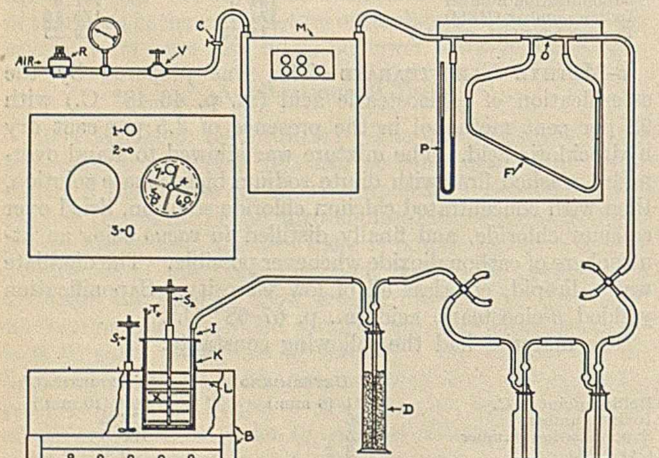

Figure 1—Apparatus for Study of Atmospheric Oxidation of Methyl and Glycol Ethers of β-Eleostearic Acid

Note—Though the significance of the figures obtained by this method has not been exhaustively studied, at present it may be said that they indicate to a considerable degree the active acidity of the oil, as well as some of its adsorptive properties. The method has shown interesting possibilities in oil studies in this laboratory and further work is being done on it.

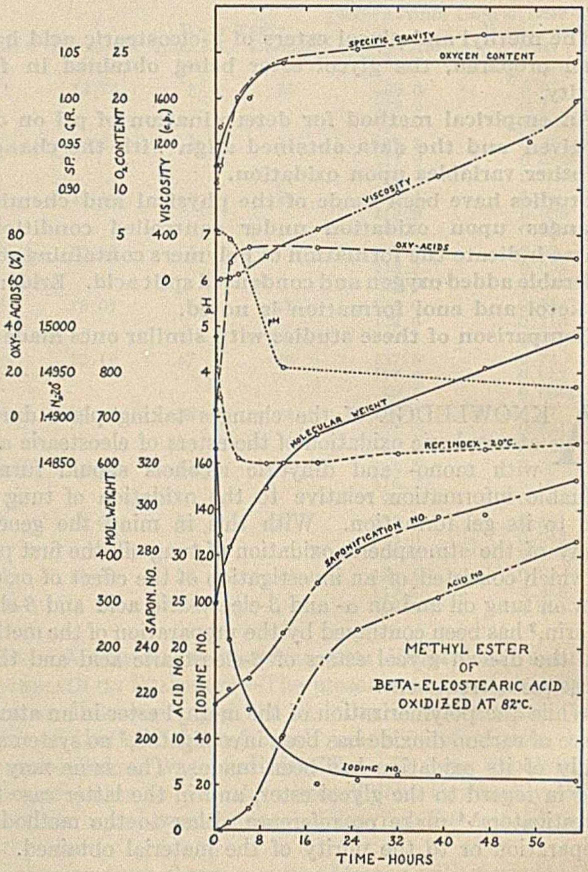

Figure 2

Experimental Procedure

The oxidation of the esters, in 400-gram lots, was conducted at a temperature of 82° C. After the material was placed in the reaction vessel, it was allowed to melt before the agitator was started and the air turned on. The air was conditioned to a relative humidity of 10 per cent at 25° C., instead of 35 per cent as in the oxidation of the eleostearic acids and the β-eleostearin. The amounts of air employed were 292 cc. per minute when treating the methyl ester and 274 cc. per minute when treating the di-acid glycol ester.

The rate of reaction of the methyl and glycol esters was accelerated by minor changes in the construction of the apparatus, and the times of processing, when compared with those for the acid and the glycerol ester, should be even greater than the figures indicate.

In addition to these two principal runs, small batches, about 150 grams, of β-eleostearic acid and its glycerol ester were treated in a similar manner and the spent air and fumes were conducted through two calcium chloride (free from CaO) tubes and then through alcohol. The amount of water given off was thus determined and the alcoholic solutions were analyzed for acid and aldehyde decomposition products.

Product Application

The product obtained upon treatment of the glycol ester was employed as the binder in a typical linoleum mix. It

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[7] *Monatsh.*, **12**, 514 (1891); **13**, 299 (1892).

[8] *Ind. Eng. Chem.*, **19**, 750 (1927).

[9] Norris, "Organic Chemistry," p. 166.

[10] Ellis, *J. Soc. Chem. Ind.*, **45**, 27, 193T (1926).

Table I—Methyl Ester of β-Eleostearic Acid Oxidized at 82° C.

Sample	Time	Iodine No.	Saponification No.	Oxy Acids	Acid No.	pH	Sp. Gr.	Mol. Wt.[a]	Refractive Index	Viscosity (25° C.)	Ultimate Analysis
	Hours			Per cent					(20° C.)	Centipoises	Per cent
1	0.0	166	215	3.2	...	7.1	0.9065	295	1.4988	8	C—75.7 H—11.78 O—12.52
2	1.0	128.49	...	...	0.0	...	0.9259	...	1.4921	24	C—71.77 H—11.25 O—16.98
3	2.5	83.00	221.5	68.1	0.8	6.9	...	419	...	61	
4	4.0	...	...	...	...	...	1.003	...	1.4855	124	
5	6.0	52.71	226.2	74.9	2.4	...	...	...	...	...	C—69.05 H—10.95 O—20.03
6	9.0	...	...	...	...	...	1.0317	545	1.4850	473	
7	12.0	41.06	246	...	10.4	4.1	...	...	1.4850	...	C—66.7 H— 9.50 O—23.80
8	18.0	20.03	268	74.8	...	...	...	662	1.4851	911	
9	25.0	22.52	282.0	...	21.9	...	1.0538	...	...	...	
10	32.0	24.35	...	...	...	...	...	...	1.4861	1622	
11	39.0	24.12	297.2	...	25.5	...	...	...	...	1913	
12	47.0	...	298	...	...	...	1.0700	810	1.4867	2542	
13	63.0	22.50	313	70.4	31.6	3.7	1.0750	888 864[b] 444[c]	1.4872	3280	C—66.55 H— 9.55 O—23.90

[a] Determined in benzene, except where otherwise noted.
[b] Determined in stearic acid.
[c] Determined in acetic acid.

showed very great capacity for absorption of filler and gave a piece of material which, after rapid maturing, had a tensile strength of 40.1 kg. per sq. cm., an elongation of 13.7 per cent at 21° C., and was extremely flexible. The material had but slight odor and possessed characteristics which made it much more desirable than similar substances made with the oxidation products of the acids or the glyceride as the cementing medium. Its probable stability on aging makes it of particular interest.

The colorless heavy oil resulting from oxidation of the methyl ester at normal temperatures has properties which suggest its possible application as a plasticizer.

Discussion

β-Methyl Ester (Table I)—This batch is characterized by vigorous oxidation accompanied by a minimum of physical change; the material takes on 13 per cent of its weight of oxygen and merely changes to a dark brown oil. This is in striking contrast to a material like β-eleostearin, which becomes a typical gel upon taking up 3 per cent oxygen.

The chemical saturation of the ester with oxygen is both rapid and complete, as shown in Figure 2. The iodine number of the material is down to 20 by 18 hours, the oxy acids are up to their maxima at 6 hours, and the ultimate analysis of the 19-hour sample checks that at 63 hours. After this brief period of oxidation dominance the variables change more gradually and uniformly owing to the extraneous influences of heat, agitation, and moisture. This condition gives rise to definite critical points on the curves where oxidation dominance is lost. The only curve remaining practically a straight line is that for viscosity, which feature suggests a constant agglomeration by heat, though undoubtedly considerably peptized by the increasing acidity of the system.

Two distinct fractions of the end product of the methyl ester oxidation have been separated on the basis of their solubility in petroleum ether. The indication of the present data is that they are each fairly simple and that the insoluble fraction is a simple polymer of the soluble one. The fraction soluble in petroleum ether may be regarded as consisting chiefly of molecules of oxidized methyl ester with split acids condensed at one or more ethenoid linkages and some free acid. The insoluble fraction shows only slightly greater oxidation than the soluble fraction. The indications are that it is a polymer of the soluble portion averaging 4 molecules (molecular weight 3.86 times that of the soluble portion). The acid number of this fraction suggests one free carboxyl to the quatre-polymer (theoretical acid number, 37.2; found, 35.6).

The evidence is conflicting as to the amount of methoxyl present in the end product, analyses varying from 3.68 per cent by the Norris method to 9.95 per cent calculated from the total acids; it is believed, however, that the second result is the more reliable. This gives a loss of methoxyl of 0.55 per cent, which goes off as formic acid and probably formaldehyde.

Apart from oxidation, the most evident feature is splitting. Rising saponification number, acid number, and pH are associated with only a 5 per cent loss of methoxyl, which is not sufficient to account for the observed rise in saponification and acid numbers. The distillate from vacuum distillation appears to be composed chiefly of split acids liberated from the polymer under the influence of heat. (Table III)

The other evident reaction is condensation of split acids at ethenoid linkages. The increase in the saponification number is 310 per cent of the acid-number rise, indicating that the larger portion of the split acids has been rebound to the molecule in such a manner that the hydrolysis produced by the caustic may free them again. Such hydrolysis would produce hydroxy acids when total acids are prepared. 6.67 per cent hydroxyl are found in the total acids and only 1.95 per cent in the end product itself.

Though no study was made of the ketol and enol groups of the two fractions, the study of them in the end product itself is of interest in the light of Ellis' work on linseed oil.[10] Carbonyl and hydroxyl were found in the proportion of one ketol group per molecule of 888 weight (theoretical 3.1 per cent CO, found 3.56 per cent; theoretical 1.93 per cent OH, found 1.95 per cent). The amount of hydroxyl in the total acids of the end product indicates one hydroxyl group per molecule of 558 molecular weight (theoretical 3.83 per cent OH, found 4.63 per cent) apart from that in the ketol.

The fact that aldehydes are found in the distillation products of the end sample and indicated in several other places suggests aldehyde condensation as an item in the polymerization. Lactone and anhydride formation are of no importance since the end sample shows only a trace of unsaponifiable matter.

Ultimate analysis of the end sample indicates that, apart from added oxygen, there is little or no change in percentage composition. With 13 per cent oxygen taken on, the change in percentage is: C, theoretical 67.2, found 66.5 per cent; H, theoretical 10.05, found 9.55 per cent.

The end product is briefly an isocolloid-like fluid consisting of thoroughly oxidized methyl ester in which is dissolved a heavier liquid which is approximately a quatre-polymer of it. The lighter liquid has taken on about three molecules of oxygen per molecule and the heavier a proportional amount. The entrance of this oxygen, though splitting the ester only slightly, splits the eleostearic acid notably. Condensation of split acids at open bonds takes place as well as the possible formation of ketol and enol groups. There is likewise indication of aldehyde formation.

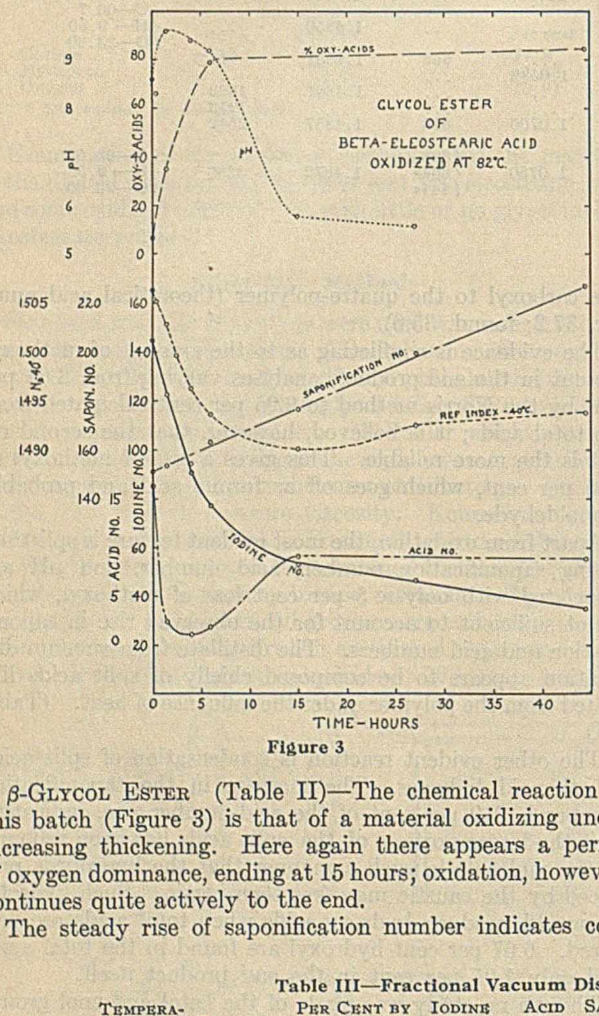

Figure 3

β-Glycol Ester (Table II)—The chemical reaction of this batch (Figure 3) is that of a material oxidizing under increasing thickening. Here again there appears a period of oxygen dominance, ending at 15 hours; oxidation, however, continues quite actively to the end.

The steady rise of saponification number indicates considerable splitting and the initial sharp drop in acid number and the differential between the later rise in acid and saponification numbers indicate condensation of acids at open linkages.

Table II—Glycol Ester of β-Eleostearic Acid Oxidized at 82° C.

Sample	Time	Iodine No.	Saponification No.	Oxy Acids	Acid No.	pH	Refractive Index	Ultimate Analysis
	Hours			Per cent			(40° C.)	Per cent
1	0.0	144.95	151.0	6.7	16.15	8.6	1.5063	C—75.3 H—12.01 O—12.69
2	0.5	...	...	...	...	8.4	1.5052	...
3	1.5	122.33	153.5	35.4	2.34	9.6+	1.5028	...
4	2.5	...	(161.1)	...	...	...	1.4997	...
5	4.0	90.28	154.1	...	1.04	9.4	1.4963	...
6	6.0	77.28	163.7	79.4	1.82	9.2	1.4936	...
7	15.0	53.05	176.6	...	9.12	5.8	1.4902	...
8	27.0	46.47	200.0	...	...	5.6	1.4926	...
9	44.5+	34.80	227.0	84.3	8.85	...	1.4938	C—66.8 H—10.61 O—22.59

The ultimate analysis of the last sample indicates an 11 per cent increase of oxygen without any other change in percentage composition: C, theoretical 67, found 66.8 per cent; H, theoretical 10.7, found 10.61 per cent. This analysis corresponds to the taking up of almost 4 molecules of oxygen per molecule of the original ester.

The evidence points to a splitting of the beta acid from one of the hydroxyls of the glycol. The hydroxyl found in the end product is 9.33 per cent, which is in considerable excess of the free OH groups in its oxy acids (it must be noted also that the method of determination does not detect hydroxyl in free glycol). This formation of the monoglycol ester would also partially explain the abnormally low total acids; the adsorbed water noted in the petroleum ether extract would account for most of the rest. The fact that the molecular weight of the total acids is higher than that of the methyl ester acids suggests greater condensation of beta acid than of split acids, as would be expected under these circumstances.

The end product is briefly a hygroscopic, colloidal gel, which consists of polymers of a well-oxidized mono-acid glycol ester in which the split-off acid and split-up acids are largely condensed at open bonds. The hydroxyls of the total acids indicate possible enol and ketol formation.

Since the residual acid in the untreated material is rapidly condensed and since splitting and condensation of split acid take place immediately, there is not much likelihood that the course of the reaction is markedly influenced by its presence.

Table III—Fractional Vacuum Distillation of Beta Methyl Ester End Product

No.	Temperature	Pressure	Per Cent by Volume	Iodine No.	Acid No.	Saponification No.	Physical Properties and General Observations
	° C.	Mm.					
1	40–45	7	0.7	...	...	...	Aldehyde containing material immiscible with water; negative test for CH_3OH; colorless
2	45–70	9	2.7	...	...	...	One-fourth colorless; three-fourths deep yellow
3	110–135	7	2.5	27.46	...	...	Green-yellow
4	135–170	6	5.7	...	102	302	Green-yellow
5	170–172	6	9.5	20.21	131	...	Brown-yellow; redistilled fraction indicates no aldehyde esters; little evidence of unchanged ester
Residue			59.7	...	...	...	Heavy black tar

Note—Material shows signs of decomposition from beginning of distillation.

Table IV—Fume Analysis

Material	Time	Acid	pH	CHO	H_2O
	Hours	Per cent		Per cent	Per cent
Beta methyl ester	0–63	Present	2.8 (Equiv. conc. HCOOH) 2.7	Present[a]	...
Beta glycerol ester	0–1	0.004 as CH_3COOH	4.1 (Equiv. conc. CH_3COOH) 3.6	0.55	0.786
	1–3	0.0065 as CH_3COOH	3.4 (Equiv. conc. CH_3COOH) 3.4	0.20	0.491
	Total	0.01 as CH_3COOH		0.75[b]	1.277
Beta acid	0–13.25	0.003 as HCOOH	2.8 (Equiv. conc. HCOOH) 3.0	0.58	0.612

[a] Fair test for formaldehyde.
[b] Probably largely acrolein from glycerol decomposition.

Fume Analysis (Table IV)—The analysis of the volatile products in the case of the methyl and glycerol esters and the acid shows that little volatile matter is given off under these conditions and this apparently is derived from both the decomposition of the alcohol radical and the acid. The water given off evidently comes from condensation as well as from decomposition.

General Relationships

The relationships of the courses of oxidation and of the end products of these esters to those of the β-eleostearic acid and β-eleostearin studied in the previous paper, as summarized in Tables V and VI, indicate a transition of properties in the order: methyl ester, glycol ester, beta acid, glycerol ester.

Table V

COMPARISON OF BETA-ELEOSTEARIC ACID AND ITS ESTERS ON OXIDATION				
	METHYL ESTER	GLYCOL ESTER	ACID	GLYCEROL ESTER
HOURS RUN	63	44	29	13
ORIGINAL MOL.WT.	294	556	280	± 878
ORIGINAL PHYSICAL PROPERTIES	WATER-WHITE LIGHT OIL	WHITE PASTE	WHITE CRYSTALS M.P. 68°	WHITE CRYSTALS M.P. 58°
IODINE NO.	LARGE DROP TO 22.5	LARGE DROP TO 35	SLIGHT DROP TO 113	SLIGHT DROP TO 124
ACID NO.	LARGE RISE	SOME RISE	LARGE DROP	SLIGHT DROP
SAPONIFICATION NO.	LARGE RISE	FAIR RISE	SLIGHT DROP	SLIGHT DROP
pH	DROP	RISE THEN DROP	RISE THEN DROP	RISE
OXY-ACIDS	LARGE RISE	LARGE RISE	MODERATE RISE (SPECIAL METHOD)	FAIR RISE
REF. INDEX	SHARP DROP—THEN RISE	DROP THEN RISE	SMALL DROP	FAIR DROP
OXYGEN ABSORBED	13%	11%	6.5%	3%
PHYSICAL PROPERTIES OF END SAMPLE	DARK BROWN OILY LIQUID	DARK BROWN, TACKY, ELASTIC GEL.	YELLOW-BROWN, TOUGH, ELASTIC GEL	YELLOWISH-WHITE, SHORT, FRIABLE GEL
% PET. ETHER. SOL.	51.7	12.86	0.7	53.4

The alcohol radical of the eleostearic acid ester influences the rapidity and thoroughness of oxygen absorption owing to the molecular size of the ester which it forms with eleostearic acid and to the physical properties of the ester under reaction conditions. The more fluid the material is originally and the more it remains so, the better the opportunity for rapid and complete saturation. This, in the case of the methyl and glycol esters, results in completeness of oxygen absorption (Figure 4).

The physical properties of the end products show the transition most interestingly. The methyl ester, after 63 hours' processing, is still fluid and distinctly oily in feel, suggesting that the molecules and micelles are of such shape, polarity, and size that internal friction is low. Its total acids are a brown, sticky liquid. The glycol ester, after 45 hours' processing, becomes a sticky, elastic gel. This transition was gradual and even the end material was somewhat fluid at the processing temperature. This suggests a material of gelling tendency, consisting largely of one phase (the surface of the gel does not dry). Such a material is doubtless one of greater molecular weight than the former and probably has more elongated or irregular molecules and micelles. Its total acids are similar to those of the methyl ester, but more viscous. The beta acid, after 29 hours, became a tough, elastic gel, incompletely oxidized and evidently of two phases (high iodine number and surface drying of gel). Its total acids are a brown, semisolid paste with slight smectic structure. The β-glycerol ester gives a short gel, which microscopic examination shows to be composed of relatively few burr-like micelles of oxidized material holding pasty, less thoroughly oxidized matter between them. Its total acids are a brown and white solid paste with strong smectic structure.

The paradoxical position of the beta acid in this series as well as other data, chief of which are the percentage hydroxyl and the properties of the series of total acids liberated from the above, leads to what is thought to be a new hypothesis concerning the function of the alcohol valency on the trend of ester oxidation and on the properties of the resulting polymer.

Fonrobert and Pallauf[4b] postulate polymerization of China wood oil by reësterification of multibasic acids, formed by the linking of acids to each other at their open bonds, with multivalent alcohol molecules of the former linking esters of the latter. A condition analogous to this arises with ketol or enol formation at ethenoid linkages of an unsaturated fatty acid, converting it into an hydroxy acid which functions as a multivalent alcohol.

Though there is conflicting evidence that β-eleostearic acid forms such an oxidation polymer, the same cannot be said of the esters studied, since they all show notable condensation of fatty acids at ethenoid linkages.

Table VI—Data on Oxidized Materials

Material	Per Cent	Iodine No.	Acid No.	Saponification No.	(OH) Per cent	(CO) Per cent	Ultimate Analysis Per cent	Mol. Wt.	Physical Properties
Beta methyl ester		22.50	31.6	313	1.85	3.56[a]	C—66.55 H— 9.55 O—23.90	888[d]	Dark brown heavy oil
Beta glycerol ester		34.80	8.85	227	9.33	...	C—66.88 H—10.61 O—22.59	...	Dark brown elastic gel
Beta acid (1)		113.16	90.6	195.5	...	...	C—71.55 H—10.30 O—18.14	...	Brown tough gel
(2)					5.45				Brown tough gel
β-Eleostearin (1)		124.21	0.52	186.0	...	...	C—75.02 H—10.86 O—14.12	...	Yellow white semigel
(2)		128.64	0.0		3.75				Yellow white semigel
Total acids beta methyl ester	95.5	40.98	...	248.0	6.67	3.4	C—65.7 H—10.73 O—23.57	558[e]	Dark brown sticky material
Total acids beta glycol ester	67.1	31.43	...	342	6.86	...	C—67.9 H—10.23 O—21.87	605[e]	Same, but more viscous
Total acids β eleostearin (2)	97.5				7.21				Brown and white solid paste; strong smectic structure
P. E. extract beta methyl ester	57	23.79	29.2				C—67.3 H— 9.59 O—23.11	390[a]	Yellow, light oil
P. E. insoluble beta methyl ester	43	20.1[a]	35.6[a]				C—65.55[a] H— 9.61 O—24.84	1505[e]	Dark brown heavy oil
Beta acid (2) total acids	97.5					5.10			Brown semisolid paste, slight smectic structure
P. E. extract beta glycol ester	12.8								Large portion water, also a light oil
Beta methyl ester blown at 25° C. 1.5 days		60.03	1.3						Heavy colorless oil (strong peroxide test)
Beta glycol ester air-dried film 1 day		55.37	18.3						Dry white, wrinkly film
Total distillation beta methyl ester[b]	20[c]							194[e]	Yellow, light oil

[a] Calculated.
[b] See Table III.
[c] By volume.
[d] Determined in benzene.
[e] Determined in stearic acid.

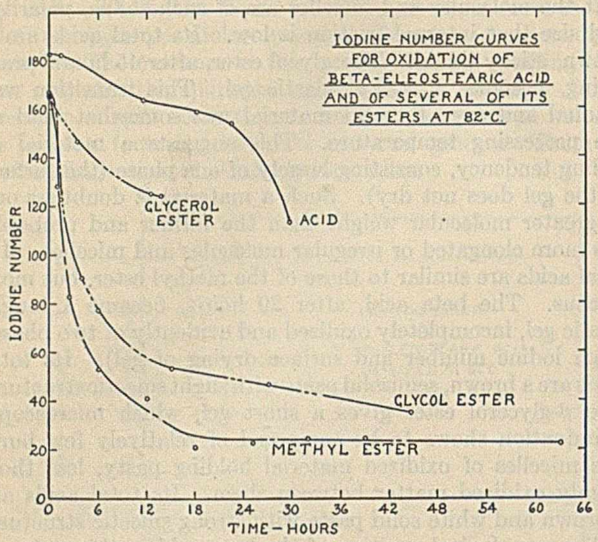

Figure 4

Since the observations indicate that the alcohol holds its acid tightly in the case of the methyl ester, that the glycol ester goes over to a mono-acid ester, and that the glycerol radical of the eleostearin decomposes (total acids rise from 91 to 97.5 per cent), it may be postulated that an important function of the alcohol valency is in determining the stability of the ester and preventing the β-eleostearic acid, with its long chain and ethenoid linkages, from condensing at open bonds, which condensation is highly favorable to polymerization and colloidal aggregation. Even if the beta acid so released does not condense at open bonds, these free, long chains would mesh with the ester polymers and, since the acid is solid at normal temperatures, would be of great assistance in gel formation.

Under this hypothesis the oxidized methyl ester may be pictured with its condensation polymer having only the simpler acids condensed at its open bonds and its quatre-polymer being more compact and regular than if these condensed acids had longer chains. The oxidized glycol ester may be visualized as the mono-acid ester with beta-acid chains condensed here and there at its open bonds and at the open bonds of the condensed acids, making possible a system composed of numerous highly complex polymers. Even though it is assumed that oxidized beta acid does not form condensation polymers, it may be pictured as giving rise to a gel by intermingling of the straight chains with oxidized and polymerized molecules which have changed in shape and size. The oxidized glycerol ester may be pictured as splitting off beta acid with subsequent decomposition of a portion of the glycerol as well as notable condensation of the beta acid at open bonds (hydroxyl rises from 3.75 to 7.21 per cent on liberation of total acids and 1.28 per cent water is given off during processing). Inasmuch as the condensation polymers of these long beta-acid chains are still linked to a considerable extent to glycerol radicals, a condition exists most favorable to polymer building and aggregation, thus precluding thoroughness of oxidation.

In brief, the end products of the esters and acids studied may be visualized, in the light of this work, as being tangles of long carbon chains deformed by oxidation and condensation.

Acknowledgment

The authors express their thanks to the Armstrong Cork Company for permission to publish the results of this investigation.

Odors and Sewage Sludge Digestion[1]

I—Effect of Sea Water on Hydrogen Sulfide Production[2]

Willem Rudolfs and P. J. A. Zeller

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SEWAGE plants in the proximity of the seaboard often produce strong hydrogen sulfide odors which are apparently due to unfiltered sea water. Sewage led directly into the sea produces also considerable odor at the places of contact with sea water. Sometimes with high tides sea water backs into sewage-disposal plants located a considerable distance inland and has been reported to affect the digestion processes. Two types of materials may be involved, sulfates and sodium chloride. A number of treatment plants in the country receive comparatively large quantities of sulfates discharged by manufacturing processes and others are affected by salt water from mines or brine from industries.

The studies reported in this paper were designed to throw light upon the following points:

(1) Effect of the presence in sea water of sulfates (Ca and Mg), sodium chloride, and a combination of the two upon the rate of sludge digestion.

(2) Effect upon gas production caused by a possible retardation of the rate of digestion.

(3) Effect upon the composition of the gas.

(4) Relation between sulfate reduction and quantity of hydrogen sulfide present in the gas.

Experimental Procedure

Ripe sludge and fresh solids were mixed on the basis of dry volatile matter in the proportion of 1:1.2. Analyses of fresh solids, ripe sludge, and sea water used are given in Table I.

Table I—Analysis of Material Used

MATERIAL	pH	SOLIDS	ASH	CHLORIDES	SULFATES	ALKALINITY
		%	%	*P. p. m.*	*P. p. m.*	*P. p. m.*
Ripe sludge	7.5	6.39	48.2	129	144	5200
Fresh solids	5.7	5.14	21.3	116	48	770
Sea water	8.0	2.74	78.4	13,050	1985	900

To these mixtures different quantities of sea water were added and the resultant mixtures analyzed (Table II). All mixtures were brought to the same volume by addition of distilled water, and incubated at 20–22° C. Gas production was recorded daily and all the gas analyzed at intervals after being collected and stored over gas-saturated water. The mixtures were analyzed again after 44 days' incubation.

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[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Paper No. 365 of the Journal Series of the New Jersey Agricultural Experiment Stations, Department of Sewage Disposal.

Table II—Analyses of Mixtures at Beginning and End of Experiment

Mixture	pH	Solids	Ash	Chlorides	Sulfates	Alkalinity	B. O. D.	Sea Water in Sludge
		%	%	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*Cc./L.*
				BEGINNING				
A	7.4	2.62	36.0	58	61	1480	2240	0
B	7.5	2.81	36.8	796	155	1420	2000	100
C	7.5	3.27	44.8	3635	550	1465	1990	500
D	7.5	3.96	50.0	7000	1020	1520	1870	1000
				END				
A	7.5	1.96	45.3	57	14.8	2805	705	0
B	7.5	2.17	46.5	710	3.3	2920	660	100
C	7.5	2.68	51.8	3410	18.1	3280	640	500
D	7.7	3.37	57.5	6710	21.4	3740	760	1000

The analyses at the end of the experiment (Table II) show that in every case digestion had progressed to the extent that the mixture could be pronounced as ripe sludge. Sludge could have been drawn earlier from *A*, *C*, and *D*, as indicated by the rate of gas production (Figure 1). There was no appreciable difference between the mixture with the smallest quantity of sea water and that which received no sea water. The percentage volatile-matter reduction and total amounts of gas produced after 44 days were as follows:

	Mixture	Volatile Matter Reduction	Gas per Gram Volatile Matter
		%	*Cc.*
A	No addition	29.8	438
C	500 cc. sea water	28.3	466
D	1000 cc. sea water	27.8	498

The percentage volatile-matter reduction of the treated mixtures was but slightly less than in the untreated mixture. This indicates some retardation of the digestion processes, but it is more definitely shown by the curves for daily gas production (Figure 1), since the initial retardation has been overcome after the more prolonged period of digestion. In the untreated material the peak of gas production occurred after 10 or 12 days, whereas with a medium amount of sea water this peak occurred after 17 days and with the largest amount of sea water after 18 days. Gas production from the untreated mixture increased rapidly from the beginning of incubation and was followed by a rapid decrease. The mixture receiving a medium amount of sea water started off with a higher gas production than the untreated mixture, followed during the first few days by a decrease and thereafter by a similar rise and fall as in the untreated mixture. The mixture with the largest quantity of sea water produced a still greater amount of gas during the first few days, but the peak comparable with those of the other mixtures was decidedly lower. The total quantities of gas produced from the different mixtures differed with the amounts of sea water added. However, the percentage methane in the gas was lowest from the mixture with the largest quantity of sea water (Figure 1).

Effect of Chlorides

From a series of experiments with sodium chloride additions to ripe sludge–fresh solids mixtures the results of two mixtures are plotted in Figure 2 as an illustration of the retardation of digestion processes attributable to chloride. The mixtures were similar to those to which sea water was added and different quantities of sodium chloride were introduced. The two mixtures used for illustration received, respectively, nothing and 10 grams of sodium chloride per liter sludge mixture. Determinations and analyses were made at weekly intervals. Although the retardation caused by the sodium chloride is not great, it was persistent and checks the slight retardation caused by sea water. It would seem, therefore, that the effect of sodium chloride and sea water on digestion is comparatively insignificant, provided sufficient ripe sludge is present to take care of the fresh solids added. Sierp[3] concluded that only comparatively high salt concentration affects the rate of organic matter decomposition, and that small quantities of sulfates are not detrimental but larger quantities (1.07 grams per liter sludge as compared with 1.02 grams per liter in our mixture) were harmful. Purvis[4] concludes that sludge decomposes very slowly when mixed with sea water. Although the writers' experiments indicate that retardation of decomposition occurs, it does not appear to be "very slow" with the comparatively large quantities of sea water added.

Hydrogen Sulfide Production

The amounts of sulfates added to the different mixtures varied from 5 to 48 mg. per gram volatile matter. All these sulfates disappeared in the course of digestion in addition to more than half the sulfates present in the original material (Table III). The total amounts of hydrogen sulfide per liter sludge varied from 9.2 to 373 cc. according to the amounts of sulfates added. The mixtures receiving about 5 mg. sulfates per gram volatile matter produced the same amount of hydrogen sulfide in the gas per liter of sludge and the same quantity per gram volatile matter destroyed as the mixture without sulfate addition, owing to the fact that some hydrogen sulfide remains in solution in the liquid.

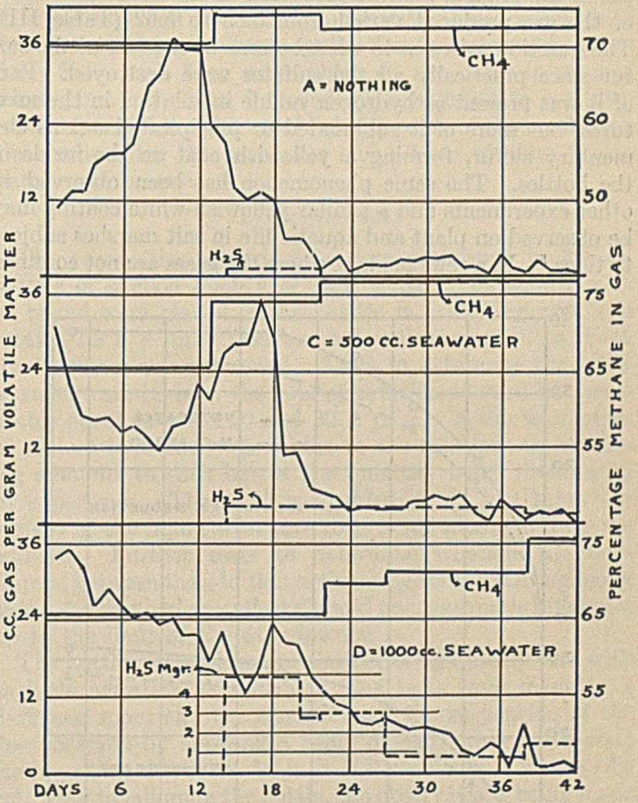

Figure 1—Daily Gas Production, Percentage Methane, and Amounts of Hydrogen Sulfide in Different Mixtures

Hydrogen sulfide in the gas varied from 0.08 to 4.83 per cent. None of the mixtures produced hydrogen sulfide in the gas during the first 14 days of incubation, although it was present in the liquid (Figure 1). Most of the hydrogen sulfide in the gas occurred during, and especially after, the peak of gasification had been reached. During the same periods of digestion nitrogenous matter is most actively decomposed. Although the percentage of hydrogen sulfide was comparatively small, odors were very strong.

The percentage of hydrogen sulfide in the total gas pro-

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[3] *Tech. Gemeindeblatt*, **29** (1926–7).

[4] *Surveyor*, **96**, 277 (1926).

Table III—Decomposition of Sulfates and Hydrogen Sulfide Production

Mixture	Sulfate per gram dry volatile matter: Beginning	Sulfate per gram dry volatile matter: End	Sulfur from Sulfate per gram dry volatile matter: Beginning	Sulfur from Sulfate per gram dry volatile matter: End	Hydrogen Sulfide Produced: Per liter sludge	Hydrogen Sulfide Produced: Per liter sludge	Hydrogen Sulfide Produced: Per gram volatile matter destroyed	Hydrogen Sulfide Produced: Per gram sulfate	H_2S of Total Gas	Sulfur Recovered in H_2S
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Cc.*[a]	*Cc.*	*Cc.*	%	%
A	3.63	1.37	1.21	0.46	0.38	9.2	1.53	25.1	0.12	2.86
B	8.73	0.28	2.91	0.09	0.38	9.2	1.50	6.96	0.08	0.65
C	30.4	1.40	10.13	0.47	2.93	70.0	13.6	24.7	0.83	1.58
D	51.5	1.50	17.17	0.50	15.53	373.0	67.8	66.5	4.83	5.62

[a] At 20° C.

duced from the mixtures with 500- and 1000-cc. additions of sea water was above the lethal dose; in fact, the mixture with the largest quantity of added sulfates produced gas with hydrogen sulfide concentration of several times the lethal dose.

The percentage sulfur of the total amounts of sulfates present in the original mixture recovered in the hydrogen sulfide of the gas produced varied from 0.65 to 5.62 (Table III). The question arises as to what became of the rest of the sulfur since practically all the sulfates were destroyed. Part of it was present as hydrogen sulfide in solution in the mixtures, but more of it sublimated or precipitated out as elementary sulfur, forming a yellowish coat on the inside of the bottles. The same phenomenon has been observed in other experiments and a similar yellowish-white coating may be observed on plant and aquatic life in salt marshes subject to tides.[5] In a sewage plant where the gases are not confined this sulfur precipitates against walls, goes off into the air, and some of it is carried out with the effluent. A thorough discussion of the sulfur cycle in sewage, including the effect of a variety of sulfates on digestion, hydrogen sulfide production, mercaptans, and other intermediate products will be published later.

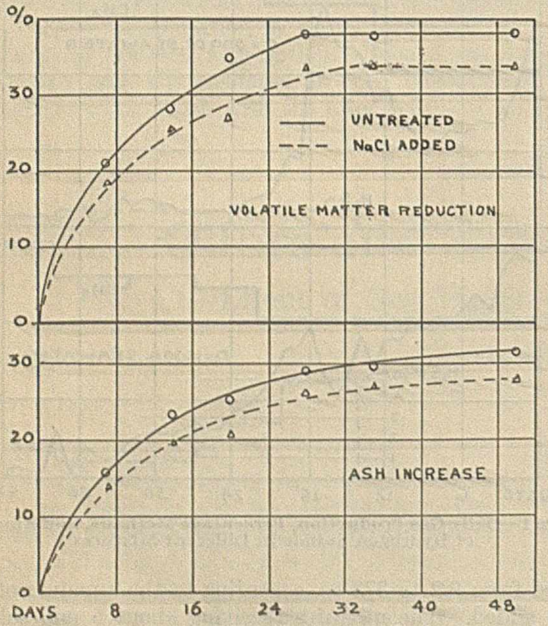

Figure 2—Percentage Volatile Matter Reduction and Ash Increase of Mixtures Receiving Sodium Chloride

The relation between sulfates and hydrogen sulfide production, together with the percentage sulfur recovered in the gas, is shown graphically in Figure 3. It can be seen that the relation is direct as soon as more than 5 mg. sulfates per gram volatile matter are added.

Sierp[3] was unable to find any hydrogen sulfide in the gas produced by mixtures of ripe sludge and fresh solids to which sulfates were added, although at the end of the experiment no sulfates were present in the liquid. He concludes that, although all sulfates were destroyed, no hydrogen sulfide formed under strictly anaerobic conditions, but only when the sludge received sufficient air—viz., H_2S-forming bacteria are stimulated and the activities of H_2S-oxidizing bacteria retarded. The experiments conducted by the writers were under anaerobic conditions, no air was allowed to enter the bottles for the duration of the experiment, and hydrogen sulfide was found not only in the liquid but also in the gas produced.

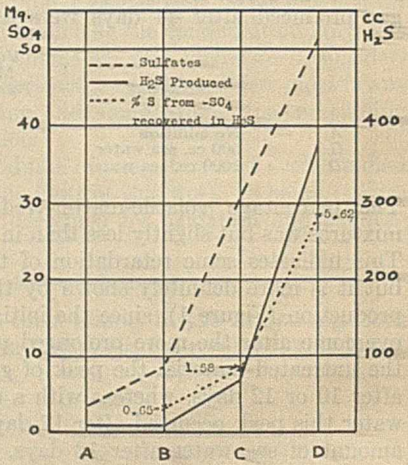

Figure 3—Sulfates Added and Hydrogen Sulfide Produced in Different Mixtures

Sea water added: *A* = 0, *B* = 250 cc., *C* = 500 cc., *D* = 1000 cc.

Summary

The digestion processes in ripe sludge-fresh solids mixtures treated with sea water and sodium chloride were slightly retarded.

The total quantities of gas produced from the different mixtures varied with the amounts of sea water added, but the percentage methane was lowest in the gas produced from the mixtures with the largest amounts of added sea water.

Practically all the sulfates added disappeared from the mixtures, but only from 0.65 to 5.62 per cent of the sulfur added in the form of sulfates was recovered in the gas as hydrogen sulfide.

Hydrogen sulfide production was greatest during and after the peak of gasification had been reached.

A large percentage of the sulfur of the sulfate added was changed to elementary sulfur.

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[5] Rudolfs, *Proc. N. J. Mosquito Extermination Assocn.*, 1925.

The Siberian Chemical Industry

Reports from the Chemical Division of the Department of Commerce indicate that lack of important consuming outlets has probably checked development of the Siberian chemical industry. Production is confined principally to basic products. Production of alkalies is little developed. There are two coal-tar plants, and ample raw material is available for a large wood chemical industry but at present it is not of much importance. The tanning industry produces all kinds of leather, with glue as a by-product. Production of matches is concentrated in four plants. The fats industry makes vegetable oils from flax, hemp, cedar nut, etc. The soap-making plants represent the highest developed branch of the Siberian chemical industry. The silicate industries include cement plants, glass factories, a porcelain factory, and a number of small pottery plants. Some of the breweries and distilleries also produce acetic acid. The pharmaceutical industry is represented by a number of plants and laboratories. The radio-active ores are being worked in Turkestan.

Effect of Salts on the Rate of Coagulation and the Optimum Precipitation of Alum Floc[1]

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The properties of the alum floc used in water purification have long been subjects of investigation. The composition of the floc is not definitely known though it is usually written as $Al(OH)_3$. It is a gelatinous substance, highly adsorptive, amphoteric, and relatively insoluble over a wide range of hydrogen-ion concentration. Miller[2] has shown that the composition varies if the precipitate is formed in the presence of different ions, owing either to the adsorption of the ions or to the formation of a basic salt. Williamson,[3] Bancroft,[4] and Rose[5] have isolated basic salts by partially neutralizing a solution of an aluminum salt with various alkalies. Miller[6] has further shown, by the precipitation of an alum floc from a solution containing oxalate and sulfate ions, that the ratio of the oxalate and sulfate ions in the precipitate is dependent upon their concentration in the solution. This strongly suggests a true adsorption phenomenon. Charriou[7] showed that divalent ions carried down by the precipitate could be displaced by ions of a higher valence, further indicating adsorption. It is possible that the variation of composition under varying conditions might be due to both adsorption and a complex salt formation. This factor has not been carefully considered in the investigations of the properties of the floc. Obviously the precipitate formed in the presence of various salts would show different properties, such as the rate of coagulation, conditions of optimum precipitation, etc.

The factor most consistently investigated has been the so-called optimum hydrogen-ion concentration for coagulation. If the floc is an ampholyte it should exhibit a point of maximum insolubility—i. e., a hydrogen-ion concentration at which the solubility of the floc is least. As the pure floc is colloidal in most of its properties, it should show its least stability at the same point. This isoelectric point has been reported by different investigators at values ranging from 4.90 to 7.20. Baylis[8] and Norcum[9] report optimum values for coagulation distinctly on the acid side of neutrality, adjusting to this value by treating the water with sulfuric acid. This was tried by the writer at the Cedar Rapids, Ia., plant, and the conditions and rate of formation of the floc did improve. Bates,[10] at the writers' suggestion, substituted an equivalent quantity of sodium sulfate and obtained identical results without affecting the hydrogen-ion concentration to any measurable degree. Theriault and Clark[11] found optimum conditions for coagulation at a pH value of 4.9 to 5.4, using 100 to 400 p. p. m. of alum in solutions buffered with phosphates. This is in accord with the observations of Baylis and Norcum, but will be further discussed later in this paper.

It becomes evident, therefore, that any attempt to establish optimum coagulation conditions must take into consideration the effect of the salts present in the water. Whether the ions of such salts are adsorbed or form a basic salt precipitate, the properties of the resultant floc will vary according to the kind and concentration of such salts. This investigation was then planned to determine what some of the effects might be, and if the salts normally present in water supplies did affect the conditions of optimum floc formation. It is not expected that all the observations and conclusions included will have a direct application to waterworks practice. Salts have been used which do not occur in natural waters, but have been included in an attempt to establish general principles which would clarify some of the conflicting ideas concerning the properties and actions of alum floc in waterworks practice.

Experimental

The coagulation experiments were performed in 300-cc. bottles of a good quality of clear glass. The solutions to be tested were placed in the bottles in a shaking rack and rotated 22 r. p. m. This was not violent enough to break the floc after it was formed. Tests to determine the effect of small variations in the rate of rotation showed no measurable effect between 20 and 30 r. p. m. A dilute solution of sodium hydroxide was added to the solutions in increasing amounts to each bottle, the quantity being determined by experience. The alkali was added slowly just below the surface of the liquid with care to prevent mixing during the addition. Further tests to determine whether the time elapsed between the addition of the reagents and the beginning of the shaking had any effect showed no measurable difference up to the limit of the experiments.

The bottles were placed in the stirrer as quickly and with as little agitation as possible. The tests were made in a darkened room and the conditions of the suspension of the floc observed by allowing a beam of light from a 100-watt lamp passing through a $^3/_4$-inch (1.6-cm.) tube 3 inches (7.6 cm.) long to fall upon the bottle, the observations being made from an angle to the beam. The Tyndall cone so produced was very well defined and the coagulation of the floc particles could be plainly seen. The change from a bright cone to a floc condition was very abrupt and could be duplicated within a few seconds in successive experiments. Observations were made at half-minute intervals at the beginning of the experiment until the more quickly coagulated samples were flocculated and then at intervals dictated by experience. On the acid side of coagulation the floc was always opaque and well-defined, but on the alkaline side it was more glassy in appearance and the time of coagulation was not so easily observed, especially at low concentrations of the salts.

The alum solution used was made by dissolving 6.84 grams of recrystallized aluminum sulfate of the formula $Al_2(SO_4)_3$-$16H_2O$ in 1 liter of distilled water. This was of such a strength that 1 cc. added to 200 cc. of water was equivalent to 2 grains per gallon (34 p. p. m.). Such a concentration represents about an average filter-plant dosage. In the sulfate experiments the solution was made up of aluminum chloride of equivalent concentration. The salts to be added were

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[1] Received August 15, 1927. Abstract of a thesis submitted by Ben H. Peterson in partial fulfilment of the requirements for the degree of doctor of philosophy in the State University of Iowa.

[2] *U. S. Pub. Health Service, Pub. Health Repts.*, **32**, 1895 (1925).

[3] *J. Phys. Chem.*, **27**, 284 (1923).

[4] *Ibid.*, **26**, 501 (1923).

[5] *Kolloid-Z.*, **15**, 1 (1924).

[6] *U. S. Pub. Health Service, Pub. Health Repts.*, **40**, 1502 (1924).

[7] *Compt. rend.*, **176**, 679 (1923).

[8] *J. Am. Water Works Assocn.*, **10**, 563 (1921).

[9] *Ibid.*, **11**, 97 (1924).

[10] Personal communication.

[11] *U. S. Pub. Health Service, Pub. Health Repts.*, **38**, 181 (1923).

made up in such concentration that 1 cc. of the solution added to 200 cc. of the sample was equivalent to 20 p. p. m. expressed as calcium sulfate. The required amount of alum and the additional salt were placed in a 2-liter flask, diluted with distilled water to the mark, well mixed, and 200 cc. of this solution placed in each of the bottles. The alkali was then added in varying amounts, the rotation begun, and the observations made as described above. The pH of the solutions was determined colorimetrically.

Results

Table I—Effect of Sodium Sulfate on Time Required for Coagulation of Alum Floc, Using Aluminum Chloride Solution and Adjusting Alkalinity with Sodium Hydroxide

Na_2SO_4—25 p. p. m.		Na_2SO_4—50 p. p. m.		Na_2SO_4—100 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.30	46	5.5	29	5.25	39
6.60	36	5.8	19	5.60	15.5
6.70	31	6.0	16	5.70	14
6.85	16	6.4	13	6.00	10
7.00	12	6.6	11	6.10	9.5
7.20	10	6.7	10	6.75	8
7.40	9	7.1	9	7.20	8.5
8.00	12.5	7.4	8	7.40	9.5
8.45	18	7.9	13	7.50	11
8.60	22	8.3	19	7.60	13
		8.5	24	7.70	17
				7.72	23
				7.75	26
				8.10	33
				8.35	48

Na_2SO_4—150 p. p. m.		Na_2SO_4—200 p. p. m.		Na_2SO_4—500 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.10	25	4.50	42	4.60	15
5.25	19	4.60	26.5	4.70	10
5.45	13	4.85	19.5	4.80	9
5.65	10	5.45	9.5	5.00	7
5.70	9	5.60	9	5.50	4.5
5.75	8	5.70	8.5	5.60	4.5
5.85	8	5.95	6.5	6.45	4.5
6.00	8	6.25	6.5	6.90	4.5
6.20	7.5	6.65	6.5	7.15	4.75
6.30	7.5	7.00	6	7.35	5
6.50	7	7.75	8.5	7.60	9
6.80	7	8.05	15	8.00	12
7.30	7	8.20	24	8.40	17
7.50	8.5	8.25	42	8.60	28
7.80	10				
8.00	15				
8.20	40				

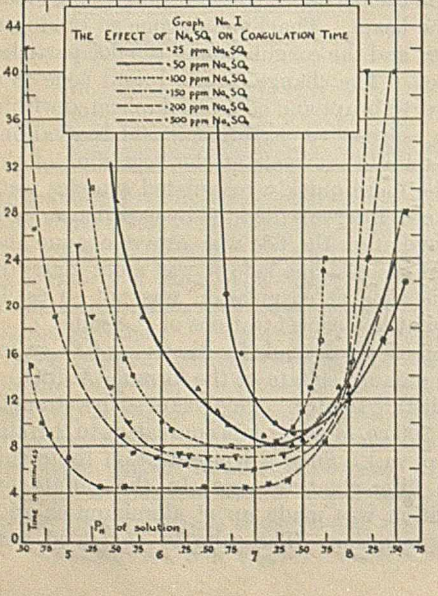
Sodium Sulfate—The effect of sodium sulfate is shown in Table I and Graph No. I. The sulfate content of a 2-grains per gallon (34 p. p. m.) dose of filter alum is equivalent to about 20.9 p. p. m. as $CaSO_4$. The results plotted in the first curve, then, show the effect of slightly more than the sulfate which would be added with 2 grains per gallon (34 p. p. m.) of filter alum. This shows a maximum coagulation at about 7.3 to 7.4 and coagulation within a reasonable length of time is between rather narrow limits. Further additions of the sulfate produced a marked effect, lowering somewhat the time required for coagulation, but not proportionately, and widening the zone of coagulation to the acid side. The effect is more marked between 25 and 100 p. p. m. than between 100 and 500 p. p. m. Water of sulfate content corresponding to 100 p. p. m. would be considered only moderately hard, and most public supplies of the Middle West would equal or exceed that amount. If, then, other factors did not influence the formation of the floc, it would form readily within a pH range of 6.0 and 7.5, with perhaps the optimum conditions at 6.75.

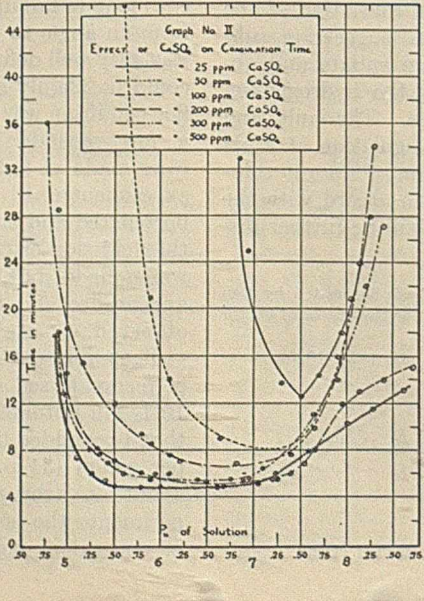
Table II—Effect of Calcium Sulfate on Time Required for Coagulation of Alum Floc, Using Aluminum Chloride Solution and Adjusting Alkalinity with Sodium Hydroxide

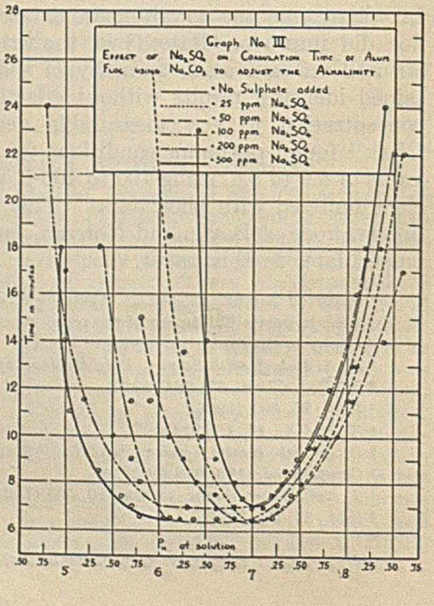
$CaSO_4$—25 p. p. m.		$CaSO_4$—50 p. p. m.		$CaSO_4$—100 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.85	33	5.60	46	4.75	36
6.95	25	5.90	21	4.90	28.5
7.30	13.5	6.10	14	5.00	18.5
7.50	12.5	6.65	9	5.15	15.5
7.70	14.5	7.40	8	5.50	12
7.93	18	8.00	18	5.80	9.5
8.25	25	7.70	13	5.90	8.5
		8.05	21	6.10	7.5
				6.20	7
				6.80	7
				7.40	7
				7.65	10
				7.90	14
				8.15	24
				8.30	34

$CaSO_4$—200 p. p. m.		$CaSO_4$—300 p. p. m.		$CaSO_4$—500 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
4.90	18	4.90	17	4.90	17.5
5.30	8	5.00	14.5	4.95	14.5
5.35	7.5	5.15	8.5	5.00	13
5.50	7	5.25	8	5.10	7
5.80	6	5.45	7	5.25	6
5.96	6	5.90	5.5	5.40	5.5
6.10	5.5	5.60	6	5.50	5
6.40	5.5	6.50	5.5	5.80	5
6.65	5.5	6.90	5.5	6.00	5
6.75	5.5	7.10	6.5	6.50	5
6.95	5.5	7.40	8	6.65	5
7.20	5.5	7.65	11	7.05	5
7.25	5.5	7.90	16	7.20	6
7.40	6	8.20	22	7.60	8
7.55	7	8.40	27	8.00	10.5
7.65	8			8.30	11.5
7.95	12			8.60	13.5
8.15	13			8.70	14.5
8.40	14				
8.70	15				

Calcium Sulfate—These experiments using calcium instead of sodium sulfate as the source of the added sulfate ion were tried to determine whether the positive ion would have any effect on the rate of coagulation. Alum floc, being a positive colloid, is stabilized by positive ions. If the calcium ion is adsorbed to a different degree of effectiveness than the sodium ion, a difference in the coagulative properties of their sulfates would be apparent. In general, little







difference is shown by a comparison of the curves in Graphs Nos. I and II, a concentration of equivalent sulfates extending the zone of rapid coagulation to about the same degree. Although there can be no doubt that the sodium and calcium ions do exert a different stabilizing influence, the difference is negligible in this particular case.

Table III—Effect of Sodium Sulfate on Coagulation Time of Alum Floc, Using Aluminum Sulfate and Adjusting Alkalinity with Sodium Carbonate

Na_2SO_4—000 P. P. M.		Na_2SO_4—25 P. P. M.		Na_2SO_4—50 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.30	31	5.90	25.5	5.80	15
6.40	23	6.10	18.5	5.90	11.5
6.50	14	6.25	13.5	6.10	10
6.80	8	6.45	10	6.25	9
6.85	7.5	6.60	9	6.40	8
7.10	7	6.80	7	6.50	7.5
7.20	7.15	6.85	6.5	6.90	6.5
7.30	8	6.90	6.5	7.00	6.5
7.45	9	7.15	6.5	7.20	6.5
7.70	11	7.50	8	7.40	7.5
8.00	14	7.75	10	7.90	10
8.10	16	8.00	11.5	8.05	11.5
8.40	24	8.10	13	8.50	15
		8.35	18	8.60	17.5
		8.60	22		

Na_2SO_4—100 P. P. M.		Na_2SO_4—200 P. P. M.		Na_2SO_4—500 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.35	18	4.5	24	4.9	24
5.70	11.5	5.0	14	4.95	23
6.10	6.5	5.2	11.5	5.0	17
6.35	6.5	5.5	10	5.05	11
6.60	6.5	5.7	9	5.35	8.5
6.80	6.5	5.8	8	5.6	7.15
7.00	6.5	6.0	7	5.7	6.5
7.20	7	6.3	7	5.8	6.5
7.65	9.5	6.6	7	6.05	6.5
7.95	11	6.6	7	6.35	6.5
8.05	13	7.0	7	6.4	6.5
8.20	18	7.2	7	6.6	6.5
8.50	22	7.35	8.5	6.95	6.5
		7.6	9.5	7.1	6.5
		7.8	12	7.25	7
		8.2	17.5	7.5	12
				7.9	17.5

SODIUM SULFATE, ADJUSTING ALKALINITY WITH SODIUM CARBONATE—On account of the similarity of the sulfate and carbonate ion it would seem probable that the carbonate ion would have an additive effect and that the result would be as if a larger quantity of the sulfate were used. In general, however, there is no noticeable effect and the results (Table III and Graph No. III) are similar to those in which the hydroxide was used to adjust the alkalinity. There was no attempt to correct for the sulfate added as the alum.

FERROUS SULFATE—Ferrous sulfate has long been used alone and with alum in water purification. In waters of high turbidity and low color its use has decreased the amount of alum necessary to effect clarification. These experiments (Table IV and Graph No. IV) show a very decided effect even in such small concentrations as 0.5 grain per gallon (8.5 p. p. m.). The time interval is lowered by one-third and the pH range is extended from 5.0 to 7.5. It would at first appear that ferrous sulfate would be an ideal coagulation aid in waters of low salt content, especially colored waters, it having been shown that colors are best removed in an acid medium; but unfortunately such colors are usually tannates, which form highly colored bodies with iron salts. The difference between the behavior of the ferrous and the sodium salts may be due to the formation of the hydroxide of iron at the higher concentrations, which affords a nucleus for the formation of the alum floc.

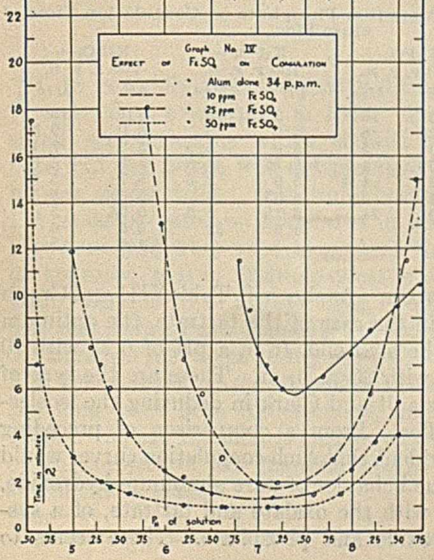
Table IV—Effect of Ferrous Sulfate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

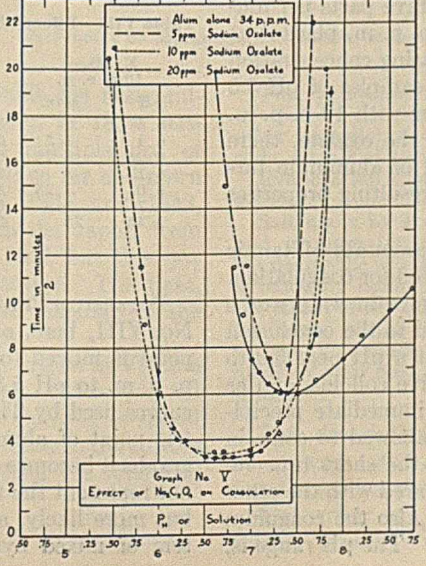
$FeSO_4$— 000 P. P M.		$FeSO_4$— 10 P. P. M.		$FeSO_4$— 25 P. P. M.		$FeSO_4$— 50 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.8	23	5.8	36	5.0	23.5	4.5	35
7.0	15	5.95	26	5.2	15.5	4.6	14
7.1	14	6.15	17	5.3	14	4.65	12
7.2	13	6.2	14.5	5.4	12	4.75	10
7.25	12	6.4	11.5	5.7	8	5.0	6
7.7	13	6.6	6	6.0	5	5.3	4
8.0	15	7.0	4	6.2	4.5	5.4	3.5
8.2	17	7.2	4	6.4	3.5	5.6	3
8.5	19	7.8	6	6.5	3	6.2	2
8.75	21	8.2	11.5	7.15	3	6.6	2
		8.6	23	7.6	3	7.1	2
		9.0	33	8.0	5	7.2	2
				8.25	7.5	7.9	3
				8.5	11	8.3	6
						8.5	8
						8.6	30

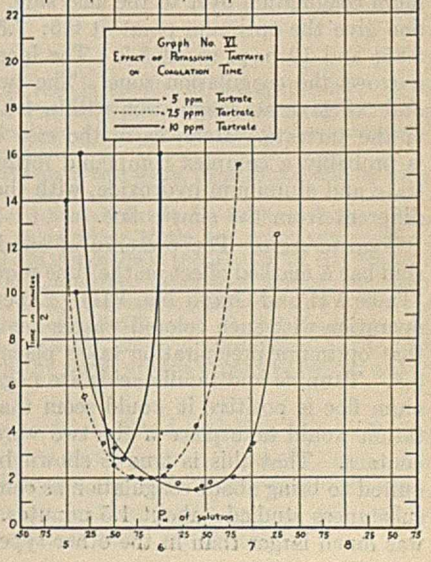
Table V—Effect of Sodium Oxalate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

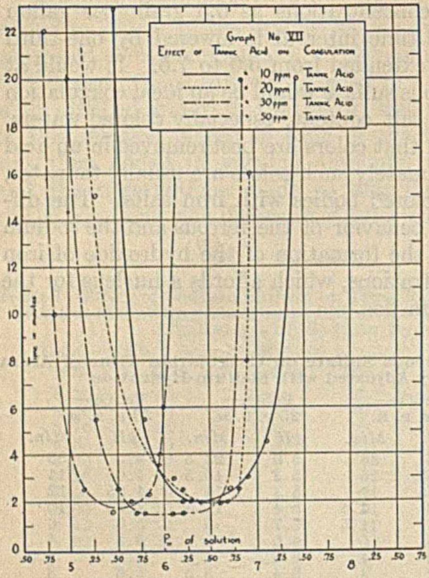
$Na_2C_2O_4$—5 P. P. M.		$Na_2C_2O_4$—10 P. P. M.		$Na_2C_2O_4$—20 P. P. M.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.5	42	5.45	41	6.6	40
5.8	25	5.25	18	6.7	30
6.0	14	6.0	12	7.05	23
6.15	9	6.2	8	7.2	15
6.3	8	6.3	8	7.3	12
6.4	7	6.6	7	7.4	12
6.5	6.5	6.7	7	7.65	16
6.6	6.5	6.8	6.5	7.8	26
6.7	6.5	7.0	7	7.85	38
6.8	6.5	7.2	8.5		
7.0	6.5	7.3	9.5		
7.1	7	7.5	12		
7.3	8.5	7.7	17		
7.4	14.5	7.8	40		
7.65	44				

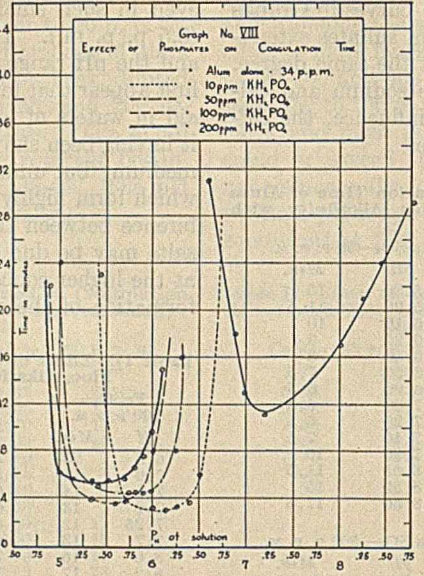
SODIUM OXALATE—The general similarity of the sulfate and oxalate ions would perhaps justify the assumption that their behavior in coagulation would be nearly identical. There is, however, a distinct difference in their relative effects. (Table V and Graph No. V) Concentrations up to 5 or 10 p. p. m. do show a decrease in the time required for coag-

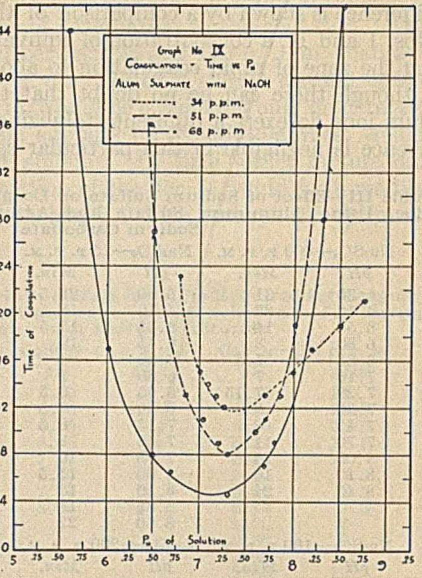












ulation and extend the zone of rapid coagulation up to a pH of about 6.0. An increase to 20 p. p. m., however, behaves very differently. The coagulation is slowed down and confined within very narrow pH limits—from 7.0 to 7.5. The significance of this specific action must lie in the formation of a basic oxalate compound with the alum floc, with resultant properties very different from those of the floc alone.

Table VI—Effect of Potassium Tartrate on Coagulation Time of Alum Floc, Alkalinity Adjusted with Sodium Hydroxide

$K_2C_4H_4O_6$—5 p. p. m.		$K_2C_4H_4O_6$—7.5 p. p. m.		$K_2C_4H_4O_6$—10 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.1	20	5.15	32	5.0	28
5.45	8	5.5	5	5.2	11
5.5	6.5	5.7	4	5.4	7
5.8	4.5	5.8	4	5.6	5.5
5.9	4	6.05	4	5.9	12
6.2	3.5	6.1	5	6.0	38
6.4	3	6.4	8.5		
6.45	3.25	6.85	31		
6.55	3.5				
6.7	3.75				
6.8	4				
6.95	6.5				
7.0	7				
7.25	25				

Potassium Tartrate—The effect of the tartrate ion is comparable with that of the oxalate ion. (Table VI and Graph No. VI) Low concentrations of the tartrate change the coagulation curves decidedly, moving the point of optimum coagulation over to the acid side. Five parts per million give the optimum point at 6.5; 7.5 p. p. m. place it at 5.85; and 10 p. p. m. at 5.5. The increasing concentration narrows the coagulation zone. The two samples of pH 5.5 and 5.8 gave no coagulation within 1 hour with 10 p. p. m. of the tartrate. Here, as in the case of the oxalate, there is probably a complex compound formed of aluminum tartrate and aluminum hydroxide, with the resulting properties different from the simple floc.

Tannic Acid—The presence of small amounts of tannic acid has a marked effect on the time required for coagulation. (Table VII and Graph No. VII) Experience in waterworks operation with such colored waters has led to the conclusion that optimum precipitation takes place at a pH near 5.0 to 5.5. Tannins and tannic acids are negative colloids, and as alum floc is positive it would seem that immediate precipitation would take place if the two were allowed to come in contact. That this is true is shown by the short time required to bring about coagulation as compared with the other substances studied—about 1.5 minutes. Also the coagulum was much larger than in the other types. The pH range is, however, very narrow and well defined. Here again it is more probable that the floc is a complex tannate. As the authors previously mentioned[8,9] were dealing with colored waters, their observations on the optimum pH for coagulation do not fix the isoelectric point of pure alum floc any more than do the experiments with the oxalate or any of the other salts studied. It does follow, however, that clarification of colored waters, if the color is due to tannic acid or its compounds, would take place in an acid medium, within narrow ranges of hydrogen-ion concentration and the exact point of the optimum results being dependent on the tannin content.

Table VII—Effect of Tannic Acid on Coagulation Time of Alum Floc

$C_{10}H_{14}O_9$—10 p. p. m.		$C_{10}H_{14}O_9$—20 p. p. m.		$C_{10}H_{14}O_9$—35 p. p. m.		$C_{10}H_{14}O_9$—50 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
5.5	23	5.1	25	5.0	20	4.75	22
5.7	10	5.3	14	5.3	5.5	4.85	10
5.8	5.5	5.95	3.5	5.5	2.5	5.15	2.5
5.95	4	6.1	3	5.7	1.5	5.45	1.5
6.05	3	6.2	2.5	5.8	1.5	5.43	1.5
6.2	2	6.4	2	6.1	1.5	5.65	2
6.3	2	6.6	2	6.2	1.5	5.85	2.25
6.4	2	6.7	2	6.6	2	6.0	6
6.6	2	6.8	2.8	6.75	9	6.25	28
6.7	2.5	6.9	8	6.85	20		
6.9	3	6.95	16				
7.1	4.5						
6.25	8						
7.45	20						

Table VIII—Effect of Potassium Phosphate on Coagulation Time of Alum Floc

K_3PO_4—10 p. p. m.		K_3PO_4—50 p. p. m.		K_3PO_4—100 p. p. m.		K_3PO_4—200 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.5	6	6.3	16	6.2	19	6.1	15
6.4	3.5	6.25	8	6.0	8	6.0	9.5
6.25	3.25	6.05	5	5.9	4.5	5.9	7.4
6.15	3	6.0	4.5	5.75	4.5	5.8	6.5
6.0	3.25	5.8	4.4	5.6	3.5	5.7	5.5
5.7	3.5	5.4	5	5.35	4	5.5	5.5
7.45	23	5.0	24	5.15	5.5	5.25	5.5
				4.9	32	5.0	6
						4.9	22

Potassium Phosphate—As shown in Table VIII and Graph No. VIII, here, as in the case of the tartrate, the optimum point is moved to the acid end, from a pH of 6.25 with 10 p. p. m. to pH 5.3, with 20 p. p. m. These are the type of curves used by Theriault and Clark in deducing the isoelectric point of alum floc. From a comparison of preceding graphs it becomes evident that such coagulation curves would not represent the true behavior of pure aluminum hydroxide, but more likely, as with the oxalate and tartrate, of a system of mixed hydroxide and phosphate. There seems to be no connection between the simple alum curve and those obtained with even small concentrations of phosphate.

Table IX—Coagulation of Alum Floc Alone with Sodium Hydroxide

Alum—34 p. p. m.		Alum—51 p. p. m.		Alum—68 p. p. m.	
pH	*Min.*	*pH*	*Min.*	*pH*	*Min.*
6.8	23	6.45	36	5.5	44
7.0	15	6.5	27	6.0	17
7.1	14	6.75	16	6.3	11
7.2	13	6.85	15	6.5	8
7.25	12	7.05	11	6.7	6.5
7.7	13	7.2	9	7.3	4.5
8.0	15	7.3	9	7.7	7
8.2	17	7.6	10	7.8	11
8.5	19	7.7	11	8.3	28
8.75	21	7.85	13	8.5	44
		8.0	19		
		8.25	36		

ALUM SULFATE ALONE—It is common waterworks practice to control the coagulation behavior by adjusting the alum dosage. In Table IX and Graph No. IX are given the results of the coagulation of three different dosages of alum in solutions of varying pH. It will be observed that the point of optimum coagulation is not materially changed, remaining near 7.25 to 7.35. Increase in alum dosage widens the zone somewhat, principally on the acid side. The time of most rapid coagulation does vary with the alum used, 2 grains per gallon (34 p. p. m.) requiring about one and one-half times as long as 3 (51 p. p. m.) and twice as long as 4 grains (68 p. p. m.).

Summary and Conclusions

One of the chief difficulties in the operation of a water plant is interpretation of the laboratory results to the plant. The effect of constant agitation on the duplication of results was among the first points investigated. A large number of experiments, in which the bottles were shaken for a few seconds to several minutes and allowed to stand during the formation of the floc, did not give results capable of duplication in a single instance. The practice of providing uniform agitation for the laboratory samples is not yet very generally used. One of the major conclusions to be drawn from this investigation seems to be the absolute necessity of some such provision in all waterworks laboratories, and further, coagulation pits should be so designed as to provide such agitation for some time, even after thorough mixing.

For plants which use streams as the source of supply the variation of floc behavior and the difficulty of holding a good floc during flood periods is more probably due to variations in the sulfate content than to variations in the hydrogen-ion concentration.

The abnormal behavior of the oxalate, tartrate, and phosphate ions shows the futility of any attempt to study the action of alum floc with varying pH if the solutions used are buffered with salts. The results so obtained define the point not of minimum stability nor of optimum coagulation of the pure floc, but of a composite of some kind entirely different in its properties. The majority of water plants use waters of hydrogen-ion concentration near neutrality and the fact that alum floc would form at all in such waters is inexplainable in the light of the experiments of Theriault and Clark. As they used solutions buffered with phosphate salts, it has been here shown that their results cannot be interpreted as indicative of the behavior of the pure floc.

Every operator has experienced the difficulties in the sudden appearance of color in the raw water. It is almost always difficult to obtain a good floc under such conditions. Operators usually prefer water of a very high turbidity to one of even a slight color. The experiments with tannic acid show the necessity of providing an acid medium under such circumstances. The optimum coagulation point observed here checks very closely with the points obtained by Baylis and Norcum, who were dealing with soft colored waters. The confirmatory experiments of Theriault and Clark are somewhat of an accident.

It must be concluded, therefore, that each water purification plant must determine the conditions of optimum floc formation for the water with which it is dealing and conclusions drawn from the operation of one plant are not applicable to another if the salt content of the water is different; also that the gelatinous material commonly thought to be aluminum hydroxide is a very complex substance, the properties of which vary widely with slight changes in the surrounding medium; and that the hydrogen-ion concentration is less of a controlling factor than the salt content of the water.

The First Multiple-Effect Evaporator[1]

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IT IS generally accepted that Rillieux built the first multiple-effect evaporator in 1843. Pecquer, in 1834, patented an apparatus which showed the multiple use of heat, but the design was not practical and so far as known it was never built. Sometime between 1834 and 1843, Degrande patented an apparatus in which the vapors from a vacuum pan were used to preheat the feed, but this was in no sense a true multiple-effect evaporator. The date, 1843, therefore, has always been taken as the date of the first real working multiple-effect evaporator.

There has just come to my attention an article in Volume I of the *Journal of the American Institute.* This journal has long since been discontinued, and Volume I is dated 1836. On page 170 there is an anonymous letter to the editors on the subject of salt manufacture in which the following statement is made:

> The manufacture of salt is simple in its operations. It is effected by the evaporation of water, and the separation of the other ingredients, contained in the water, from the muriate of soda, or salt of commerce.
>
> Evaporation is carried on in two ways, by artificial and by solar heat.
>
> Salt made by artificial heat—that is by boiling—costs more, and is more impure than when made by solar evaporation; yet nearly the whole of the salt made in the interior of the country is made by boiling. An improved process of boiling, by using the steam of one boiler to heat another, where the salt is formed, has been, within a few years, introduced at the Kenhawa salt springs, Va., which makes a salt, equal in appearance, to the best made by solar heat, but the works are too expensive for use on the seaboard.

This description is certainly the description of a multiple-effect evaporator, at least seven years, and possibly more, before the earliest date hitherto known for this type of apparatus.

The writer will be much interested if anyone can supply further information on this early installation.

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[1] Received November 2, 1927.

Coagulation Studies at the Washington Suburban Sanitary District[1]

Robert B. Morse,[2] Carl A. Hechmer,[3] and S. T. Powell[4]

Washington Suburban Sanitary District, Hyattsville, Md.

The Washington Suburban Sanitary District, comprising an area of approximately 96 square miles in the Maryland suburban section of Washington, receives its water supply from the Northwest Branch of the Anacostia River. The water is treated at two rapid sand filtration plants, one at Hyattsville and the other at Burnt Mills. The intake for the Burnt Mills works is about 6 miles above the Hyattsville intake.

The Hyattsville plant, with a designed capacity of one million gallons daily, supplies the smaller part of the water. Water enters the works from a gravity feed main 2 miles in length through an over-and-under baffled, rectangular mixing chamber, the period being about 5 minutes at normal rate of flow. From the mixing chamber the water flows to the coagulating basin in which the settling period is slightly less than one hour. The filters are of conventional construction. Lime is added to correct the hydrogen-ion concentration as the water enters the filtered water reservoir.

At Burnt Mills the plant is of a temporary nature, installed to meet a rapidly increasing demand before permanent works could be provided. It has a normal capacity of 2.5 million gallons daily but is operating successfully at a considerably higher rating. Raw water is pumped from the stream to the coagulating basin and chemicals for coagulation are added to the water in the low-lift suction main. A thorough mix with the water is obtained in passing through the centrifugal pumps and no destruction of the floc is noticed. The coagulating basin is of steel, circular in shape, with inlet and outlet diametrically opposite each other. It has a settling period of slightly over 30 minutes, figured on total displacement. There are four circular, wooden tub filters, with mechanically operated rakes. Lime is introduced as the filtered water passes from the filters to the filtered water reservoir.

Operation of Hyattsville Plant

Prior to March 15, 1927, alum alone was used for coagulation for turbidities under 100 p. p. m. in the raw water at the Hyattsville plant. With higher turbidities it was always necessary to add soda ash. The natural alkalinity of the raw water ranges from 18 to 22 p. p. m. Experiments were made from time to time using lime, and combination of lime and soda ash, with alum, to improve coagulation. Efforts were made to determine the optimum range of hydrogen-ion concentration for complete precipitation, but with little success. The turbidity of the raw water changes rapidly, varying from 5 p. p. m. in clear, dry weather to as much as 5000 p. p. m. after heavy rainfall. Low alum doses resulted in filter effluents with turbidities over 1.0 p. p. m. at times, and frequent objectionable tastes in the tap water after the addition of chlorine. Higher alum doses gave filter effluents with turbidities averaging 0.2 p. p. m. and a reduction in taste after chlorination. With high turbidities the large doses of alum necessary for effective coagulation lowered the pH value of the filter effluents and small amounts of aluminum hydroxide were carried through the filter in solution. The addition of a correspondingly greater dose of lime after filtration resulted in deposits in the clear-water reservoir which gave the water a cloudy appearance.

Since March 15 liquid sodium aluminate has been used with varying doses of alum. This treatment has resulted in the elimination of many of the difficulties formerly experienced and the results to date indicate that the combined treatment is warranted. With the use of a constant dose of 0.2 grain per gallon of sodium aluminate we have been able to decrease the alum and lime doses and eliminate the application of soda ash. By reference to Charts I-A, I-B, and I-C, which cover the operation of the plant for the first 6 months of this year, the saving in chemicals will be noted. It is apparent that, although the turbidity of the raw water fluctuated over practically the same range, there was a marked reduction in the dose of alum applied after the use of sodium aluminate was started. Prior to the use of sodium aluminate the average dose of alum from January 1 to March 14 was 1.25 grains per gallon. From March 15 to June 30, with a constant dose of 0.2 grain per gallon of sodium aluminate, the average alum dose was 0.55 grain per gallon. During the period when no sodium aluminate was used, the average amount of lime applied to the filtered water was 0.88 grain per gallon. After starting the sodium aluminate treatment it was possible to reduce the amount of lime to 0.3 grain per gallon. Formerly it was necessary to use soda ash to effect complete coagulation during high turbidities, and an average dose of 0.29 grain per gallon was used from January 1 to March 14. Since using sodium aluminate it has been possible to eliminate the soda ash.

The sodium aluminate is purchased in steel drums of 50 gallon capacity. The material is applied as a 2 per cent solution, the dose being controlled by a gravity orifice box. The solution is introduced at the same point as the alum and is conducted to the point of application through a rubber hose.

Better floc formation has been noted over the entire range of turbidities, and the reaction is more rapid. The coagulum is well formed when the water has passed only half-way through the mixing chamber. This condition did not exist when alum alone or when alum and soda ash were employed. The floc formed by this treatment is much larger than was formerly noted and settles more rapidly. As a result the water leaving the subsidence basin contains less suspended matter.

The raw-water supply at times contains colloidal clay. This condition is most pronounced during falling turbidities. Much difficulty was formerly experienced in effecting good coagulation and filtration during these times. The colloidal clays resisted coagulation to a marked degree and occasionally passed through the basin and filters, resulting in cloudy filter effluents. Control of the plant during such periods was difficult. The application of sodium aluminate has practically overcome this problem. The exact chemical reactions responsible for this phenomenon have not been established.

As a result of the reduced doses of alum the treated water

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[1] Presented before the Division of Water, Sewage, and Sanitation at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

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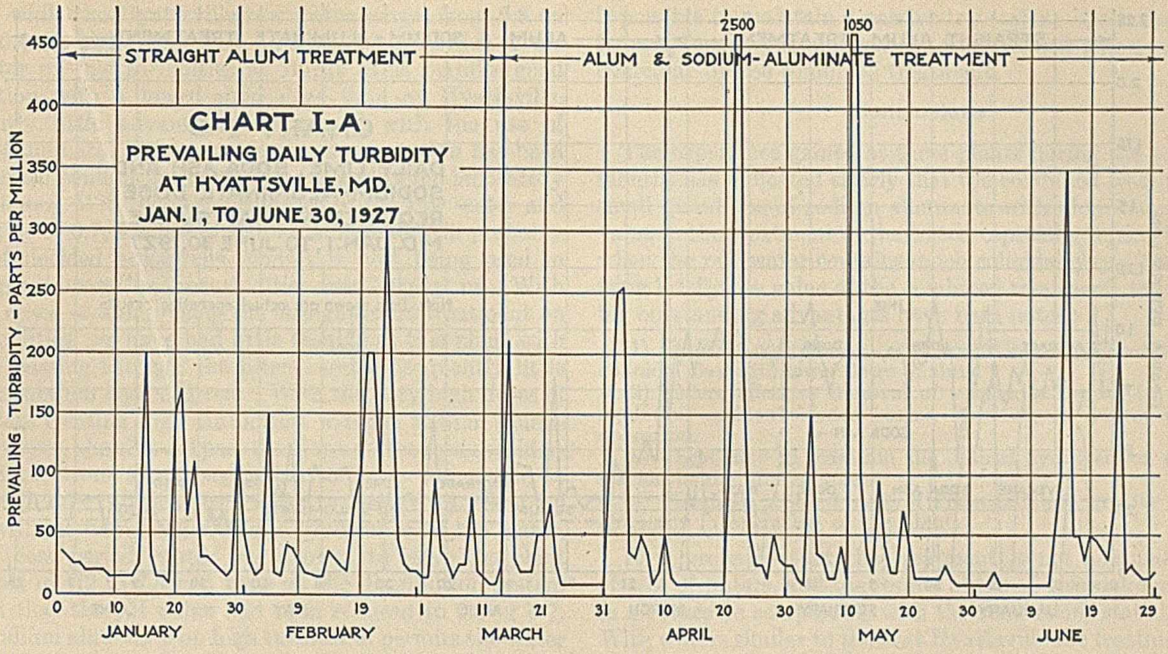
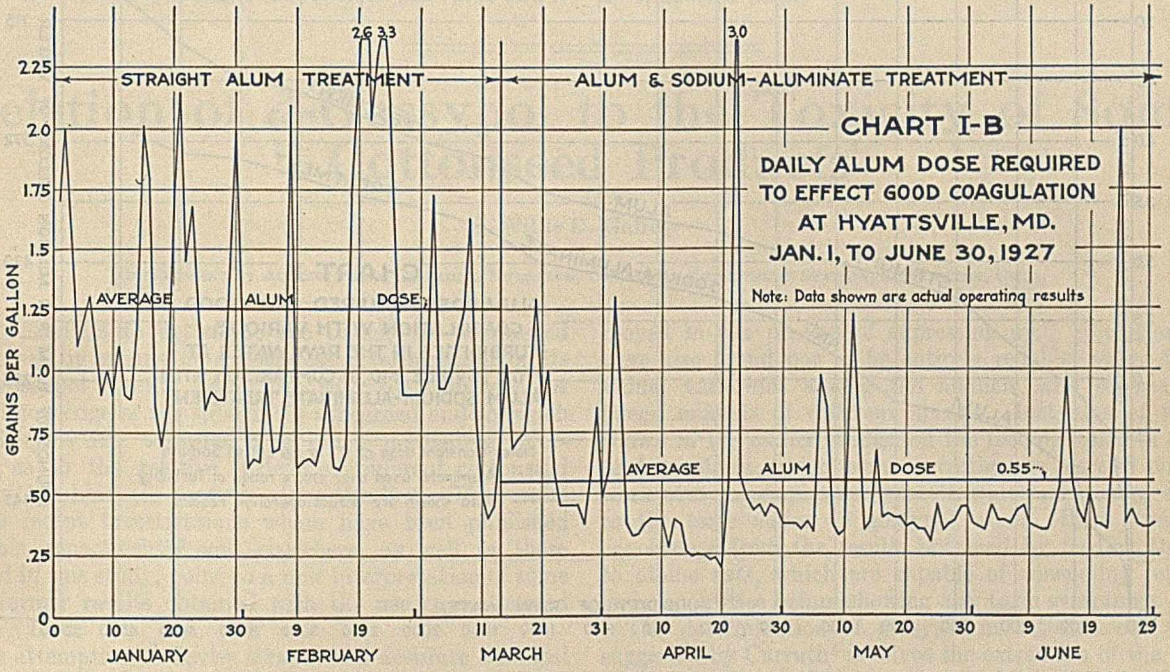
[3] Department engineer, Washington Suburban Sanitary District.

[4] Consulting chemist, Baltimore, Md.





has a lower hydrogen-ion concentration, which in turn requires smaller amounts of lime to produce the desired pH value. It has also been possible to control effectively the turbidity of the filtered water to within 0.2 p. p. m. and to accomplish this without the passage of alumina through the filters. No secondary coagulation has been noted in the clear-water reservoir and the appearance of the tap water has been improved materially. An interesting coincidence in conjunction with the sodium aluminate treatment was the consumers' comments on the improved quality of the water.

With straight alum treatment it was necessary to maintain a pH value of 8.0 in the filter effluents in order to keep the pH value of the tap water slightly above 7.0 at distant points on the distribution system. The increase in the hydrogen-ion concentration was probably due to the precipitation of lime in the mains. This condition was noted especially during the winter months, owing to retarded chemical reaction on account of the low temperature of the water. Since the water mains are all 4 feet or more under the ground, the temperature rises as the water passes through them in winter, thus aiding after-coagulation. It is anticipated that many of the difficulties encountered during cold weather will be eliminated with the sodium aluminate treatment. This prediction seems warranted since less after-coagulation will take place and smaller amounts of lime will be required to maintain the desired pH value in the treated water. A pH value of 7.4 to 7.6 is now maintained in the water leaving the plant. The tap water on the far ends of the distribution system was found to be above 7.0.

It has also been possible to reduce the dose of chlorine slightly and maintain practically a sterile water as a result of the improved filter efficiency since sodium aluminate treatment was introduced.

A study of the operating records has been made to determine the amounts of alum required for good coagulation with

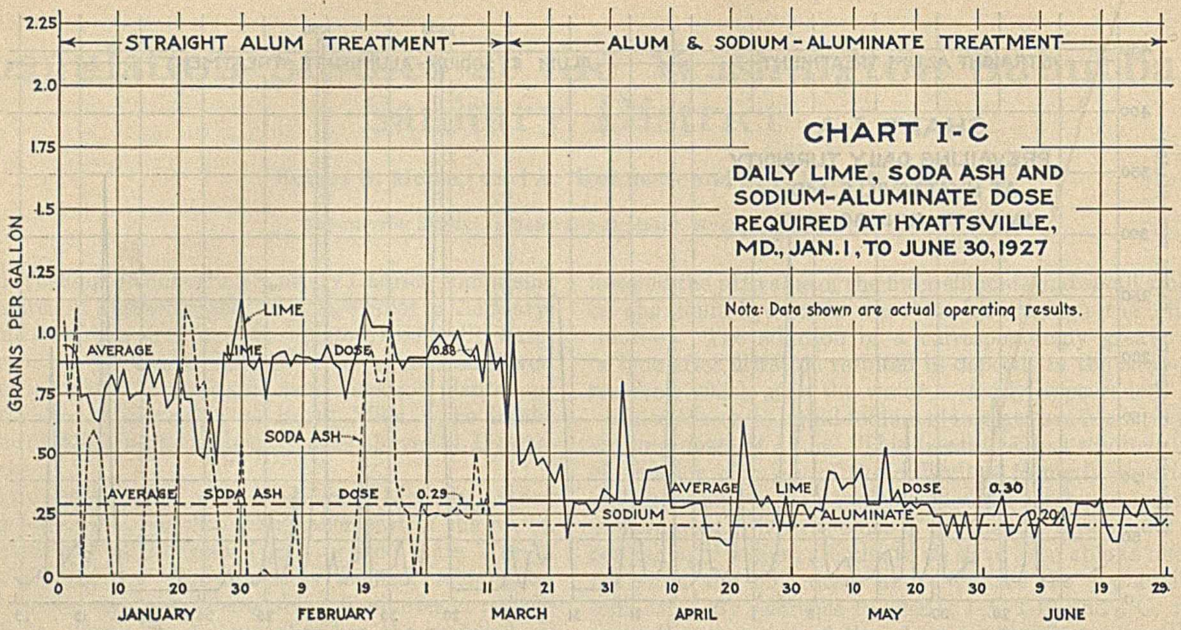


CHART I-C

DAILY LIME, SODA ASH AND SODIUM-ALUMINATE DOSE REQUIRED AT HYATTSVILLE, MD., JAN. 1, TO JUNE 30, 1927

Note: Data shown are actual operating results.

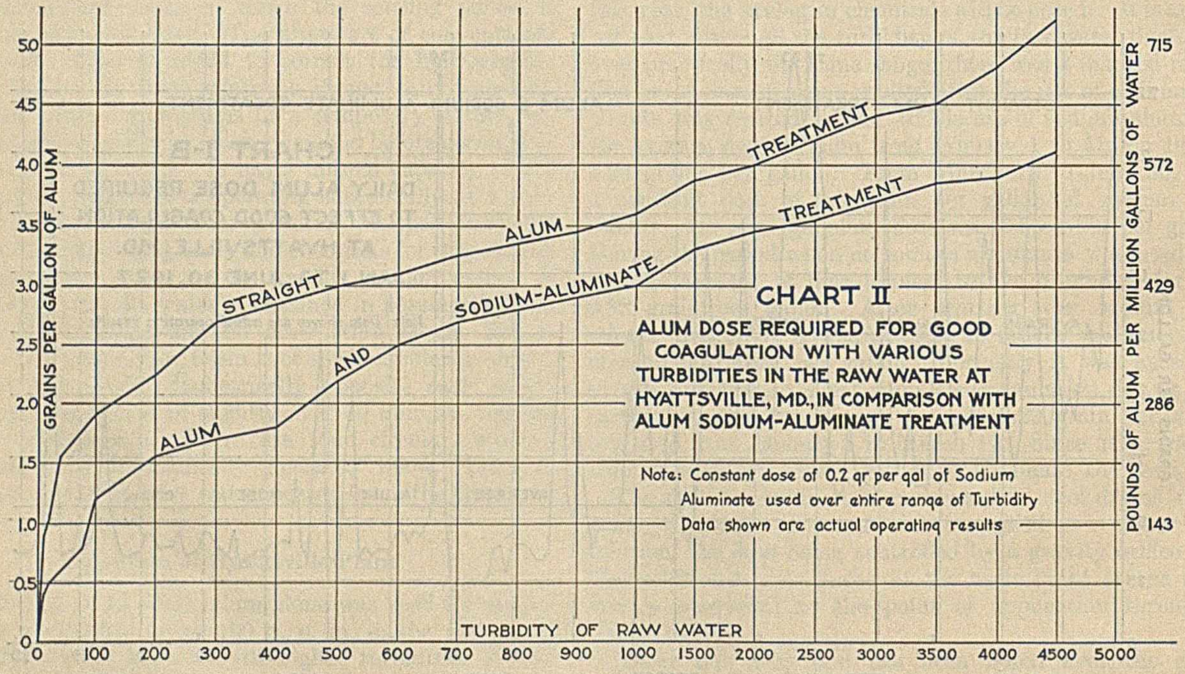


CHART II

ALUM DOSE REQUIRED FOR GOOD COAGULATION WITH VARIOUS TURBIDITIES IN THE RAW WATER AT HYATTSVILLE, MD., IN COMPARISON WITH ALUM SODIUM-ALUMINATE TREATMENT

Note: Constant dose of 0.2 gr per gal of Sodium Aluminate used over entire range of Turbidity
Data shown are actual operating results

various turbidities in the raw water. The results are shown on Chart II in comparison with the amounts of alum required with similar turbidities when 0.2 grain per gallon of sodium aluminate was applied in conjunction with alum. The amounts of alum used for the various turbidities as shown on this chart are not comparable with the doses of alum shown on Chart I-B. The turbidity as shown on Chart I-A is the prevailing turbidity during the day and the chemical doses on Chart I-B are based on the total amounts actually applied. From these curves it will be noted that the amount of alum required is consistently lower with the sodium aluminate treatment.

The actual saving in dollars and cents, based on the average amounts of chemicals used during the two periods, was comparatively small. The cost per million gallons of water treated before using sodium aluminate was $2.97. During the period when sodium aluminate was used the cost per million gallons of water treated was $2.87, a saving of $0.10 per million gallons. The alum, lime, and soda ash were purchased in car lots, while the sodium aluminate has been purchased in smaller quantities. The cost of these various chemicals per 100 pounds f. o. b. our filter plant are: alum, $1.50; lime, $0.50; soda ash, $1.60; and sodium aluminate, $5.50. By purchasing sodium aluminate in car lots a somewhat lower price could be obtained, thereby effecting a greater saving than shown above.

Experience at Burnt Mills

The value of sodium aluminate in the treatment of water at the Burnt Mills plant has been apparent only when the raw water is of high turbidity. Sodium aluminate has been used only one month at this point and there are insufficient data to report definite conclusions. Although water for this plant is taken from the same stream as that for the Hyattsville works, the pH value of the raw water is considerably higher, particularly on low turbidities, than at Hyattsville. The pH of the raw water at Burnt Mills ranges from 7.4 on extremely low turbidities to 6.7 on high turbidities, while the Hyattsville raw water ranges from 6.8 on low to 6.4 on high turbidities. The higher pH value of the raw water on low turbidities at Burnt Mills permits good coagulation with a lower alum dose than at Hyattsville. Apparently little advantage was gained with the use of sodium aluminate, and its use in regular operation has been discontinued pending the completion of additional laboratory experiments. With higher turbidities in the raw water and a pH value of 6.7, the use of sodium aluminate will probably prove of decided advantage, and it is now being used in regular plant operation for turbidities over 300 p. p. m. With the low doses of alum, using the straight alum treatment on low turbidities, we have had little trouble at this plant with alumina passing through the filters, and consequently little after-coagulation has occurred. With the very high doses of alum when treating high turbidities without sodium aluminate, however, alumina did pass the filters and caused considerable trouble from after-coagulation. It was impossible to add enough lime to the filtered water to maintain a pH of 7.8 or 8.0 without imparting a milky appearance to the water. During these periods water was allowed to leave the plant with a pH of 7.2 to 7.4 and tests on the distribution system revealed that the pH value had been reduced to 6.8 or 6.7. Using sodium aluminate on high turbidities permits the water to be filtered with only a slight reduction in pH value and it is possible to maintain a passive tap water. Colloidal interference, formerly troublesome at times at this plant, has been overcome by the combined treatment.

Conclusions

The experience gained at these plants during the past few months has indicated clearly that the combined treatment of small quantities of sodium aluminate with alum has specific value in the treatment of the water, especially during periods when the raw water contains much colloidal clay. Summarizing briefly the value of the combined treatment, the following outstanding advantages have been noted:

(1) Rapid coagulation with complete agglomeration of colloidal clay with lower doses of alum.

(2) More effective removal of suspended matter in the coagulation and subsidence basins, resulting in improved filter operation.

(3) Less lime to maintain the desired hydrogen-ion concentration in the filtered water.

(4) Slightly reduced cost of chemicals and greater over-all efficiency in operation of the plant.

It is probable that the treatment is not adapted to all classes of waters, and the results obtained elsewhere may not in all cases be comparable with the conclusions stated above. With waters similar to those at Hyattsville the treatment will be of specific value.

Relation of *d*-Gossypol to the Toxicity of Some Cottonseed Products[1]

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Attempts to determine the toxicity of cottonseed meal by means of a chemical determination of its gossypol content have met with little success. A lack of knowledge of the substances concerned and to which the toxicity is due, together with much misleading information as to the relative toxicity of different cottonseed products, has hindered progress along this line. The results of more recent investigations which have been published from this department[2,3] and elsewhere, as well as those obtained in this study, point to a new interpretation of some of the former results obtained with the use of cottonseed meal as a food.

While attempting to devise a rapid and accurate chemical method for the determination of gossypol in cottonseed meal, the fact was revealed that the gossypol content as determined was not indicative of the toxicity of the meal. This might at first appear contradictory to the results of Schwartze and Alsberg,[4] in which it was demonstrated that the toxicity of cotton seeds is due entirely to gossypol and is directly related to the amount of this substance present. That these investigators were cognizant of considerable variation between the gossypol content of cottonseed meal and the seeds from which it is produced is shown in their use of cottonseed kernels in their studies in preference to the meal "in order to eliminate any effect upon the toxicity of the seed resulting from the heat and pressure employed in the process of expressing oil." Biological tests were also found not to be entirely reliable, owing to individual variations among the animals, and especially between animals of different species. Instances of this are shown in the earlier studies on the feeding value of cottonseed meal, in which some investigators carried out their work with guinea pigs and rabbits, which are very susceptible to the toxic action of gossypol, while others drew their conclusions from the results obtained by feeding the meal to albino rats, which are capable of consuming relatively large quantities before showing any toxic symptoms.

The determination of gossypol in cotton seeds as first suggested by Carruth[5] involves the extraction of the ground seeds with ether, which removes the oil and gossypol and is followed by the precipitation of the gossypol with aniline. Schwartze and Alsberg[6] were able to make the method more nearly quantitative by precipitating the gossypol from a petrolic ether-oil solution. In both cases the gossypol is first removed from the seeds by ether, in which it must be completely soluble if the method is to give quantitative results. Previous experimentation has shown that if the ground seeds are heated previous to the extraction a portion of the gossypol becomes insoluble and cannot be removed by the usual organic solvents. Since cottonseed meal is produced from the seeds after thorough heating, this condition seemed to be responsible for the unsuccessful attempts to correlate the toxicity of the meal with its soluble gossypol content. The extent of this change of gossypol from a soluble to an insoluble form will depend upon the length of time of heating, the temperature attained, and the amount of moisture

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[1] Received July 27, 1927. Published with the permission of the Director of the Oklahoma Experiment Station, who originated a study of the factors influencing the gossypol content of cottonseed meal in this laboratory.

[2] Gallup, *J. Dairy Sci.*, **9**, 359 (1926).

[3] Gallup, *Ind. Eng. Chem.*, **19**, 726 (1927).

[4] *J. Agr. Research*, **28**, 173 (1924).

[5] *J. Biol. Chem.*, **32**, 87 (1917).

[6] *J. Agr. Research*, **25**, 285 (1923).

present. As the gossypol is decreased by this heating there is a decrease in the toxicity of the seeds, although not in the same proportion, and the seeds remain toxic long after the soluble gossypol has entirely disappeared, as shown by chemical determinations for this substance. Continued heating, especially in the presence of excess moisture, destroys the insoluble gossypol and ultimately yields a product which is free of both forms of gossypol and almost, if not entirely, deprived of any toxic properties. Proof of this is given in a previous article.[3]

The insoluble form of gossypol, which has been given the name "*d*-gossypol," may be a combination of gossypol, with some other constituent in the seeds or a single compound formed by a rearrangement of the gossypol molecule through the agency of heat, or perhaps an oxidation or hydrolytic product. Schwartze[7] has indicated that the formation of this substance may be due to a physico-chemical property of gossypol, "such as its tendency to become bound or adherent to the meal." In the form in which it has been isolated from the heated seeds it resembles gossypol, and some investigators[8] believe it to be a single compound similar to, but not identical with, gossypol. That this form of gossypol which occurs in relatively large amounts in cottonseed meal is not toxic has been suggested by Sherwood,[9] although Carruth[10] in an earlier investigation suggested that it might be the substance responsible for the toxicity of cottonseed meal, rather than the soluble form which is found in the seeds. The results reported in this investigation are in harmony with the latter suggestion. Since a rapid chemical method for determining the toxic substances in cottonseed meal was desirable, it appeared necessary first to confirm previous indications of the toxicity of *d*-gossypol.

Note—The term "*d*-gossypol" is employed throughout this paper to denote that form of gossypol which is practically insoluble in ether and formed at the expense of gossypol when the seeds are heated. There is some controversy as to the identity of *d*-gossypol and its existence as a compound separate from gossypol but the different solubility of the two substances has made it necessary to distinguish one from another. Carruth[10] has suggested the name "*d*-gossypol" for the less soluble form.

The data obtained in this investigation broadly indicate the extent to which gossypol and its related compounds, in particular *d*-gossypol, are responsible for the toxicity of certain cottonseed products.

Gossypol was converted to a less soluble form called *d*-gossypol by heating cotton seeds in an electric oven for several hours. The extent of this change was observed by chemical determinations of the two compounds and the decrease in the toxicity of the seeds determined by feeding experiments. It was found that the toxicity decreased as the time of heating was increased and that the toxicity was due to that form of gossypol which could not be removed from the heated seeds by extraction with ether. This gave evidence of the toxicity of *d*-gossypol.

The investigation was continued with the use of cottonseed meal, which contains only traces of ether-soluble gossypol but relatively large amounts of *d*-gossypol. The meal proved to be toxic when fed in large amounts to animals but, in spite of its higher content of *d*-gossypol, was much less toxic than the heated seeds. It is pointed out that the present chemical methods for the determination of gossypol and its related compounds do not suffice as a measure of the toxicity of heated cottonseed products.

Experimental Methods

Albino rats were used in this investigation, since they are less susceptible to "cottonseed injury" and can be fed cottonseed products for a greater length of time without fatal results than most experimental animals. In fact, their resistance to the effects of gossypol, and especially *d*-gossypol, is such that some investigators have stated that cottonseed meal is not toxic for them.

EXPERIMENTS USING COTTON SEEDS—Two varieties of cotton seeds were used, one containing small amounts and the other relatively large amounts of gossypol, but neither showing the presence of *d*-gossypol. The cottonseed meal used was of good quality, bright yellow meal showing traces of gossypol and an average amount of *d*-gossypol quite comparable with the amounts found in other meals examined in this laboratory. In order to convert the gossypol in the seeds to *d*-gossypol and note the decrease in the toxicity of the product, the seeds were ground and heated in thin layers in an electric oven at 110° C. for different lengths of time which varied from 10 minutes to 16 hours. Gossypol and *d*-gossypol determinations were made on the seeds before and after such treatment and some of the products so formed were fed in adequate diets to albino rats. (The change in the gossypol content of these seeds under this treatment is given in a previous paper.[3])

Gossypol Determinations. These determinations were made in a manner similar to that suggested by Schwartze and Alsberg,[6] in which 50 grams of the ground seeds are extracted with anhydrous ether in a Soxhlet extraction apparatus for 24 hours. The extract is evaporated at a low temperature and the residue taken up with about ten times its volume of petrolic ether. After standing overnight, the solution is filtered and 1 cc. of aniline added, the flask being shaken until the aniline is completely dissolved. This is set aside for precipitation to take place, which requires about 7 days, and at the end of this time the precipitate of aniline and gossypol is collected in a weighed Gooch crucible. The precipitate is washed several times with petrolic ether and the crucible and contents are dried for 4 hours at 105° C. and weighed.

d-Gossypol Determinations. The method suggested by Sherwood[9] was followed, in which 50 grams of ground seeds, after thorough extraction with ether, are digested with 100 cc. of hot aniline for 5 minutes. The temperature is kept constant at 110° C. and the mixture stirred constantly. The material is filtered through a Büchner funnel while still hot, using suction to remove the excess aniline, and when cool is thoroughly washed with ether. The ether is recovered from these washings by distillation and the residue added to the main filtrate with the aid of a little ether. The aniline is then distilled from the filtrate until about 10 cc. remain, which are washed into a small beaker with ether and set aside for precipitation of the aniline *d*-gossypol compound. This precipitation also requires about 7 days and the precipitate is handled in the same way as described for gossypol. Calculation of the gossypol and *d*-gossypol in these precipitates is made by multiplying the weight of the precipitate by the factor 0.74.

The growths made by rats on two of these products, together with the percentage of *d*-gossypol in the rations, are given in Group 1 of Table III. These results give strong evidence of the toxicity of *d*-gossypol, since the heating process when continued for 1 hour completely converted the gossypol to *d*-gossypol, although the seeds remained toxic even after heating for 16 hours. Such may not always be true, as is shown later, and the length of time of heating necessary to bring this change to completion appears to depend somewhat upon the amount of gossy-

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[7] *J. Oil & Fat Ind.*, **3**, 173 (1926).

[8] North Carolina Expt. Sta., 42nd Annual Report.

[9] *J. Agr. Research*, **32**, 793 (1926).

[10] *J. Am. Chem. Soc.*, **40**, 647 (1918).

pol originally present. Furthermore, the methods for determining these two forms of gossypol are subject to some error.

Another lot of cotton seeds containing 0.423 per cent gossypol, which is considerably more than was originally present in the first group of seeds, was ground and divided into three portions. One portion was completely extracted with ether, which removed the gossypol and oil. The second portion was first heated as described above for 2 hours and then extracted. The third portion was similarly heated for 4 hours and only half of it extracted with ether. Another lot of the same seeds was autoclaved at 20 pounds (1.4 kg.) steam pressure, as previously described,[3] which process is effective in destroying the toxic properties of the seeds. The products were examined for gossypol and *d*-gossypol and fed to albino rats in the rations shown in Table I.

Heating the seeds for 2 or even 4 hours did not completely convert the gossypol to *d*-gossypol as was expected, which no doubt was due to the relatively large amount originally present. Although longer heating would accomplish this, it would also tend to destroy the *d*-gossypol, which was undesirable, and 4 hours of heating was selected as the optimum length of time for producing the best yields of *d*-gossypol in these particular seeds. Ether extraction of the heated seeds was accomplished for the purpose of removing any soluble gossypol and thereby leaving a product containing only the *d*-gossypol.

Table I—Cottonseed Rations

(Figures in per cent)

Ration number	33	35	36	38	39	40	41	42
Cotton seeds (0.42% gossypol)	35							
Cotton seeds, extracted		26.2			26.2		26.2	
Cotton seeds, autoclaved for 2 hours (0.218% *d*-gossypol)			35					
Cotton seeds, heated 2 hours, extracted (0.341% *d*-gossypol)				26.2				
Cotton seeds, heated 4 hours, extracted (0.40% *d*-gossypol)						26.2		
Cotton seeds heated 4 hours (0.09% gossypol, 0.30% *d*-gossypol)								35
Extract of 2-hour heated seeds (0.878% gossypol)					8.8			
Extract of 4-hour heated seeds (0.37% gossypol)							8.8	
Refined cottonseed oil		8.8		8.8		8.8		
Wheat	60	60	60	60	60	60	60	60
NaCl	1	1	1	1	1	1	1	1
$CaCO_3$	1	1	1	1	1	1	1	1
Cod-liver oil	3	3	3	3	3	3	3	3

The results of this feeding work, together with the amounts of the two forms of gossypol in the various rations, are tabulated in Group 2 of Table III.

The heated, unextracted seeds represented products containing both forms of gossypol, while the extracts of the heated seeds which were used in combination with unheated seeds freed of gossypol by extraction, represented gossypol in amounts much less than were found in the extract of unheated seeds. A direct comparison was made possible, therefore, between the extract and the residue of seeds heated for 2 and 4 hours, the former containing soluble gossypol and the latter the insoluble or *d*-gossypol.

Experiments Using Cottonseed Meal—For the purpose of extending the investigation with the use of a cottonseed product more widely used as a feed than are the seeds, a sample of cottonseed meal containing 0.92 per cent *d*-gossypol was obtained. One portion of the meal was dampened and autoclaved as described in the experiment with the seeds and another portion was thoroughly extracted with ether and the oil so removed replaced with refined cottonseed oil. These products, after their gossypol and *d*-gossypol contents were determined, were incorporated in the rations shown in Table II.

Table II—Cottonseed Meal Rations

(Figures in per cent)

Ration number	25	26	27	52	53
Cottonseed meal (traces of gossypol, 0.92% *d*-gossypol)	45				
Extracted meal + refined cottonseed oil (0.92% *d*-gossypol)		45			
Autoclaved meal (0.54% *d*-gossypol)			45		
Basic ration				90	90
Ether extract of meal (traces of gossypol)					10
Cottonseed oil refined				10	
Wheat	50	50	50		
$CaCO_3$	1	1	1		
NaCl	1	1	1		
Cod-liver oil	3	3	3		

Since this meal showed only a trace of gossypol, it appeared desirable to determine if an ether extract of the meal which would contain this small amount of gossypol could produce the usual toxic symptoms in animals if incorporated in their diet in large quantities. As a control, a ration containing the same amount of refined oil was to be used. The ether extract was added to a growing ration in amounts equal to 10 per cent of the ration and in which amounts it provided over twice as much gossypol as could be present if added as cottonseed meal with the meal composing 45 per cent of the ration. If the toxicity of cottonseed meal is due to the ether-soluble gossypol alone, then such a ration as this should be extremely toxic, provided this particular sample of meal showed toxic properties. More elaborate work of this kind dealing with the production of a non-toxic meal will be given in a subsequent paper. The above rations are presented in Table II and the growth made by the animals is included in Group 3 of Table III.

Discussion

A study of the data presented in Table III reveals a rather astonishing situation as regards the growth of the animals on the rations containing different amounts of the two forms of gossypol.

Group 1 shows the usual decrease of *d*-gossypol and de-

Table III—Average Growth of Rats on Cottonseed Product Diets

RATION NUMBER	GOSSYPOL IN RATION	*d*-GOSSYPOL IN RATION	NUMBER OF ANIMALS	DURATION OF EXPERIMENT	INITIAL WEIGHT	FINAL WEIGHT	GAIN	LOSS	DAILY GAIN	LIVED	DIED
	Per cent	*Per cent*		*Days*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*		
					GROUP 1—COTTON SEEDS						
34	...	0.083	4	20	69	60	...	9	...	.	4
29	...	0.040	4	90	45	85	40	..	0.4	4	.
					GROUP 2—COTTON SEEDS						
33	0.148	...	4	30	61	48	...	13	...	2	2
35	...	...	4	60	71	205	134	..	2.2	4	.
36	...	0.076	4	60	59	177	118	..	1.9	4	.
38	...	0.090	4	45	76	66	...	10	...	3	1
39	0.077	...	4	45	74	89	15	..	0.3	4	.
40	...	0.104	4	30	121	104	...	17	...	4	.
41	0.032	...	4	30	110	172	62	..	2.0	4	.
42	0.032	0.104	4	35	55	51	...	4	...	4	.
					GROUP 3—COTTONSEED MEAL						
25	Trace	0.414	4	150	64	201	137	..	0.9	4	.
26	...	0.414	4	150	72	211	139	..	0.9	4	.
27	...	0.243	4	150	68	231	163	..	1.1	4	.
52	...	...	4	40	48	111	63	..	1.6	4	.
53	Trace[a]	...	4	40	49	110	61	..	1.5	4	.

[a] Two and one-half times as much gossypol as in ration 25.

struction of gossypol which takes place when ground cotton seeds low in gossypol are heated for a sufficient length of time. Along with this change there is a decrease in the toxicity of the seeds as shown by the growth of the animals. The seeds in ration 29 were heated sixteen times as long as those in ration 34.

In Group 2 the decline of the animals receiving ration 33 gives evidence of the toxicity of the gossypol in the raw seeds, while the excellent growth made by animals receiving the unheated, extracted seeds points to the complete removal of gossypol by ether extraction of the unheated seeds. These results are representative of a large number obtained in this laboratory with different varieties of cotton seeds. The destruction of this toxic substance by steam heat, as reported in previous papers, is again demonstrated in results obtained with ration 36, which was composed of autoclaved seeds, while its incomplete destruction and the formation of *d*-gossypol under conditions of dry heating for the same and longer periods of time are shown in rations 38 to 42 in Table I and supported by the growth of animals receiving these rations as presented in Group 2 of Table III.

That the insoluble gossypol which is formed by heating the ground seeds for 2 and 4 hours, and which cannot be removed by ether extraction, is toxic, is shown by the decline of the animals receiving these products in rations 38 and 40, the former containing 0.090 per cent and the latter 0.104 per cent *d*-gossypol. The amount of unchanged gossypol obtained from seeds by ether extraction after heating for 4 hours was much less than was present after 2 hours of heating, being so low in the former case that the animals receiving ration 41, in which the extract was incorporated, made good gains over a short feeding period.

The growths made by animals in Group 3 receiving rations 25, 26, and 27, which were made up of cottonseed meal and contained the largest amount of *d*-gossypol of all the rations reported here, are in striking contrast to those reported immediately previous. The meal contained 0.92 per cent *d*-gossypol, which could not be removed by ether extraction or completely destroyed by autoclaving for 1 hour. There was present, therefore, in rations 25 and 26, about four times as much of this compound as in any of the cottonseed rations, and yet the animals whose diets were restricted to these cottonseed meal rations made the best growth. That their growth was still below normal is made apparent by comparison with the results obtained with the use of ration 27, containing the autoclaved meal and less *d*-gossypol. Furthermore, the general condition of these animals, the number of breeding failures, and high death rate among the young born, which are not included in these data, are indicative of a toxic factor which can be greatly reduced by autoclaving the meal. This statement is supported not only by the one feeding trial reported here, but by several others to be reported in their proper order. The point to be emphasized is that the insoluble gossypol found in cottonseed meal is much less toxic than the insoluble gossypol produced by simply heating the seeds, and the chemical determination for this compound does not, therefore, suffice as a measure of its toxicity.

In order to account for these differences in toxicity, reference was made to the studies reported by Carruth,[10] in which several forms of gossypol are given consideration. Two of these are reported as being formed from gossypol by heat—one called *b*-gossypol and produced along with considerable black resinous material on heating the isolated gossypol to 186–190° C.; and the other, *d*-gossypol, formed in the seeds during the cooking process which precedes the expression of the oil at the oil mill.

It would hardly seem that *b*-gossypol could be formed under the dry heating conditions reported here, since the temperature was maintained around 110° C. at all times and there was no indication of the formation of dark resinous material. The seeds did develop a yellow color characteristic of *b*-gossypol, which is more intensely yellow than gossypol but also characteristic of ground seeds which have been stored for some time and is the usual color of the commerical meal. Furthermore, almost quantitative yields of the insoluble gossypol have been obtained by heating the seeds as described which could not result if any large amount of resinous material was being formed by the conversion of gossypol to *b*-gossypol during the process. The final solution of the problem may be found in the fact that gossypol breaks down in the seeds at a temperature of 100° C., but when isolated and subjected to test-tube reactions it withstands a temperature up to 186° C. It is quite possible that this compound as it exists in its original state in the seeds is quite different from that which has been isolated. That the isolated gossypol is toxic to the same degree as seeds containing similar amounts of this substance has been demonstrated.[4]

With little evidence to support the view that *b*-gossypol is a factor determining the toxicity of the heated cotton seeds, attention was given to the amount of *d*-gossypol remaining in seeds which had been autoclaved for 2 hours and which had no harmful effects when fed to animals, as in ration 36. Ration 34, containing only slightly more *d*-gossypol produced by dry-heating the seeds for one hour, was extremely toxic and ration 29, containing little more than half as much, was also quite toxic. Evidently some factor other than the *d*-gossypol as determined by the present chemical methods must be taken into consideration in order to approximate the toxicity of these products. The method of preparation of the meal becomes more important in this respect than the determination of its *d*-gossypol content, and as yet sufficient data of this nature in an attempt to find a correlation between the toxicity of a cottonseed meal and its *d*-gossypol content as affected by oil-mill processes have not been obtained.

That the presence of moisture is necessary for the destruction of the toxic properties of cotton seeds during the cooking process at the oil mill seems to be an established fact. It is also well known that the condition of the seeds as regards their moisture content during this process will determine to some extent the amount of oil which can be later expressed from the seeds. For this reason the addition of water is often practiced when cooking very dry seeds, but the amount is small and apparently much less than is necessary for the destruction of the toxic principle. Very few samples of meal examined in this laboratory have contained unchanged gossypol in sufficient amounts to be of physiological importance. The *d*-gossypol has always been found in relatively large quantities, although its toxic properties have been decreased to a degree much less than can be accomplished by simply heating the seeds in a dry condition. In view of these findings the manner of cooking the seeds assumes importance, not only in the production of oil, but in improving the quality of the meal.

Conclusion

The toxicity of cottonseed meal may be due not only to the presence of ether-soluble gossypol as it is found in cotton seeds, but also to the presence of what appears to be a decomposition product formed during the heating of the seeds previous to expressing the oil, and given the name *d*-gossypol.

The toxicity of the meal studied was not reduced by removal of the small amount of ether-soluble gossypol which it contained, nor was this form of gossypol present in sufficient amounts to produce toxic symptoms in animals when the extract was fed in excessive quantities. When the meal is heated in the presence of moisture, as in autoclaving, it loses its toxic properties although it may still contain a small amount of *d*-gossypol.

Although cotton seeds are extremely toxic, they also may be rendered non-toxic by autoclaving in a wet condition. By heating the seeds for a short time in a dry condition the gossypol becomes partially converted to the insoluble form and a separation made of the two by extraction with ether. The insoluble gossypol so produced is much more toxic than the insoluble form found in cottonseed meal or in seeds which have been subjected to steam heat. The determination of *d*-gossypol by the present chemical methods is not a safe criterion for estimating the toxicity of cottonseed products.

Acknowledgment

The writer's thanks are due to V. G. Heller and N. B. Guerrant for their constant interest and advice during the progress of this work.

Germicidal Efficiency of Sodium Hydroxide and Sodium Hydroxide-Carbonate Mixtures at the Same H-Ion Concentration[1,2]

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IT HAS been suggested that the H-ion concentration might be employed as an index of the germicidal efficiency of alkaline washing solutions. Observations with sodium hydroxide, sodium carbonate, and trisodium phosphate indicated very clearly that the H-ion concentration was not a dependable measure of the relative germicidal efficiencies of these alkalies.[3] Thus at pH 12.15 and 70° C. the killing times for 99.9 per cent of about a million bacterial spores were approximately 5 and 36 minutes for the trisodium phosphate and sodium hydroxide, respectively.

Many of the washing compounds consist of sodium hydroxide or mixtures of sodium hydroxide and carbonate. It was the purpose of the following observations to ascertain whether sodium hydroxide and mixtures of the hydroxide and carbonate at the same H-ion concentration were equally effective as germicides.

The procedure employed was to determine the surviving bacteria after various periods of exposure to the alkali solution and ascertain the time for effecting a reduction of 99.9 per cent. The organism employed was a spore-former of the *Subtilis* group. The details as to preparation of the test culture and technic of disinfection were identical with those previously described in studies on the effect of concentration of sodium hydroxide and temperature on disinfection.[4]

Experimental

SODIUM HYDROXIDE AND SYNTHETIC HYDROXIDE-CARBONATE MIXTURES—In this series of experiments normal alkali solutions were prepared by mixing various quantities of normal sodium hydroxide and normal sodium carbonate. The germicidal efficiencies of these mixtures at 50° C. were then compared with those of sodium hydroxide solutions of the same H-ion concentration.

Table I—Composition of Alkali Solutions

pH	SODIUM HYDROXIDE SOLUTION		SODIUM HYDROXIDE AND CARBONATE MIXTURES			
			NaOH	Na_2CO_3	NaOH	Na_2CO_3
	N	*% by wt.*	*Parts*	*Parts*	*% by wt.*	*% by wt.*
13.20	0.48	1.92	1	2	1.3	3.5
13.32	0.725	2.90	1	1	2.0	2.7
13.40	0.843	3.40	2	1	2.7	1.8

The composition of the various solutions is indicated in Table I. The results are shown graphically in Figures 1 and 2. They may be summed up as follows:

At pH 13.20 a 0.48 *N* sodium hydroxide was only slightly more efficient than a normal alkali mixture consisting of 1.33 per cent sodium hydroxide plus 3.5 per cent sodium carbonate. The hydroxide effected a reduction of 99.9 per cent of the exposed bacteria in 40.9 minutes, as compared with 43.7 minutes for the alkali mixture.

At pH 13.32 the sodium hydroxide solution (0.725 *N*) was more effective as a germicide than the normal alkali mixture consisting of 2.0 per cent sodium hydroxide and 2.7 per cent sodium carbonate. The killing time for 99.9 per cent of the exposed bacteria at 50° C. was 22.8 minutes for the hydroxide and 31.1 minutes for the mixture.

At pH 13.40 and 50° C. the hydroxide (0.8425 *N* or 3.4 per cent) effected a reduction of 99.9 per cent in 15 minutes as compared with 18 minutes for the carbonate-hydroxide mixture (2.7 per cent NaOH + 1.8 per cent Na_2CO_3).

The H-ion concentration does not seem to be an accurate index of the relative germicidal efficiencies of solutions of sodium hydroxide as compared with hydroxide carbonate mixtures.

SODIUM HYDROXIDE AND A COMMERCIAL ALKALI WASHING COMPOUND—A widely used commercial washing compound consisting of a mixture of sodium hydroxide and carbonate was employed, the concentration being adjusted to give a pH of 13.18 for the 50° and 60° C. series. This corresponded to a 0.5 *N* sodium hydroxide which gave pH 13.20. The concentration of the commercial washing compound on titration using methyl orange indicator was equivalent to a normal alkali, and contained 1.99 per cent NaOH and 2.66 per cent Na_2CO_3 on a weight basis.

Figures 3 and 4 show the results obtained at 50° and 60° C., respectively. It is apparent that the commercial washing compound at pH 13.18 was a better sterilizing agent than sodium hydroxide at approximately the same reaction (pH 13.20). Thus at 50° C. the killing time of 99.9 per cent of the exposed bacteria was 34 minutes for the commercial compound as compared with 40.8 minutes for the hydroxide, while at 60° C. the killing times were 8.5 and 11.75 minutes, respectively.

An analysis of the test materials shows that the commercial compound in the concentration used contained practically as much caustic alkali as the pure sodium hydroxide. The results therefore indicate that the presence of the carbonate in the commercial product served to increase the germicidal effect of the sodium hydroxide present, although the pH was not appreciably affected.

Another series of observations on the relative germicidal efficiency of sodium hydroxide and the commercial washing compound described above was carried out at 70° C. with

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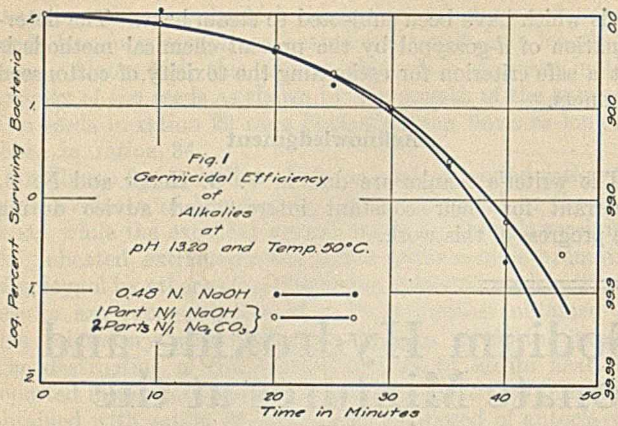
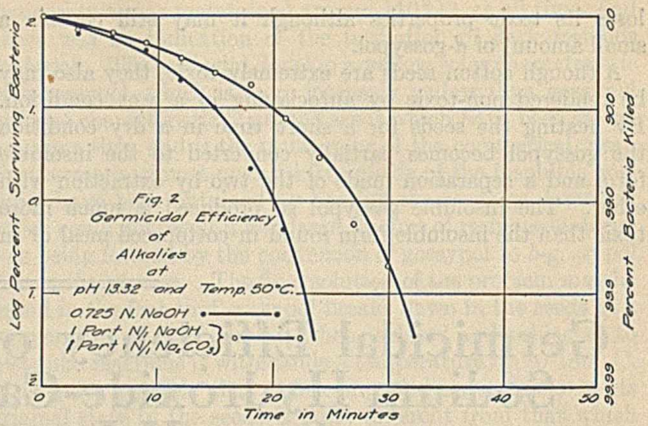
[1] Received June 29, 1927.

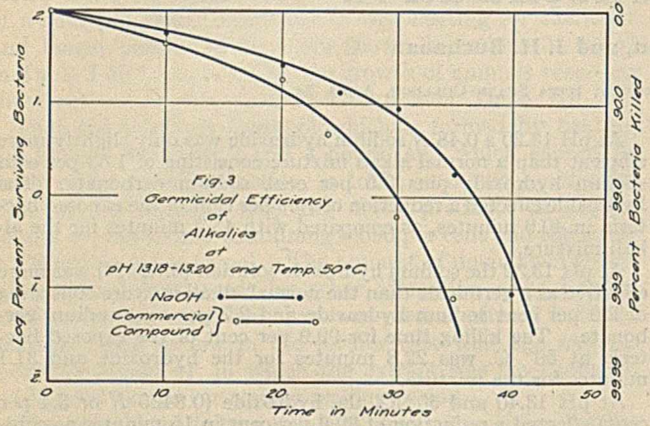
[2] These studies were made possible through a fellowship maintained by the American Bottlers of Carbonated Beverages at Iowa State College.

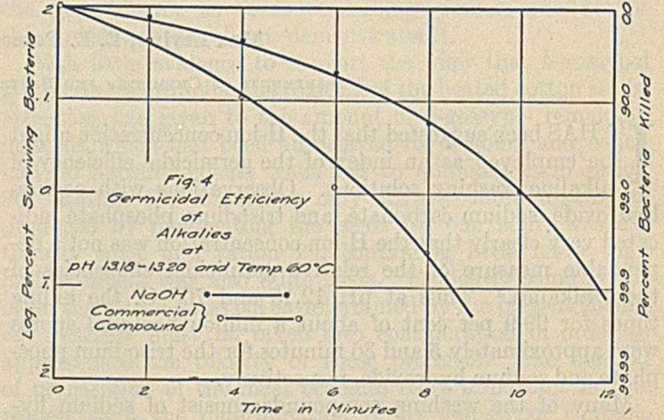
[3] Levine, Peterson, and Buchanan, *Ind. Eng. Chem.*, **19**, 1338 (1927).

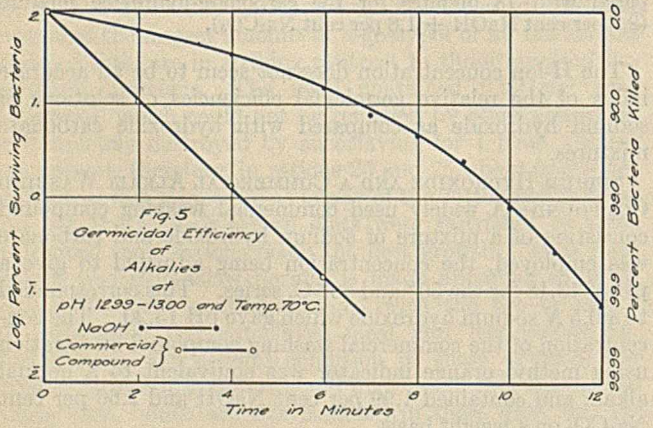
[4] *Iowa State College J. Science*, **1**, No. 4, 379–394 (1927).











weaker concentrations of the alkalies. A 0.25 *N* sodium hydroxide (1.0 per cent) with a reaction pH 12.99 was compared with a solution of commercial compound at pH 13.0. On a titration basis (methyl orange) the solution of commercial compound was equivalent to 0.5 *N* alkali and contained 0.995 per cent sodium hydroxide and 1.33 per cent sodium carbonate. The results are indicated in Figure 5.

At 70° C. the commercial washing compound at pH 13.0 effected a reduction of 99.9 per cent of exposed bacteria in 6.3 minutes, as compared with almost 12 minutes required by sodium hydroxide at pH 12.99. The concentration of sodium hydroxide in the two test solutions was practically the same (1.0 per cent), but the commercial compound contained in addition 1.33 per cent sodium carbonate. This additional carbonate did not affect the H-ion concentration of the mixture appreciably, but the germicidal efficiency was markedly increased.

The H-ion concentration (expressed at 30° C.) was not a dependable index of the relative germicidal efficiency of the commercial compound as compared with pure caustic, and the higher the temperature the greater was the discrepancy between these two determinations.

Discussion

At a constant temperature and H-ion concentration (determined at 30° C.) sodium hydroxide and hydroxide-carbonate mixtures were not equally efficient germicides. Thus it is seen from Table II that at pH 13.18 to 13.20 and a temperature of 50° C. the commercial alkali killed in 34 minutes, the sodium hydroxide in 40.8 minutes, and the hydroxide-carbonate mixture in 43.7 minutes—a variation of 22.6 per cent in killing time.

The titratable alkalinity was also unsatisfactory as an index of relative disinfecting power, for the 0.5 *N* hydroxide was less efficient than one of the 1.0 *N* hydroxide-carbonate mixtures but more efficient than the other.

Table II—Relation of Composition of Alkalies at pH 13.18–13.20 to Killing Times at 50° C.

Sample	Alkalinity by Titration	Concentration NaOH	Concentration Na_2CO_3	Killing Time
	N	*Per cent*	*Per cent*	*Minutes*
NaOH	0.5	2.00	0.00	40.8
NaOH-Na_2CO_3 mixture	1.0	1.30	3.50	43.7
Commercial washing powder	1.0	1.99	2.66	34.0

A comparison of the commercial alkali with the 0.5 *N* sodium hydroxide is extremely interesting. These two solutions contained practically the same quantities of sodium hydroxide (1.99 and 2.00 per cent), but the commercial product had in addition 2.60 per cent of sodium carbonate. The presence of the carbonate did not measurably change the H-ion concentration, but the killing time was reduced from 40.8 minutes to 34.0 minutes. From unpublished available data we can say that the disinfecting action of the sodium carbonate (2.66 per cent) at 50° C. was nil. It is therefore believed that the presence of the carbonate enhanced the germicidal efficiency of the hydroxide.

If the commercial alkali is compared with the hydroxide-carbonate mixture, it will be noticed that they had the same reaction (pH) and were both normal alkalies by titration, but the killing times were very different—namely, 34.0 and 43.7 minutes, respectively. Evidently neither the total alkalinity nor the H-ion concentration alone is a direct measure of the germicidal powers of these alkalies. Other factors are involved.

It is conceivable that the undissociated sodium hydroxide, rather than the OH ion, penetrates the bacterial cell. In this case the concentration of undissociated sodium hydroxide becomes the determining factor in the germicidal efficiency of alkalies. The addition of sodium carbonate to the hydroxide would result in an increase in the concentration of undissociated sodium hydroxide and thus increase the germicidal action. Because of the difficulty of measuring H-ion concentration at this high alkalinity, the change due to addition of the carbonate would not be readily detected.

The determination of H-ion concentration in the range pH 13.00 to 13.50 is subject to considerable error, and may therefore lead to anomalous results. Thus the commercial alkali (1.99 per cent NaOH plus 2.66 per cent Na_2CO_3) gave a pH of 13.20, whereas an artificial mixture of approximately the same composition (2.0 per cent NaOH + 2.70 per cent Na_2CO_3) was pH 13.32. These H-ion readings corresponded to sodium hydroxide concentrations of 0.5 *N* and 0.725 *N*, respectively. The germicidal efficiencies of the commercial alkali (pH 13.20) and the artificial mixture (pH 13.32) were similar (killing times of 34 and 31.1 minutes, respectively), whereas the killing times for the corresponding sodium hydroxide solutions, on a pH basis, varied from 40 minutes at pH 13.20 to 22.8 minutes at pH 13.32. Thus the artificial mixture and commercial alkali were about equally efficient germicides and superior to a 0.5 *N* and inferior to a 0.725 *N* sodium hydroxide. On comparing these solutions on the basis of H-ion concentration it is seen that the artificial mixture was less efficient and the commercial alkali more efficient than sodium hydroxide. This anomalous result is due to the difficulties inherent in determination of H-ion concentrations of solutions of alkalies in the range pH 13.00 to 13.50. A variation of 0.1 in pH is equivalent to a change of 1.0 per cent sodium hydroxide. Readings closer than 0.05 pH could hardly be obtained under very carefully controlled conditions. Herein lies a most serious obstacle in attempting to evaluate germicidal efficiencies of alkalies on a pH basis.

Summary

The H-ion concentration was not a direct measure of the relative germicidal properties of sodium hydroxide as compared with sodium hydroxide-carbonate mixtures.

At pH 13.2 to 13.4 and 50° C. the sodium hydroxide-carbonate mixtures contain less caustic alkali than the pure sodium hydroxide, and are less efficient germicides.

On comparing sodium hydroxide with a commercial washing solution containing the same amount of sodium hydroxide (and in addition sodium carbonate) at pH 12.99 to 13.20, the commercial product was found to be the better germicide, indicating that the sodium carbonate enhanced the disinfecting powers of the sodium hydroxide. This effect of the carbonate increased with temperature.

It is suggested that the undissociated sodium hydroxide rather than the hydroxyl-ion concentration may be the controlling factor in disinfection with alkalies.

The Scientific Use of Nitrogen Fertilizers[1]

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The controlling factor in determining the market price of fertilizer nitrogen is the cost of the synthetic production of compounds of this element. Improved technic is being applied to large-scale synthesis of compounds containing high percentages of nitrogen. As a result this element can be delivered to the field at a unit cost that is sufficiently low to offer attractive possibilities in a much enlarged use of it in crop production.

It has been pointed out that,[2] notwithstanding the requirements of crop plants and the deficiences of soils, that plant-food compound which is available in the largest amounts in any country is used in largest proportion by the farmers of that country. Thus American farmers use more phosphates, Chilean farmers more nitrates, and German farmers more potash salts than do the farmers of other countries in which these materials are not so abundant.

Within certain limits some fertilizer salts can be substituted for others with equally good effect. For example, phosphates stimulate bacterial fixation of nitrogen and thus serve as an indirect source of this element. Their correct use results in an enlarged root system of the plant, which increases its foraging power for potash and other nutrients in the soil. Thus, comparative trials of the same number of pounds each of a 2–12–2 and a 4–8–4 analysis may show almost identical effects on the crop during the earlier years of the test.

The abundance of phosphates in this country and their low price makes it possible to use them more nearly up to the limit of their efficiency. They not only serve as sources of the elements phosphorus and calcium for direct use of crop plants, but also produce desirable indirect effects at a cost that is often less than that for which these effects can be secured by other means.

A further explanation of the use of larger amounts of that fertilizer material which is available in greatest quantity at a low price is the research that is fostered by the syndicates which have the product for sale and the propaganda which follows up each advance that is made in the knowledge as to the more efficient use of the material. Research finds the places where and the means by which a fertilizer salt can be made most effective. Propaganda and sales effort put the salt in these places and get it used efficiently. In the event that the same effect can be secured by the use of either of two salts, price ultimately becomes the determining factor in deciding which will be used.

The foregoing statements anticipate, in part, the story that is now being written for synthetic nitrogen. This element is being taken from the air in large amounts. Enormous quantities of its salts will eventually be synthesized and at a lower cost per unit of nitrogen. Intensive studies are being made of possible means of securing greater returns for each

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[1] Presented before the Division of Fertilizer Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] Curtis, *Am. Fertilizer*, **64**, No. 13, 73 (1926).

pound of nitrogen applied. The effects of the other elements in the nitrogen-bearing compounds are also being investigated. The world is being combed for places wherein the economic, climatic, edaphic, and biotic factors are best suited to the use of larger amounts of nitrogen. In Germany, where the nitrogen-fixation industry is best established, the consumption of fixed nitrogen for fertilizer purposes increased from 185,000 tons in 1913–14 to 335,000 tons in 1924–25. One may confidently anticipate further rapid increases in the consumption of nitrogen fertilizers not only in Germany but in the other important agricultural countries as well.

Whereas, until quite recently, farmers were limited in their selection of nitrogen carriers to Chilean nitrate, sulfate of ammonia, and the various by-product organic ammoniates, they may now choose from cyanamide, nitrate of lime, ammonium nitrate, ammonium sulfate-nitrate, ammonium phosphate, ammonium chloride, and urea as well. These, and additional nitrate of soda and sulfate of ammonia, are now being synthesized in quantity. Possibilities in the economic production of other nitrogen compounds are also being investigated. By reason of the opportunity for choice, it is possible to fit the carrier of nitrogen more nearly to the requirements than formerly and thus to increase the profit from its use.

Factors Influencing Choice of Nitrogen Carrier

Various factors are involved in determining the choice from among these nitrogen carriers. Consideration must be given to the form in which the nitrogen occurs in the compound; to the secondary effects of other elements, radicals, or compounds that are present in the material; to the nature of the soil and the climate; to the requirements of the crop to be grown; and to the applied cost of a unit of nitrogen as compared with the algebraic sum of the values of the several effects produced by the quantity of each material that is required to supply that amount of nitrogen.

In so far as the form of nitrogen is concerned, carriers of the element may be conveniently grouped into nitrates, ammonium compounds, amides, and by-product organics. In general, the order of the rate at which the nitrogen of these various groups of materials becomes available to crop plants is that in which they are named above. Thus the nitrogen of nitrates is usually immediately effective while that of the other materials requires varying periods of time before its full effects are secured. The time factor depends upon the soil and the weather conditions as well as upon the nature of the nitrogen carrier and the requirements of the crop. Differences in the effectiveness of the nitrogen of these various groups of materials, often noted in comparative tests in which they have been applied at planting time, can be overcome in large part by regulating the time of application with regard to the nature of the material and the period at which the full effect of its nitrogen is desired.

Usually the availability of the nitrogen of ammonium compounds is placed at 90 and of high-grade organics at 80, if that of nitrates is given a rating of 100. Tests have shown, however, that if the ammonium salt is applied 10 days or 2 weeks in advance of planting the crop or previous to the time at which the full effect of the nitrogen is desired, it will often be equally as effective as a nitrate. In many regions of heavy rainfall and on sandy soils the advantage lies with the ammonium salts and high-grade organic carriers of nitrogen in that their nitrogen is retained by the soil in contrast to the serious losses by leaching that may occur from the use of nitrates. In such cases nitrates may produce as good results as ammonium salts and organics, if fractional applications are made as additional nitrogen is required by the crop.

Under conditions in which the soil is highly saturated with water for some time, the nitrogen of nitrates is ineffective, probably by reason of its loss in elemental form as a result of denitrification. The frenching of tobacco and the yellow appearance of corn and other crops in wet areas in a field are evidence of nitrogen starvation resulting from nitrate reduction. Crops such as paddy rice, which grow normally under flooded conditions, must have their nitrogen supplied in some other form, normally as ammonium salts. There is evidence to support the belief that potatoes, buckwheat, and other crops which grow well on quite acid soils also use ammonia nitrogen as such. The grasses seem to be capable of taking up large amounts of ammonia and of converting it very rapidy into proteins. In fact, the use of heavy dressings of nitrate nitrogen on pastures has been found to be objectionable, since under certain weather conditions the nitrates are absorbed by the grass more readily than they are converted into amide or protein nitrogen and therefore tend to accumulate in concentrations that are toxic to livestock.

Nitrates have a distinct advantage in regions of sparse rainfall, for here the rate of ammonification and oxidation of ammonia to nitrates is too slow. Soils of such regions are normally not acid in reaction and the plants that are there grown are those which utilize the nitrate nitrogen to best advantage. Nitrates may also be preferred in times of drought in humid climates. For rapidly growing vegetables, for short-season crops such as barley, for regions of short summers, and for cold, backward seasons the nitrate is quite likely to be more effective than is any other form of nitrogen.

Ammonium, calcium, potassium, and sodium nitrates may produce very different effects, depending upon the nature of the soil and the needs of the crop for their cations. Potassium and ammonium, having known values for plant-nutrition purposes, are sold at their commercial valuation. Sodium and calcium, although they produce certain well-known effects on crops and soils, have no commercial rating when combined with the nitrate radical. The sodium may serve as a partial substitute for potassium in the fertilizer in so far as its effect on the crop is concerned. Continued heavy applications of sodium nitrate tend to effect the deflocculation of soils. This is decidedly objectionable in the case of those that contain considerable percentages of clay but may be of distinct advantage in sandy soils. In irrigated regions where trouble is experienced with alkali the use of sodium nitrate increases the difficulty.

Calcium nitrate is in many ways an ideal source of nitrogen in that the calcium ion not only has no objectionable effect on most plants but is, in general, extremely useful in improving soil conditions for the growth of plants. Solution culture studies have shown that if the nutrient solution is out of balance by reason of an excess of any other cation the calcium ion is the most generally effective in bringing the culture solution back to a condition of non-toxicity. Many soils are unproductive because of a deficiency of calcium for neutralizing or balancing purposes. In this lies the explanation of the usefulness of liming materials. The high solubility of calcium nitrate gives its calcium a greater value for some soil and plant purposes than has the calcium in the carbonate form.

The one outstanding characteristic of all nitrogen compounds, except the nitrates and cyanamide, is their acid effect when applied to the soil. As the nitrogen of ammonia, urea, or by-product organics, as well as that which is fixed by soil bacteria, is nitrified in soils, its acid effect becomes apparent. In proportion as the nitrate radical is built up into protein form by plants it is removed from the field of action. In general, however, the recovery in the crop of the added nitrogen does not exceed 50 per cent of the amount applied. The remainder may be utilized in part by soil microörganisms, in which case it is also stored in protein forms. The permanently acidulating effect is measured by the amount of nitrate which escapes in the drainage water. This varies from very small amounts in grass-covered soils to quite large amounts in soils under clean cultivation that carry no growing vegetation during considerable portions of the year.

The simplest case is that of urea in that in this material no fixed acid or basic constituents, other than nitrogen, are present. A somewhat more complicated problem is presented by the chloride and sulfate of ammonia. These salts on oxidation in the soil leave, in addition to nitric acid, equivalent quantities of hydrochloric and sulfuric acids, respectively. Chlorine is of little value to plants; therefore most of the hydrochloric acid acts on the soil to form salts that are later carried away in the drainage water. In the case of the ammonium sulfate the effect is somewhat less marked by reason of the utilization of a part of the sulfur in the formation of proteins in crop plants and in soil microörganisms. However, the continued use of sulfate of ammonia on acid soils has effects that cannot be ignored.

From 100 pounds of pure sulfate of ammonia approximately 95 pounds of nitric acid and 75 pounds of sulfuric acid are liberated in the soil. The quantity of pure limestone required to neutralize these amounts of acid is nearly 150 pounds. It may therefore be said that for every 100 pounds of sulfate of ammonia applied to the soil in no case will more than 150 pounds of pure limestone be required to neutralize the acid that may be produced. In proportion as this nitric and sulfuric acid is utilized by crop plants and soil microorganisms the quantity of lime required for neutralizing purposes is reduced.

With increasing acidity soils reach a point of equilibrium at which it is difficult to effect a further increase either in their hydrogen-ion concentration or in their base-absorbing capacity. The quantity of limestone required to neutralize the acid effect of an application of sulfate of ammonia is, therefore, also dependent upon the degree to which the soil complex has already been depleted of its basic constituents. Most of the cropping in humid regions is on soils the pH of which is between 5 and 6. Under these conditions it seems entirely safe to assume, both from theoretical and experimental grounds, that not more than 50 pounds of calcium carbonate will normally be required to counteract the increase in acidity resulting from the use of 100 pounds of sulfate of ammonia on the soil. There is evidence also that when ordinary acid phosphate and sulfate of ammonia are applied together at the rate of about 3 pounds of the former to 2 of the latter no acidulating effect on the soil results. The mixing of sulfate of ammonia and nitrate of soda, or the alternate use of sulfate of ammonia and either nitrate of lime or nitrate of soda, merits consideration in this connection.

If the soil contains carbonates, as is the case in semihumid regions and in areas in which irrigation is necessary, the use of acid-forming carriers of nitrogen is preferable. Most soils in humid regions are not improved for crop-producing purposes by further acidulation. This is particularly true for the growing of such high lime-requirement crops as sugar beets, alfalfa, celery, and onions. It is of much less significance in the case of potatoes, oats, rye, cotton, and alsike clover.

The regular use of liming materials is an essential part of a scientific farming program in humid climates. Following an application of lime, however, ammonia salts are often more effective than nitrates, especially in the production of plants that grow best on acid soils or which are attacked by disease organisms that are favored by soil conditions approaching neutrality, as is the case with tobacco and potatoes. In proportion as lime is not used or as the time advances between applications of lime, nitrates are quite likely to give better results except as some factor other than soil reaction is involved.

When one considers the differences in the nature of soils as, for example, between sands and clays or between those of irrigated deserts and those of tropical regions; the variations in the climatic conditions as between regions of frequent showers and relatively slow rates of evaporation and areas like the Corn Belt that are often subjected to considerable periods of drought between times of heavy rainfall; the differences in the requirements of plants as between the acid-tolerant grasses of putting greens and acid-sensitive cabbages; he is impressed with the need for a considerable variety of nitrogen fertilizers having a wide range in their chemical properties.

Bacterial Fixation

It has been a somewhat current belief that our chief dependence for nitrogen to replace that lost through crop removal and in the drainage water must be based on bacterial fixation. This point of view originated when fertilizer nitrogen was very expensive; when practically the only source of nitrogen was Chilean nitrate of soda, the supply of which was known to be limited; and before much was generally known as to the scientific use of nitrogen fertilizers. Investigation has shown the possible efficiency of the several groups of bacteria which function in this capacity. Continuous cropping experiments with wheat indicate that the yield can be maintained indefinitely at about 10 bushels per acre without the use of either manure or fertilizer. By applying phosphate and potash fertilizers this yield can be raised 3 to 4 bushels. It is probably safe to assume that non-symbiotic nitrogen-fixing organisms can be depended on to accumulate enough nitrogen to meet the requirements for the production of one-fourth of the maximum yield of wheat. On this assumption it then remains to consider the legume program as a means of securing the additional nitrogen required in the production of full yields of wheat and other crops.

The evidence shows that neither in the more extensive nor in the more intensive systems of farming is it economical to grow adequate acreages of legumes to meet this requirement. In the intermediate systems of farming in the Corn Belt there seem to be two very definite possibilities of maintaining the supply of nitrogen in the soil at a fairly high level with economy. One of these lies in the growing of sweet clover as a green manure and the other in the adoption of a regular rotation of grain crops and legumes, the feeding of these crops on the farm, and the careful saving and returning of the manure to the field.

The sweet clover green-manuring program seems especially well adapted to the needs of the Corn Belt. Sown in the wheat or oats, a fairly heavy growth is often made during the same season. A second rank growth, containing as much nitrogen as 1000 pounds of sulfate of ammonia, often takes place in the spring before it is necessary to plow it under for corn. This is enough nitrogen to meet the needs of a 100-bushel corn crop. Green materials like sweet clover, having a high ratio of nitrogen to carbohydrates, undergo very rapid nitrification, particularly during the early summer months. In fact, the very dark green color sometimes noted on young corn plants following the plowing under of sweet clover indicates that so much available nitrogen is at their disposal as to have an injurious effect.

It is well to keep in mind that only a portion of the nitrogen accumulated by a legume comes from the air. In proportion as there is available nitrogen in the soil the nitrogen-fixing organisms fail to function in this capacity. The level to which the nitrogen content of the soil can be raised by fixation processes is not necessarily as high as would be required to supply sufficient available nitrogen for maximum yields, particularly of those crops which do not immediately follow the plowing under of the legume crop. In proportion as the legume crops are harvested and removed from the field the quantity of nitrogen added to the soil is lessened. It is of interest in this connection to note that alfalfa is often very much benefited, both in getting started and after several years of growth, by applications of available nitrogen.

Notwithstanding the possibilities of the legume program, if one were to analyze the practices on one hundred typical Corn Belt farms or had available for study an accurate record of what takes place on any one farm during a century of farming, he would be convinced that a state of emergency as to the nitrogen supply exists and bids fair to continue to exist indefinitely. Fertilizer nitrogen has the advantage that, no matter how much a well-planned legume program offers for the future, today's emergency need for this element can be met. However high the content of organic nitrogen in the soil may be, the rate at which this nitrogen is supplied to the plant at critical periods in its growth may be entirely inadequate. Of interest in this connection is the fact that soil microörganisms may compete with the crop plant for available nitrogen under conditions in which the organic matter that is worked into the soil is high in its content of carbohydrate materials and low in nitrogen. This is the case when cornstalks, straw, coarse manure, and many types of weeds are plowed under.

A study of the legume program also raises doubts as to whether this is necessarily the cheapest means by which protein can be secured for feeding purposes and sufficient amounts of nitrogen can be provided for the growing of non-legume crops. The cost of protein in legume hays and pastures has never been adequately compared with its cost in nitrogen-fertilized, non-legume hays and pastures. This comparison is of particular interest for an area such as the New England States, where the climatic conditions are especially favorable to the grasses. The relative costs of nitrogen in legumes and fertilizers also merit consideration in proportion to the rise in land values and labor costs and the reduction in the cost of the synthetic production of the compounds of this element.

Climatic Conditions and Problem of Drought

Central European grain and root farmers not only grow legumes and produce and use large amounts of manure, but add liberal dressings of nitrogen fertilizers to their crops as well. Much higher acre yields of crops than are produced in the United States are the result. One must keep in mind that the climatic conditions in Central Europe are much more favorable to high yields of the small grains, potatoes, and root crops, and therefore to the advantageous use of nitrogen on these crops, than are those of the Corn Belt of this country. For example, in Berlin, Germany, it rains during 170 days of the year and there are only 44 entirely clear days annually. In Des Moines, Ia., the days having rain are 84 and the number of clear days 187. Other important differences in the climatic conditions become apparent on detailed study of this problem. The remarkably high yields of wheat secured by the heavy use of high-nitrogen fertilizers in Germany, Holland, and England probably cannot be duplicated over any very large area of land in this country with the present intensity of our agriculture and the varieties of wheat that are now being grown. A very important problem for all but the more northern and northeastern parts of the United States is the breeding of such types of cereal crops as will be better able to withstand the droughty conditions under which we are farming. Definite progress has already been made in this direction.

The problem of drought is in many ways the most serious one with which the crop grower has to deal. In the Corn Belt especial precautions must be taken to conserve the moisture supply. Phosphates have certain advantages in stimulating root growth and permitting greater resistance against drought. By bringing wheat and oats to earlier maturity they escape the drier weather of July and August. Under these conditions nitrogen must be used in such a manner and amounts as to prevent excessive vegetative growth or delay in maturity. Excessive use of phosphates on corn and tobacco tends to bring these crops to maturity too early in the summer before the drought is broken, unless this effect is counteracted by the use of nitrogen and potash. If large amounts of available nitrogen are present in the soil at seeding time, rank vegetative growth may be produced at the expense of root development and early maturity. If the nitrogen is applied somewhat later in the growth of the plant, its effect may be largely an improvement in quality and yield of grain.

In the Great Plains region considerable difficulty is experienced in effecting the decay of organic matter by reason of inadequate moisture supply. Manure, unless well rotted and rightly used, may have disastrous effects. The growing of legumes robs the soil of water and brings about conditions of drought for the crop that follows. Under such conditions it will be seen that readily available fertilizer nitrogen applied at the proper time has certain advantages over that which is present in the soil in the form of legume and other crop residues.

In the production of grass and of hay crops other than legumes, lack of nitrogen is usually so seriously a limiting factor that even the root systems of the plants fail to develop adequately. This is because these crops have the capacity to consume large amounts of nitrogen while the conditions in the soil during their growth are such as to bring nitrification almost to a standstill. The evidence indicates that, in spite of the enormous increase in vegetative growth produced as a result of the use of nitrogen top dressings, the grass is usually less subject to drought than when nitrogen is not used. This same drought resistance has been noted with nitrogen-treated fruit trees when grown in sod culture. This indicates that very large amounts of nitrogen must be applied to grass before the nitrogen-carbohydrate ratio in the upper portions of the plants becomes such that vegetative growth takes place at the expense of the development of adequate root systems.

Time of Feeding

Experiments in the technic of feeding plants show certain advantages in being able to supply them with nitrogen at particular stages in their growth. Soluble nitrogen is applied to apple trees a few weeks in advance of the blossoming period. Tomato growers desire a small amount of readily available nitrogen to start the plants, slowly available nitrogen until the blooming period, and more highly available nitrogen after the fruit is set. Strawberries should have a light application of nitrogen in the spring of the first year after planting and heavy dressing of nitrogen in the early fall for a heavy set of fruit the following year. Some of the best farmers in Europe apply phosphate and potash fertilizers at seeding time for winter cereals and use most of the nitrogen as a top dressing before growth starts in the spring. The protein content of wheat can be increased by applying nitrate at the heading stage. Many other possibilities suggest themselves.

Pasture Maintenance and Improvement

One of the outstanding problems in the world's agriculture is that of pasture maintenance and improvement. Long experience with this problem has led to the general adoption by progressive farmers of a program of pasture management in which use is made of phosphate and liming materials, and some potash, to stimulate the growth of clovers in the pasture, in order to secure adequate amounts of atmospheric nitrogen to meet the requirements of the grasses of which the pasture is largely composed. This system results in an alternation of clovers and grasses and when systematically practiced is fairly satisfactory. While attention has frequently been called to the possibility of using nitrogen fertilizers as a substitute for the clover scheme, little has been done in this direction because of the relatively high cost of fertilizer nitrogen and the low cost of protein feeds. The release of synthetic nitrogen for agriculture altered the ratio between the costs of these materials. As a result new experiments with nitrogen fertilizers on pastures and meadows were begun at a number of different points in Central Europe.

Early in these tests two facts of fundamental importance were discovered. One is that by the use of heavy applications of nitrogen fertilizers, in addition to the phosphate-limestone program, very young grass can be made to contain such a high amount of protein (reported as high as 28.6 per cent of the dry matter) that only high-producing cows can take full advantage of its milk-making qualities. The other is that not only is the carrying capacity of the pasture very considerably increased, but the pasture season begins several weeks earlier in the spring and continues later in the autumn.

As a result of several years of investigation of this problem a combined system of pasture and meadow management has been developed which, with various modifications, is now under way on a number of farms in England, Holland, and Germany. The system involves dividing the combined meadow and pasture land into eight to ten fields; treating the land with phosphate, limestone, and potash as required; adding from 50 to 100 pounds of nitrogen as ammonia salts or urea per acre, half before growth starts in the spring and the remainder at suitable intervals during the growing season; starting the milch cows on that field on which the grass first reaches a height of about 4 inches and having enough cows to eat the best of this grass in 3 or 4 days, then turning them into the next field; following the milch cows with dry cows, calves, or other animals whose protein requirements are not so high, to clean up the remainder of the grass; and using for hay such fields as are not required for pasture until later in the season. In England it is believed that this is the most revolutionary discovery as relates to the agriculture of that country that has been made in the last forty years.

Synthetic Nitrogen Released for Agriculture

Following the World War European countries found it difficult, by reason of unfavorable exchange rates, to purchase American concentrated feeds, on which they had long depended for protein, primarily for feeding and secondarily for fertilizer purposes. At the same time the synthetic nitrogen compounds that were being produced on a large scale were no longer required for munition purposes and were released for agriculture. The question then arose as to the extent to which it might be possible to use this nitrogen as a means of overcoming the necessity of importing American feeds and foods. The period of depression through which the farmers of the United States are passing testifies somewhat as to the success of their efforts in this direction.

The synthetic-nitrogen industry of Germany claims that in Central Europe 1 pound of nitrogen, intelligently used, can be depended on to produce 20 pounds of grain, 100 pounds of potatoes, 150 pounds of sugar beets, 45 pounds of hay, or 20 pounds of milk. An examination of the experimental evidence indicates that these figures are not too high for the climatic conditions that there obtain, for the varieties of crops which are grown, and for the relatively high acre rates at which nitrogen is being applied.

Place of Nitrogen in Fertilizer Analyses

In eastern United States phosphoric acid is not so dominant in fertilizer analyses as it is farther west. Nitrogen percentages are considerably higher. This has been explained on the assumption that the excessive use of phosphates has built up a reserve of phosphoric acid in the soil with the result that it is no longer the plant-food constituent that is in greatest deficiency. The explanation probably lies, however, in the better moisture relationships that there obtain as a result of which nitrogen comes into the leading role. It is further evident that in proportion as the effects of drought are overcome to the end that higher acre yields are produced, whether by plant breeding, improvement in soil management, or the development of more scientific methods of plant feeding, nitrogen is quite likely to occupy a more prominent place in fertilizers.

Optimum Application

Contrary to the original law of the minimum, as formulated by Liebig and later modified by Mitscherlich, it now seems probable that, except as the lack of water or of some nutrient is a limiting factor, a greater return of crop per unit of fertilizer applied can be secured from moderately heavy than from light applications. The curve of increase, instead of being a straight line or logarithmic, is believed to be of the sigmoid type. The crop increase per unit of nitrogen applied is at first small, then increases rapidly, and later decreases as the rate of application becomes quite high. Certain American field data lend support to this conception of the increased effectiveness of heavier applications of nitrogen. This is particularly significant with reference to fertilizer practice in this country, since nitrogen is normally used in very small amounts both in field experiments and in practice.

Future Possibilities

Attention should be called to some very interesting possibilities in the further use of nitrogen fertilizers. A few years ago some investigations were reported from Rothamsted, England, on the production of artificial manure made from straw and similar materials by reënforcing them with nitrogen, phosphoric acid, and lime in sufficient amounts to meet the needs of the bacteria of decomposition. For a time the process was viewed with considerable skepticism, but continued investigation reveals that it is entirely feasible. A material can be produced that has all of the desirable qualities and none of the undesirable ones of the product of animal origin. Furthermore, the cost of this artificial manure is probably no greater than that of the animal manure produced on the average American farm, if consideration is given to all of the items which should enter into cost accounting in manure production.

This introduces the subject of what may be termed "factory farming." It may not be well to speculate too far or to raise any false alarms, but one would not go amiss perhaps to call attention to some interesting possibilities that are being investigated in the production of synthetic foods capable of replacing high-protein feeds for animals and meat and milk for humans, without loss of palatability. There is no longer any question but that such foods can be produced and at a cost that is not prohibitive. In fact, they are now being manufactured and sold in considerable amounts. Steinmetz, commenting on this problem, said:

> Within a century or two or even a shorter time we could supply the food demands of the World not through the cultivation of new areas for the growing of wheat but by producing it through microörganisms which would be raised on suitable mineral products without depending upon sunlight.

Highly important economic adjustments among the various agricultural areas of the world are sure to result from an abundance of nitrogen. China and India, where fertilizers have never been used, are now being propagandized and are becoming interested. Russia, almost three times the size of the United States and with vast areas of excellent farming land, is an unexplored field. The great plains of Hungary and Roumania can be made to produce double their present yields when fertilizers are applied. The tropical regions of the world, where nitrogen is an especially important constituent in the fertilizer, have enormous possibilities, as yet untouched, in the production of crops for use in the manufacture of clothing and of carbohydrate foods. Vast areas of level land, capable of producing high acre yields, are to be found in Brazil and the neighboring countries of South America. In Canada conditions are especially favorable for the use of large amounts of nitrogen in the growing of cereal crops. English agriculture is taking on new life as a result of its having been found possible, with liberal dressings of nitrogen fertilizers, to grow enough pasture on one acre to support two steers or milch cows, instead of requiring two acres or more for one animal unit. Germany now feels entirely capable of feeding herself.

The immediate effect of cheaper and more abundant supplies of nitrogen will probably be that of raising the yield on the better farming land and forcing a larger acreage of other land into pasture and forest. This will reduce the percentage of the total population that can profitably be employed in agriculture and release more workers for industry.

Notes on the Clerget Factor and Deerr Method of Double Polarization[1]

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In 1915 Noel Deerr outlined a method for the Clerget determination of sucrose. The inversion was made with sulfuric acid. To this was added aluminum sulfate and then barium hydroxide to neutrality. This gave a precipitate of aluminum hydroxide and barium sulfate, leaving none of the inverting reagents in solution. The method did not prove satisfactory. By changing certain details of acid concentration and time and temperature of inversion, however, it was found possible to get satisfactory results, the Clerget constant being 141.7. A description of this method is preceded by a discussion of double polarization in general and the errors incident to the various methods proposed—that is, neutral direct polarization, with acid inversion and acid invert polarization; neutral invert polarization, the acid being neutralized by a base and the equivalent quantity of salt being added to the direct polarization; neutral direct polarization and neutral invert polarization, using invertase.

THE determination of sucrose in the presence of optically active substances is dependent upon the principle of invert polarization which is expressed in the following formula:

$$S = \frac{DP - IP}{141.66 - \frac{T}{2}}$$

In determining this formula using c. p. sucrose the direct polarization is assumed to be 100. The invert polarization is determined for the half-normal weight of 13 grams inverted, diluted to 100 cc., and read at 20° C., with the bichromate cell in the saccharimeter.

Clerget Factor

In calculating this formula the rotations of glucose and fructose at 20° C. in approximately fourth-normal concentrations are taken as strictly additive and, using the older values of specific rotation for glucose and fructose, the double invert reading should be −31.66° at 20° C. The correction $T/2$ is accurate at 20° C., and is sufficiently accurate within the range of 15° to 25° C., in determining the factor 141.66. When one attempts to verify this factor experimentally, however, higher figures are always obtained, ranging from 141.7 to 142. Using the more recent values for specific rotation and the ratio between this and the Ventzke scale, the figure is still higher. Zerban confirmed the work of Vosburgh, and obtained a value of 142.05. Subsequent redeterminations by Zerban, confirmed also by Brewster, raised this value to 142.09. The official factor for the invertase method is 142 according to the A. O. A. C. Methods for 1925, and is at present 142.1 [tentatively].

This probably means that the rotations of glucose and fructose dissolved together and diluted to 100 cc. are not strictly additive, but the presence of the one makes unnecessary a certain amount of water and thus increases slightly the real concentration of the other.

If the original solution for direct polarization contains reducing sugars, the factor must again be altered because the specific rotations of glucose and fructose vary with concentration. It is possible to allow for this if glucose and fructose are present in equimolecular quantities, but ordinarily there is more glucose than fructose and then it is rather difficult to get a factor which is strictly correct, though the error is practically negligible.

There is also the matter of quartz compensation for rotary dispersion, which is fairly close for sucrose, using light filtered through the bichromate cell, but not so close for glucose and fructose. This error is practically negligible.

For the purpose of this article we shall assume the old factor of 141.8, which is the figure obtained several years ago by Hudson, inverting with invertase.

Methods for Invert Polarization

In ordinary technical work there are two methods for invert polarization. The first is the invertase method, which takes too long for commercial purposes, is rather expensive, and must be used under carefully controlled conditions. The newer invertase preparations are sufficiently concentrated

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[1] Presented before the Division of Sugar Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

to decrease the amount of time necessary, but the other objections still maintain.

While it is probable that the invertase method will eventually become the standard commercial method, at the present time most invert polarizations are made after acid hydrolysis. These have been standardized as far as concentration is concerned, until now it is agreed to invert not more than the half-normal weight, and to polarize at as near 20° C. as possible. Hydrochloric acid is ordinarily used.

Method. To 50 cc. of solution containing not more than a half-normal weight of the sample, 10 cc. of hydrochloric acid of 1.1029 (20°/4° C.) specific gravity of 25° Brix at 20° C., are added, the flask being rotated. This is then heated to 67° C. in 2.5 minutes and kept at 67° C. for 5 minutes with occasional shaking, the temperature not being allowed to rise higher than 69° C. The flask is then cooled in water to 20° C. and the solution polarized, the temperature being read to 0.1° C.

This is the present official method, and the Clerget formula used with it employs the factor 143 for the half-normal weight at 20° C., the temperature correction being $T/2$, and the concentration correction being $+0.0676(M-13)$, where M represents the grams of total solids in 100 cc. of the invert solution read in the polariscope. For half-normal weights, therefore, the concentration correction is practically zero. The factor 143 is affected considerably by concentration; for a normal solution it would be 143.88, for a 1 per cent solution it would be practically 142.2. This table of concentration corrections is accurate when there are no reducing sugars in the solution taken for direct polarization, but since the rotation of fructose is very considerably increased in the presence of hydrochloric acid, the direct polarization taken in neutral solution when reducing sugars are present is higher than it would be in acid solution, assuming no inversion of the sucrose. This, too, can be allowed for to some extent if glucose and fructose are present in equal proportions in the direct polarization, but where the glucose is in excess, as is ordinarily the case in technical analyses, the correction is difficult to make. Moreover, while the rotation of fructose is increased by hydrochloric acid, fructose itself is gradually destroyed by hydrochloric acid at 70° C. and above. At 78° C. the destruction in 8 minutes is sufficient to reduce the factor from 143 to about 141, though there is no regularity as to the lowest value. This destruction is quite noticeable at 75° C., where the factor falls to about 142. At 73°, at 71°, and even at 70° C., figures were obtained all lower than 143. In fact, it is difficult to say that there is no destruction of fructose at the official temperature of 67° C. It is highly probable that under the ordinary laboratory conditions, where the interior of the inversion flask is 67° C., the exterior may be heated locally to several degrees above 70° C., which is certainly the danger mark. Local overheating, therefore, will give too low figures for sucrose. To avoid overheating, attempts have been made to invert for a longer period at a lower temperature, but these methods have not been widely accepted inasmuch as the increased time is the very thing the technical chemist wishes to avoid. Moreover, for every deviation from the prescribed method a different factor must be employed and different tables calculated. For this reason acid invert polarization with neutral direct polarization is the method ordinarily employed.

In order to avoid the obvious defects in this method, the invert solution was neutralized with sodium or ammonium hydroxide, thus replacing hydrochloric acid with sodium or ammonium chloride. Salts also affect the polarization of the invert sugars, however, and Saillard therefore proposed that an equivalent quantity of the salt be added to the direct polarization in order to compensate. This method is slightly wrong in theory. It assumes that a definite amount of salt will affect the rotation of all sugars in the direct polarization solution, irrespective of their concentrations, to the same extent that it affects the reducing sugars produced by the inversion of sucrose. The error introduced here is not great, particularly in the method worked out in considerable detail by Jackson and Gillis. However, the acid is frequently neutralized by adding a drop of phenolphthalein and then titrating with sodium hydroxide to neutrality. Neutrality to phenolphthalein is really alkalinity, the pH being about 9, and the optical activity of the sugars is somewhat reduced even in slightly alkaline solutions. Moreover, if any acid other than hydrochloric is used for inversion, and if anything other than sodium hydroxide is used for neutralization, it is necessary to calculate new factors because the different salts affect the rotation of the sugars differently.

All these objections, therefore, are arguments for the general use, even commercially, of the invertase method, the only alternative being a method in which the reagents used for inversion are removed from the solution before the final reading is taken. In 1915 a method to accomplish this was proposed by Deerr.[2]

Deerr Method

Solutions—*A*. A saturated solution of 0.52 *N* barium hydroxide (strength depending considerably on temperature). *B*. A solution of aluminum sulfate and sulfuric acid made by dissolving 165 grams of crystallized aluminum sulfate in water, adding 135 cc. of 1 *N* sulfuric acid, and making up to 1000 cc.

A is titrated against *B*, and *B* is diluted so that 25 cc. of *A* are equivalent to 15 cc. of *B*. (Deerr recommended phenolphthalein as indicator.)

Direct Reading—Fifty cubic centimeters of solution to be analyzed are placed in a 100-cc. flask, 25 cc. of solution *A* are added and, after mixing, 15 cc. of solution *B* are run in with agitation during the addition. The volume is then completed to 100 cc. with the addition of 0.1 gram of sodium hyposulfite in certain cases. The filtrate is used to obtain the direct reading, which is decreased by 0.7 per cent to compensate for the volume of the precipitate formed; or the volume may be completed to 100.7 cc.

Inversion Reading—Fifty cubic centimeters of material to be analyzed are placed in a 100-cc. flask, 15 cc. of solution *B* are added, the flask is placed in a water bath, and the temperature maintained at 95° to 97° C. for 20 minutes. (In 1921, Deerr recommended inversion at temperature of boiling water for 30 minutes.) After cooling, 25 cc. of solution *A* are added, and the inversion reading is obtained exactly as the direct reading. The sucrose is calculated by the usual formula

$$S = \frac{D - I}{K - \frac{T}{2}}$$

where D and I are the direct and inversion reading, respectively, K is a constant varying with the dilution, and T is the temperature of observation. In both D. P. and I. P. solutions barium sulfate and aluminum hydroxide, being precipitated in the solutions, act as satisfactory clarifying agents.

Deerr claims for this method:

(1) Direct and invert readings are taken under identical conditions.

(2) Disturbing influences of lead salts or of the reagents used for inversion are eliminated.

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[2] *Intern. Sugar J.*, **17**, 179 (1915).

(3) It is practically suited to analyses where separation of dextrose and levulose are required.

(4) The filtrate is well adapted for the determination of reducing sugars.

These claims are justifiable, but the method has attracted very little attention. In the laboratory of the Audubon Sugar School it was tried out a number of times with unsatisfactory results, which may have been the experience of others. In 1925 the writers undertook this work to find out what was wrong with so ingenious a method.

Investigation of Deerr Method

Sucrose (c. p.) was prepared in the usual way. The polariscope had been standardized by the Bureau of Standards and the slight corrections found were introduced in all readings. The light was filtered through a standard bichromate cell. All polariscope tubes used were measured and found correct. All flasks and pipets were calibrated.

The constant for the half-normal weight obtained by Deerr was 141.2. Under the same conditions the writers obtained 140.1. A series of the writers' determinations of the Clerget constant compared with those given by Deerr shows that there is a constant difference of about 1.5, Deerr's being the greater. An attempt was therefore made to examine the various factors that might affect the value of the constant.

Time of Inversion—Deerr recommended inversion at from 95° to 97° C. for 20 minutes and also at 100° C. for 30 minutes. The writers' results indicate that for 100° C. the uncorrected invert reading for 15 minutes is −12°, for 20 minutes −13.7, and for 25 minutes −13.4. Inversion is therefore complete in 20 minutes. At 95° C. the invert reading for 20 minutes is −9.3, for 25 minutes −12.8, for 30 minutes −13.7, and for 35 minutes −13.5. In each case there is increased destruction of fructose when the boiling is continued longer. It is also clear that with the concentration of acid used, 30 minutes is necessary at 95° C.

Influence of Excess of Reagents on Specific Rotation of Sugars—As Deerr's method calls for the neutralization of the sulfuric acid, with barium hydroxide, the excess of either one due to incomplete neutralization will have a disturbing effect upon the specific rotation of invert sugar. An excess of 5 cc. of the acid solution *B* decreases the direct polarization of the half-normal solution from 49.9 to 49.8, this being probably due to inversion. An excess of 5 cc. of the barium hydroxide (solution *A*) decreases the direct polarization from 49.9 to 49.3, however. An excess of 5 cc. acid solution *B* added to the invert polarization increases it from 13.7 to 13.9. An excess of 5 cc. of barium hydroxide solution decreases the invert polarization from 13.7 to 11.5. It is therefore evident that exact neutralization should be obtained if possible and, in particular, there should be no excess of alkali.

Volume of Precipitate—Deerr found the volume occupied by the precipitate of aluminum hydroxide and barium sulfate to be 0.07 cc. All the present writers' figures gave 0.62 cc. Since the difference is so small they used Deerr's figures at the outset.

Inasmuch as there is an evident destruction of fructose when the acid inverting solution is kept in boiling water for 20 minutes, it was concluded that, although the general principle of Deerr's method is sound, the method as proposed is unsatisfactory. Therefore an attempt was made to invert at room temperature (27° C.), at 55,° and at 68° C., using Deerr's acid concentration.

Half-normal sucrose was added to 15 cc. solution *B*, and the mixture heated, cooled, and diluted to 100 cc. The results are shown in Table I.

Table I

Temperature of Inversion	Time of Inversion		Polarization
° *C.*	*Hours*	*Minutes*	° *V.*
	Initial polarization		49.9
27	1	12	49.7
	19	50	46.5
55		30	46.7
	1	30	40.6
68		30	36.2
	1	30	17.4

It is evident that the pH of the sulfuric acid employed for inversion was too low, and a larger quantity was taken so that the time might be shortened.

Hydrochloric acid of 1.1028 specific gravity is about 6.1 *N*. A half-normal weight of sugar dissolved to 50 cc. plus 10 cc. of this hydrochloric acid gives a total volume of 60 cc. with approximately normal hydrochloric acid concentration. This is the solution generally heated to 68° C. for 7 minutes in order to secure complete inversion of the sucrose. The inverting agent being the hydrogen ion, and the dissociation of this strength of hydrochloric acid being 79.6 per cent, the effective hydrogen-ion concentration would be approximately 0.8 *N* and the velocity of the hydrolysis would be determined by this value.

Two hundred and fifty-eight cubic centimeters of sulfuric acid, 0.8354 specific gravity, diluted to 1 liter give about a 9.1 *N* solution. Ten cubic centimeters of this solution plus 50 cc. of the sugar solution give 60 cc. of about 1.5 *N* acidity. Sulfuric acid of this strength is about 53 per cent ionized, so this acid invert solution would have a hydrogen-ion concentration of about 0.8 *N*, nearly that of the conventional hydrochloric acid solution. A solution of this strength was therefore made up, but the amount of precipitate obtained from 10 cc. by neutralization with barium hydroxide was too great, so that 5 cc. only were added for the inversion, thus giving a hydrogen-ion concentration practically 0.43 *N*. Using this solution the figures were obtained in Table II.

Table II

Temperature of Inversion	Time of Inversion		Polarization (Uncor.)	Temperature
° *C.*	*Hours*	*Minutes*	° *V.*	° *C.*
	Polarization of sample		49.9	26.5
	Initial polarization		49.0	26.5
27	1	2	+36.8	27.0
	24	0	−14.6	24.7
	47	0	−14.85	26.5
	48	0	−14.85	26.5
68		7	−14.8	26.5
		10	−14.8	26.5
		12	−14.8	26.5
		15	−14.8	26.5

We therefore get a maximum invert reading in the conventional 7 minutes at 68° C., but as it is not lowered by heating for 10 minutes it might be safer to do so.

Modified Deerr Method

Based on the fundamental principle of Deerr's method, which requires the complete removal of the inverting agent and clarification by precipitation of alumina within the solution, the following modifications were devised:

Solutions—*A*. A 0.5 *N* solution of barium hydroxide, which is made by dissolving 79 grams $Ba(OH)_2 \cdot 8H_2O$ in 1 liter of water and filtering.

B. Aluminum sulfate solution made by dissolving 190 grams of crystallized aluminum sulfate, $Al_2(SO_4) \cdot 18H_2O$, in water and making up to 1 liter.

C. A sulfuric acid solution made by diluting 129 cc. of sulfuric acid of 1.8354 specific gravity to 500 cc.

D. Rosolic acid indicator solution made by dissolving 0.5 gram rosolic acid in 50 cc. ethyl alcohol and 50 cc. water.

A is titrated against *B* with rosolic acid as indicator and B is adjusted so that 25 cc. of *A* exactly neutralizes 15 cc. of *B*. *A* is titrated against *C* and the value noted.

Direct Polarization—Fifty cubic centimeters of material to be analyzed are introduced in a 100-cc. flask, 25 cc. of solution *A* are added, and, after mixing, 15 cc. of solution *B* are run in with agitation. The volume is then completed to 100 cc. with the addition of 0.1 gram sodium hydrosulfite in certain cases. The filtrate is used to obtain the direct polarization, which should be decreased by 0.6 per cent to compensate for the volume of precipitate formed.

Invert Polarization—Fifty cubic centimeters of material to be analyzed are introduced into a 200-cc. flask and 5 cc. of solution *C* are added. The flask is then placed in a water bath of 73° C. and a thermometer is inserted in the flask. The temperature of the sugar solution should reach 68° C. in 3 minutes, and then be kept at 68° C. for 7 minutes. The contents of the flask should be mixed from time to time to insure a uniform temperature. At the end of the heating period the flask is rapidly cooled to about room temperature. Fifteen cubic centimeters of solution *B* and 3 drops of rosolic acid solution are then added, and the whole titrated with 0.5 *N* barium hydroxide until the solution is distinctly pink. It is brought back to the neutral point by adding about one drop of solution *C*, diluting to mark, filtering, and polarizing. The invert polarization thus obtained should be decreased by 0.89 per cent to compensate for the volume of precipitate formed.

Examination of Modified Deerr Method

Volume of Precipitate—Theoretically, the volume of the precipitate of aluminum hydroxide and barium sulfate obtained when 25 cc. of 0.5 *N* barium hydroxide solution neutralizes 15 cc. of the aluminum sulfate solution is 0.464 cc. The sulfuric acid used proved on titration to be 8.5 *N*. Five cubic centimeters of this solution theoretically give barium sulfate with a volume of 1.17 cc. Fifteen cubic centimeters of aluminum sulfate and 5 cc. of the sulfuric acid solution give a precipitate with a volume of 1.63 cc., according to theory.

By experiment, the volume of the precipitate from 15 cc. aluminum sulfate solution was found to be 0.60 cc., and that from the 5 cc. of sulfuric acid, 1.17 cc., the two precipitates together having a volume of 1.77 cc.

These volume corrections were determined experimentally several times, with identical results. The figures are close enough to the theoretical for all practical purposes.

Note—In calculating the above theoretical volume for the precipitate the specific gravity of barium sulfate was taken as 4.5 and that of aluminum hydroxide as 2.3. The actual volume of the latter precipitate is somewhat greater owing to the gelatinous nature of aluminum hydroxide which seems to keep a certain amount of water from mixing with the rest of the solution, or possibly to hold it in loose chemical combination.

Indicator—Phenolphthalein changes color at pH = 9, which is too alkaline. To avoid the excess of barium hydroxide, rosolic acid is used, which changes color at pH = 7.

Rosolic acid has a red color in alkaline solution and yellow in acid solution. It is almost colorless in neutral solution and hence does not interfere with polarization. It is optically inactive.

Concentration of Acid—Thirteen grams of sucrose in a solution of 0.8 *N* acid require approximately 2 minutes to be completely inverted at 65° C.; in 0.4 *N* acid about 4 minutes. In the official method 0.8 *N* acid should result in complete hydrolysis in about 2 minutes at 65° C. The heating is continued to 7 minutes to allow for the depressing action on hydrogen-ion concentration of any organic salts in the original sample and particularly of the lead subacetate added in clarification. All excess acid and unnecessary time of heating, however, must result in increased destruction of fructose.

In the Deerr method lead subacetate is not used, and there is a minimum depression of the H-ion concentration. Hence, 7 minutes' heating at 65° C. with 0.4 *N* sulfuric acid should give complete hydrolysis with a minimum effect of the action of acid and salts on the rotatory power of the sugars.

Color and Clarification of Solution—For ordinary 96 degree sugars the clarification for D. P. and I. P. is satisfactory. For second and third sugars, also for sirups and molasses, 0.1 gram sodium hydrosulfite may be added to the neutral solution just before diluting to mark. The hydrosulfite depresses the sucrose polarization a little and should be omitted if possible, especially in the direct polarization.

Value of Clerget Constant—Since the Clerget constants chiefly employed in the analysis of sugarhouse products are those corresponding to half and quarter-normal sucrose solutions, it was deemed advisable to determine the constants for such solutions. The results are as follows:

0.5 *N* Solution	0.25 *N* Solution
141.6	140.96
141.7	140.91
141.8	140.81
Av. 141.7	Av. 140.89

Approximately 1 degree decrease in the original reading (I. P.) corresponds to 0.1 decrease in the value of the Clerget constant. Before the constants at other concentrations are determined, we can use this correction approximation without introducing serious errors.

The above results show that the Clerget constant determined by this method is in very close agreement with the old theoretical value of 141.66 and the old invertase value of 141.7 and 141.8.

In the writers' determinations of the constant 141.7 it was necessary to work at room temperatures, which ranged from 26° to 32° C. This is too far from the standard (20° C.) for the temperature correction *T*/2 to be accurate. Several individual determinations made at lower temperatures gave slightly over 141.8. Assuming that the invertase value of 142.1 is correct, the constant 141.8 would indicate that there is a slight destruction of fructose, and possibly of glucose, in acid hydrolysis at 68° C. This destruction is comparatively small and the change in the constant is considerably less than that brought about by the presence of the inverting reagents.

In this connection, however, it is necessary to emphasize a fact which is sometimes overlooked. In research laboratories it is reasonably simple to determine to within 0.1° C. the temperature of the solution to be read in the polariscope. In technical laboratories this is not so easily done, and an error of over a half degree might readily enough be introduced, which, however, would mean a change in the factor of ±0.3. This fact, taken in connection with the influence of time and temperature of inversion and the necessity for reading the invert solution at some temperature other than 20° C., would seem to make the technical Clerget determinations not so accurate as they are ordinarily assumed to be.

Analysis of Molasses by Modified Method

In order to test this method under extreme conditions several samples of blackstrap were taken for analysis. The following are some of the observations made during the course of the experiments:

1—The color of the molasses obscures that of the indicator. Therefore, titration within the solution cannot be done accurately. It is necessary to determine previously the amount of barium hydroxide solution required to neutralize solutions *A* and *B*. This necessitates in turn the use of the constant strength barium hydroxide solution, which is about half-normal at saturation.

2—A 200-cc. flask was used for the inversion on account of the volume of 0.5 *N* barium hydroxide solution added for neutralization.

3—To get a solution sufficiently decolorized it was sometimes necessary to add 0.1 gram of sodium hydrosulfite to the neutral solutions just before diluting to mark.

4—It was found that the eighth-normal solution employed could frequently be read in a 400-mm. tube.

5—The volume correction for the D. P. was taken as 0.6 cc.; that for the I. P. was taken as 1.77 cc., which could probably be raised to 2 cc. by changing the concentrations of solutions *B* and *C* slightly. This would simplify considerably the arithmetic involved.

6—If care is not observed, the final volume will be too great. The 0.6 cc. volume correction means a decrease of the reading by 0.6 per cent when the total volume is 100 cc., and of 0.3 per cent when it is 200 cc. Similarly, for the 1.77 cc. correction, we have 1.77 per cent for 100 cc., and 0.89 per cent for 200 cc.

PROCEDURE—*Direct Polarization.* Twenty-six grams of the sample are placed in a 200-cc. flask and diluted to mark. Fifty cubic centimeters of this solution, containing 6.5 grams of molasses, are introduced into a 200-cc. flask, 25 cc. of solution *A* are added, followed by 15 cc. of solution *B* (and 0.1 gram of sodium hydrosulfite if necessary). The solution is diluted to mark, filtered, and polarized in a 400-mm. tube. The reading is decreased by 0.3 per cent and multiplied by 4 to reduce to normal.

Calculation *A:*

50 cc. of sample + 25 cc. solution *A* [$Ba(OH)_2$] + 15 cc. solution *B* [$Al_2(SO_4)_3$] = 90 cc.

This cannot conveniently be diluted to 100 cc.; hence the 200-cc. flask is used. By weighing off 6.5 grams of molasses, this can be transferred to a 100-cc. flask with about 30 cc. of water. Solution *B* can be made stronger and only 10 cc. taken. This would give a volume of 30 + 25 + 10, or 65 cc., which can be shaken and diluted to mark in a 100-cc. flask.

$$\text{Reading} \times \frac{8}{N} \times \frac{200\ \text{mm.}}{400\ \text{mm.}} \times \frac{200 - 0.6}{200} = R \times 4 \times 99.7\ \text{per cent}$$

Invert Polarization. Fifty cubic centimeters of solution containing 6.5 grams of molasses are introduced into a 200-cc. flask, 5 cc. of solution *C* are added, and the solution is inverted as previously described. After cooling, 15 cc. of solution *B* are added and the whole is neutralized with the exact amount of solution *A*, previously determined by titrating 5 cc. of *C* and 15 cc. of *B* against solution *A* using rosolic acid as indicator, introduced into the solution through a buret. One-tenth gram of sodium hydrosulfite is added if necessary and the solution diluted to mark, filtered, and polarized in a 400-mm. tube. The reading is decreased by 0.88 per cent for the volume of precipitate and multiplied by 4 to reduce to normal. The sucrose is calculated as usual, using the following factors and interpolating between these values: half-normal, 141.7; fourth-normal, 140.9; eighth-normal, 140.6.

Calculation *B:*

50 cc. sample + 25 cc. solution *A* + 15 cc. solution *B* + 5 cc. solution *C* (H_2SO_4 8.5 *N*) + 85 cc. solution *A* [$Ba(OH)_2$ 0.5 *N*] = 180 cc.

This is too large a volume for convenient dilution to 200 cc. Here again, by weighing the 6.5 grams as above and increasing strength of *B*, the volume can be brought to about 160 cc. which can be shaken and diluted to 200 cc. easily.

$$R \times \frac{8}{N} \times \frac{200}{400} \times \frac{200 - 1.77}{200} = R \times 4 \times 99.12\ \text{per cent}$$

Some difficulty in handling the large quantity of precipitate was anticipated, but this disappeared after a little practice. Although filtration was somewhat slow, the precipitate settled rapidly and the solution could be decanted into the filter paper in fairly clear condition.

The D. P. sugar solution needs no deleading when used for the determination of reducing sugars. Actual tests show very little more time spent than in the conventional methods of double polarization. The writers believe that this modified method embodies the fundamental principle and avoids certain intrinsic errors found in the original description of the Deerr method.

Comparison of Modified Deerr Method with Herzfeld Method

	Direct Polarization		Invert Polarization	
	Modified Deerr	Herzfeld	Modified Deerr	Herzfeld
Normality	*N*/8	*N*/4	*N*/8	*N*/8
Tube, mm.	400	200	400	200
Original reading corrected for zero point, ° V.	6.0	5.9	− 2.9	− 1.5
° V. corrected for volume of precipitate	5.98	5.9	− 2.87	− 1.5
° V. reduced to normal basis	23.92	23.6	−11.48	−12.0
Temperature, ° C.	32.6	30.6	32.6	30.2
Clerget constant used	140.6	141.93		
Sucrose in molasses, calcd. per cent	28.4	28.1		

Acknowledgment

In order to check the volume corrections and constants used in this investigation, Prof. F. J. Robichaux very kindly consented to repeat the determinations. His results agreed exactly with the ones obtained by the writers, who wish to thank him for his very valuable assistance.

A Small High-Pressure Autoclave[1]

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SOME time ago the writers had occasion to agitate a liquid, metal catalyst, and hydrogen under as great pressures as could be conveniently obtained and at temperatures below 200° C. The excellent papers of Ernst[2] on this subject had not then appeared, and the writers were left to their own resources, which led them to devise an autoclave capable of working at 2000 pounds pressure per square inch and 200° C., agitation being developed by rocking instead of by an ordinary rotating stirrer.

The apparatus, shown in the drawing, consists essentially of a shell, *A*, manufactured and tested for service at 3000 pounds pressure per square inch, into which may be placed a reaction tube of glass, copper, nickel, or other suitable material. These reaction tubes are sealed at both ends and have a small opening in the middle. At the center of the shell, connection is made to a hydrogen cylinder by means of a $^5/_{16}$-inch flexible copper tube, tested to 5000 pounds pressure. After filling the reaction tube about one-third full and closing the shell with a screw cap, hydrogen may be introduced and the shell rocked to cause the liquid in the reaction tube to rush from end to end.

This action is a very important feature of this autoclave. Picture the liquid in the shell at rest in a horizontal position. Suddenly one end rises, the liquid rushes downward, strikes

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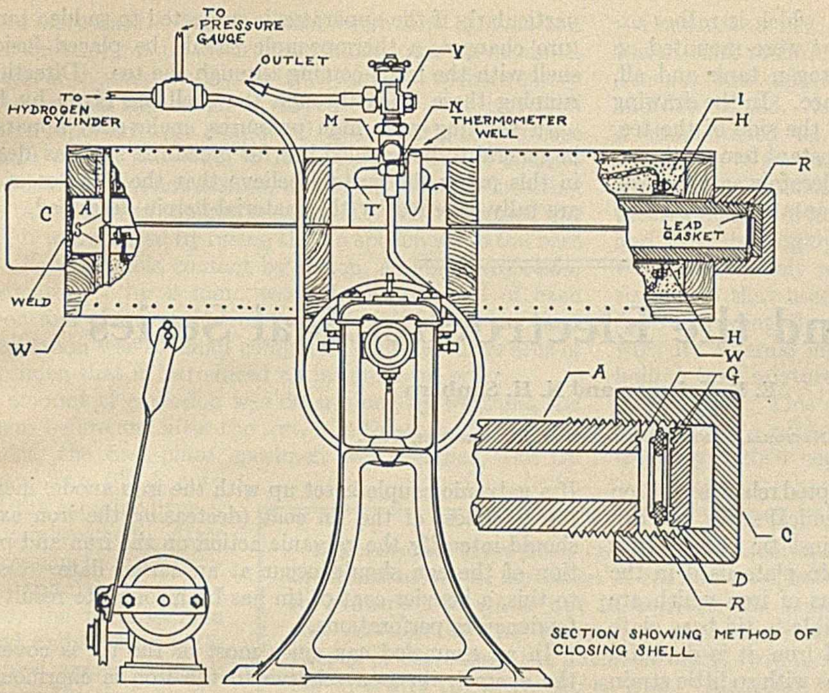
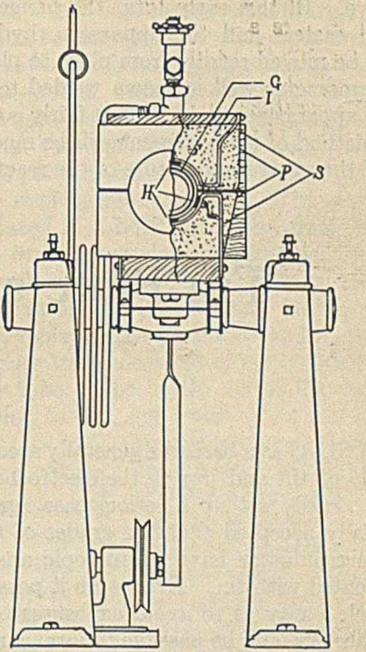
[1] Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Ind. Eng. Chem.*, **18**, 664 (1926); *Chem. Met. Eng.*, **34**, 151 (1927).



SECTION SHOWING METHOD OF CLOSING SHELL



the end of the reaction tube, curves upward and back and, falling, plunges into the stream of downward rushing liquid, setting up a swirling motion which entraps quantities of gas in the form of bubbles. The action is very similar, mechanically, to what occurs on a large scale when an ocean wave comes into shore, rises, curves over, plunges downward, and comes up a swirling mass of water, air, foam, and sand. A reaction mixture absorbed more hydrogen in this apparatus in 6 hours than the same mixture at the same temperature and pressure absorbed in 20 hours where it was agitated by a horseshoe stirrer at 100 r. p. m.

The size of this apparatus may be varied within rather wide limits, but the one illustrated is designed to handle about 1200 cc. of liquid. The shell is made of two pieces of 3-inch, double-extra-heavy hydraulic steel pipe, 18 inches long; two 3-inch double-extra-heavy steel caps, and a tee of the same material. The two pieces of pipe are screwed into the tee, *T*, and one end is closed by a cap, *C*. It is advisable to weld these three joints. The open end of the pipe is machined so that it presents a perfectly true face. In the center of this face an annular groove, *G*, $^1/_{16}$ inch deep, is turned. A steel disk, *D*, the same diameter as the pipe, has two similar grooves cut in one face, so that when it is placed against the end of the shell, *A*, the two grooves will span the groove in the face of the pipe. Lead gaskets, *R*, with annular ridges to fit into these grooves are cast from a special mold. The method of assembling these parts is shown in the enlarged sectional drawing. It is advisable to cover the gasket and threads with a graphite pipe-joint compound to insure a tight closure and ease of opening. With this apparatus hydrogen has been held at 1500 pounds pressure for 2 weeks with absolutely no leakage.

The method of connecting the copper tube to the shell may vary according to operating conditions. In the apparatus shown there is a Tobin bronze tee, *M*, with a male thread which fits into the iron tee, *T*. A standard hydrogen valve, *V*, is fitted into this bronze tee and is attached to a pigtail connection through which the pressure may be released or the apparatus evacuated before introducing the hydrogen. The copper tube is connected to *M* by a hydrogen nut, *N*, and a short nipple. This nipple may be replaced by a valve if it is desired to maintain pressure in the apparatus when the hydrogen cylinder is removed. These valves are unsatisfactory at temperatures above 100° C., but if they are raised 10 or 12 inches from the shell by means of a short length of double-extra-heavy pipe, a working temperature of 250° C. may be maintained without harm. It could also be arranged to place the valves near the hydrogen cylinder and connect the copper tube to *T* by means of a short nipple. The iron tee is used only to give wall thickness sufficient for connecting the brass tee, thermocouple leads, etc., by means of threads. If larger pipe is used, the wall thickness may be sufficient to warrant drilling and tapping the pipe itself, thus eliminating the tee.

The copper tube on this particular machine is 15 feet long, which includes three bends around the shaft. A special tee is placed in the tube from which a lead goes to a recording pressure gage. It is an open question how long these tubes will stand up under the bending to which they are subjected, but four of them have been in operation for over 400 hours and there is as yet no sign of deterioration.

Heating is accomplished by eight 12-inch space heaters, *H*, mounted around the shell on strap-iron supports, *S*. By means of a three-heat switch (not shown in the drawing) wattages of 1760, 880, and 440 may be obtained. Low heat will maintain a temperature of 130–160° C. The insulation, *I*, is of asbestos cement protected by a sheet iron covering, *P*. The upper half of the insulation, containing two of the space heaters, is built so that it may be removed, thus enabling the shell to be taken out for examination or repair. Connection between the upper and lower heaters is made by a flexible connection and plug.

The apparatus is operated by a motor-driven reducing gear. The crank makes 12 revolutions per minute and is constructed from $^1/_2$-inch strap iron, a 5-inch pulley, a pillow block, and cap screws. The method of assembly is shown in the drawing. Two rockers of the size shown are driven from one of these gears, which indicates that the power requirement is very small.

The base, *W*, on which the shell and heaters rest is mounted by means of a flat box on a shaft, which in turn is supported by ordinary hangers. In an earlier type of autoclave the hydrogen cylinder was directly attached to the under side of this base and was connected by a rigid tube to the shell, doing away with the long flexible tube, which is rather expensive. In this early form the hangers were mounted on swivel casters and the apparatus, hydrogen tank and all, could be moved readily from place to place. In the drawing a thermometer well is shown welded to the side of the tee. If the apparatus is to be used at fairly constant temperatures, this method of measurement will be moderately satisfactory, but if the exact temperature of the reactants is required, and particularly if the apparatus is subjected to sudden temperature changes, a thermocouple should be placed inside the shell with the leads coming through the tee. Directions for running these leads through the shell are given by Ernst.[2]

In working with high pressures, make-shift apparatus is in general to be avoided but for pressures such as described in this paper the writers believe that the dictates of safety are fully satisfied by the material herein described.

Tin Plate and the Electrochemical Series[1]

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USING as a basis the generally accepted relative position of tin and iron in the electrochemical series, one can easily set up a serious case against tin plate. It is generally accepted that the grades of tin plate used in the canning industry have microscopic areas of iron which are not coated with tin. Even were it possible to tin base plate in such a way as to avoid exposures of iron, it is doubtful whether it would be possible to form cans with so little strain on the metal that the tin coat would not be fractured. According to the usual electrochemical series tin would be the cathode in any galvanic couple set up between the tin and iron. Since the area of tin is so large in proportion to the anodic iron, corrosion of the iron at the exposed points would be greatly intensified, resulting in excessive solution of iron at such points and eventually in perforation of the can. In the types of can in which a cut edge of the tin plate is directly exposed to the contents, it would cause excessive solution of the iron at this point.

In a series of articles Mantel and Lincoln[2] develop such a case. They state that certain foods, such as the non-acid vegetables, do not perforate, while the more acid fruits tend to perforate the can. They further state that in the nonperforating products, although the tin is cathodic when tin and iron electrodes are first introduced into these products, the direction of the current shortly reverses itself and the tin becomes anodic. They ascribe this reversal of the current in the less acid vegetables to film effects which render the iron passive. According to them, this film results from the greater conductivity of the electrolyte due to the added salt with which these products are canned, and they suggest that salt might have a similar effect with fruits.

That salt renders iron passive is not in harmony with the general effect of chlorides on passivity. Moreover, these authors have failed to refer to extensive experiments[3] in which salt has been found not to decrease perforation, or to the fact that tomatoes and many other vegetables frequently canned without salt show no tendency to perforate.

The case against the tin can as outlined above fails to take into account most of the results experienced in its commercial use. The pitting of a plain tin can resulting in perforations is an unusual type of corrosion. The usual corrosion in such cans is not local but generally spread over the entire surface of the tin. In the case of the type of can having a cut edge exposed to the contents there is no excessive solution of iron. If a galvanic couple is set up with the iron anode, increasing the thickness of the tin coat (decreasing the iron exposed) should intensify the galvanic action on the iron and perforation of the can should occur at an earlier date. Contrary to this, a heavier coat of tin has been found to result in less tendency to perforations.

In an enameled can since most of the tin is covered by the enamel, its area relative to the iron is enormously reduced. If tin functions as the cathode, the intensity of its action should be reduced by the enamel. On the contrary, enameled cans tend to perforate enormously more than plain cans. For these reasons and others, some of those connected with the canning industry have realized for some time that there are many things about a tin can which cannot be explained on the basis of tin acting as the cathode while the iron acts as the anode. A number of experiments have therefore been conducted to learn the definite relationship of tin and iron to one another in this respect.

Methods

Since this is the first of a series of reports, some detail as to the procedure will be given. It is highly important in this connection to conduct all corrosion experiments or electrical measurements in the absence of air, since the corrosion commonly encountered in canned fruits is in the absence of air. The methods employed were devised with this in mind. The experiments have involved the use of various solutions of organic acids commonly found in fruits as well as the fruits themselves. This report will be confined to the results obtained with fruits only.

When fruits were used, they were ground in a meat grinder and diluted with water in the proportion of three parts of fruit to two parts of distilled water, with the exception of grapefruit, which was used without additional water. After the water was added, the fruit was heated to boiling and boiled for a few minutes to expel any gases within the cells of the fruit and to secure sterilization.

CORROSION TESTS—The corrosion experiments were made in wide-mouthed glass bottles having a capacity, with a stopper inserted, of 135 cc. The bottles containing the corrosion specimens were filled with the boiling fruit, a one-hole rubber stopper firmly inserted, and while pressure was still being exerted on the rubber stopper, a glass rod was introduced into the hole of the stopper. The bottles were then cooled as rapidly as was permissible without danger of breakage. In most cases they were probably cooled completely within 15 to 20 minutes. The stoppers were then firmly clamped down by means of screw clamps made for the purpose, and thereafter the bottles were held at room temperature.

For corrosion specimens finished base plate and cold rolled

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] *Canning Age*, **7**, 847 (1926); *Iron Age*, **119**, 843 (1927); *Can. Chem. Met.*, **11**, 29 (1927); Preprint of paper at 51st Meeting of the American Electrochemical Society, Philadelphia, Pa., April 28 to 30, 1927.

[3] Clark, *Canner*, **1923**, Convention number, p. 149; Kohman and Sanborn, *Ind. Eng. Chem.*, **16**, 290 (1924).

sheet tin were used. The specimens were 2.54 by 7.62 cm. (1 by 3 inches), cut on an ordinary hand squaring machine. The edges of the base plate were lightly ground with an emery wheel to smooth any rough or frayed edges. All corrosion tests here reported were conducted with a strip of the base plate and of the sheet tin in each bottle. When contact of the specimens was not desired, this was avoided by inserting a glass tube between the two specimens. When contact was desired, it was secured by fusing the tin specimens to the base plate. To make this contact by fusion, a small projection, approximately 1 by 2 mm., was left on the end of each specimen and these projections were fused to one another. The projection was so small compared with the entire area of the specimen that it introduced an insignificant error.

The amount of corrosion was determined by weighing the specimens before and after the test. In the case of the fused specimens, the base-plate specimen was weighed, the tin specimen then fused onto it, and the combined specimens again weighed. After the corrosion test the combined specimens were weighed, the tin specimen removed, and the base-plate specimen again weighed. To remove the tin from the projection of the base plate, it was melted by holding in a small flame at the point of fusion and immediately wiped off with a dry towel after being removed from the flame. It was found that tin specimens could be fused to the base plate in this manner and again removed without altering the weight of the base-plate specimen more than 0.1 mg.

Experiments have been conducted to determine the mechanism of the corrosion of tin and iron, both when in contact and when not in contact, in fruits and the relation of the results to the electrochemical theory of corrosion. It has been found that in a number of fruits tin is anodic to iron. Although not all fruits have been studied, the data indicate that this is a rather general condition in canned fruits. Many of the facts which did not conform to the older idea that tin is cathodic to iron are readily explained in accordance with these new findings. Electrical measurements have likewise been made and they bear out the results of the corrosion tests that tin is anodic to iron. The nature of corrosion in fruits is distinctly different from that in solutions of the fruit acids. The results are in harmony with commercial experience.

Before weighing, all specimens were pickled in 3 per cent sulfuric acid solution for 3 minutes at 80° C. All base-plate specimens for any one experiment were pickled simultaneously in a beaker. To avoid their lying against one another, glass rods were set up between the individual specimens. Likewise, all the tin specimens were pickled simultaneously for each experiment. When the pickling was complete, most of the pickling solution was decanted off, a small amount being left in to avoid oxide formation, the specimens covered with warm water, taken out individually, and thoroughly dried by wiping with a clean towel and weighed. When contact was desired, the fusion was made after the pickling.

Various methods of preparing the specimens were tried. Polishing reduced the corrosion of the iron, but increased the corrosion of the tin. Pickling is simple and gave satisfactory checks on duplicate specimens.

It is recognized that it is virtually impossible to start any corrosion experiment of this kind without contamination by at least minute quantities of oxygen or oxides of the metals. Furthermore, it was considered possible, as corrosion progressed, that the products of corrosion might have some effect on the nature of corrosion. Bottles were opened for the sake of convenience at intervals of 19, 67, 310, and 810 hours. The first opening was believed to include the effect of any oxygen or oxides of the metal that might have been introduced in the beginning of the experiment, as well as the effect of the high initial temperature. The subsequent openings were expected to reveal any change in the nature of corrosion as it progressed.

Electrical Measurements—To supplement these corrosion tests preliminary electrical measurements were made. The potential difference between tin and base-plate electrodes was determined. Likewise their individual potentials against a standardized tenth-normal calomel cell were measured. Electrodes of tin and base plate 2.54 by 7.62 cm. with narrow projections extending through the rubber stopper were pickled 3 minutes in 3 per cent sulfuric acid solution at 80° C. and then thoroughly washed free from acid. The electrodes were immediately placed in a bottle of boiled fruit mixture similar to that used in the corrosion experiments. A glass tube extending through the stopper into the fruit mixture, with its external end extending into a small beaker of the boiling fruit mixture, replaced the glass rod used in the corrosion tests. This glass tube consisted of two sections connected with a rubber tube. The bottle containing the electrodes was then cooled in running water while the beaker into which the open tube extended was left uncooled, making it possible to sterilize the contents of the bottle and keep them sterile during cooling. When the contents were cool, the glass tube extending into the beaker of hot fruit mixture was transferred into a tube of mercury, which acted as a seal to avoid bacterial contamination and exclude atmospheric oxygen. Electrical contact was established between the electrodes and the calomel half-cell by removing the tube from the mercury seal and placing it in a connecting vessel containing potassium chloride. The rubber connecting tube was kept closed with a screw clamp at all times except when making potential readings, in order to prevent the diffusion of potassium chloride into the fruit mixture.

Results

In Table I are given all the results obtained when contact was made by the fusion method. Similar results have been obtained with other fruits using other means of contact. The duplicates illustrate the extent to which agreement was obtainable by this method. No selection of results has been made in this table. It is therefore evident that satisfactorily close checks have resulted, with the exception of cherries, in spite of the fact that the corrosion medium was not homogeneous. This medium was not homogeneous for several reasons. It contained the fruit pulp as an insoluble constituent. The bottles were all filled from one large flask and it was impossible to secure a perfect distribution of fruit pulp throughout all the bottles, since some fruit pulps tend to settle while others tend to float. Moreover, as the corrosion progressed the fruit colors were gradually bleached around the specimens, causing non-uniformity throughout the corrosion medium. The cause for variations in cherries is not definitely known.

It is evident from Table I that the corrosion of the base plate was decreased very materially by being in contact with tin and that the corrosion of the tin was greatly increased because of its contact with base plate. In fact, when in contact the tin was much the more corroded of the two metals. The question arises—why does the tin show so much less corrosion when not in contact with base plate? Polarization

Table I—Loss in Weight of 19.4 Sq. Cm. (1 by 3 Inches) Specimens of Base Plate and Sheet Tin in 135 Cc. of Fruit, Both when the Two Specimens Are Not in Contact and when in Contact

(Figures in milligrams)

Fruit	19 Hours				67 Hours				310 Hours				810 Hours			
	Fe		Sn		Fe		Sn		Fe		Sn		Fe		Sn	
	No contact	Contact	No contact	Contact	No contact	Contact	No contact	Contact	No contact	Contact	No contact	Contact	No contact	Contact	No contact	Contact
Grapefruit	1.0	0.6	0.2	2.8	2.1	0.4	0.2	4.5	9.3	0.7	0.9	12.1	24.0	0.8	1.2	18.9
	1.3	0.3	0.3	4.6	1.9	0.6	0.2	4.7	9.2	1.0	1.0	12.3	24.4	0.9	1.0	20.0
													22.4	0.7	1.0	20.8
Av.	1.2	0.5	0.3	3.7	2.0	0.5	0.2	4.6	9.3	0.9	1.0	12.2	23.6	0.8	1.1	19.9
Pineapples	1.3	0.6	0.5	1.5	2.0	1.0	0.7	2.4	7.2	1.7	1.0	10.4	20.3	2.8	1.3	21.8
	1.3	0.4	0.5	1.7	1.9	0.8	0.7	3.0	7.5	2.0	1.0	10.1	20.3	3.0	1.4	
													20.4		1.4	24.7
Av.	1.3	0.5	0.5	1.6	2.0	0.9	0.7	2.7	7.4	1.9	1.0	10.3	20.3	2.9	1.4	23.3
Strawberries	1.7	0.7	0.6	3.5	3.0	0.6	1.1	6.2	13.5	1.3	2.4	17.1	27.0	3.7	3.3	37.4
	1.8	0.7	0.7	3.2	3.2	0.7	0.9	6.4	13.9	1.3	2.5	17.1	33.2	2.1	2.8	35.2
													37.6		3.5	
Av.	1.8	0.7	0.7	3.4	3.1	0.7	1.0	6.3	13.7	1.3	2.5	17.1	32.6	2.9	3.1	36.3
Blackberries	2.1	1.2	1.1	3.1	4.1	1.7	2.5	8.2	16.3	4.9	5.5	30.5	49.6	8.2	7.3	69.6
	2.0	1.0	1.2	3.1	4.0	1.5	2.5	8.1	15.5	5.1	5.6	31.3	46.0	8.6	7.5	71.1
													42.5		7.1	
Av.	2.1	1.1	1.2	3.1	4.1	1.6	2.5	8.2	15.9	5.0	5.6	30.9	46.0	8.4	7.3	70.4
Rhubarb	1.3	0.8	0.6	4.6	2.6	0.8	1.0	11.3	8.8	1.2	2.5	32.4	17.1	1.0	4.6	57.1
	1.4	0.7	0.6	4.3	2.4	0.8	1.0	10.8	8.1	1.1	2.3	33.2	17.6	1.2	3.9	57.6
													17.6	1.2	4.5	59.1
Av.	1.4	0.8	0.6	4.5	2.5	0.8	1.0	11.1	8.5	1.2	2.4	32.8	17.4	1.1	4.3	57.9
Black (Bing) sweet cherries, pitted	27.1	15.8	0.6	1.8	25.5	20.6	1.6	4.0	28.3	21.7	3.1	12.9	43.9	19.0	3.3	14.2
	27.1	16.5	0.7	1.7	29.3	20.0	1.5	3.9	34.2	20.1	2.8	14.0	48.0	30.8	3.7	17.5
	22.7		0.9											27.8		21.5
Av.	25.6	16.2	0.7	1.8	27.4	20.3	1.6	4.0	31.3	20.9	3.0	13.5	46.0	25.9	3.5	17.7
Red sour cherries, pitted	26.9	8.3	0.7	2.4	37.2	8.6	0.9	5.3	24.4	24.2	1.4	7.9	60.6	38.0	1.2	9.3
	29.3	8.2	0.6	2.4	25.9	11.6	0.8	5.3	21.9	18.5	1.3	8.7	60.6	47.5	1.5	7.1
						16.5		4.8	35.3		1.2					
Av.	28.1	8.3	0.7	2.4	31.6	12.2	0.9	5.1	27.2	21.4	1.3	8.3	60.6	42.8	1.4	8.2

seems to be an important factor and a further study of it in this respect is planned. The relative homogeneity of the two metals must also be considered.

The data in Table II show the effect of varying the relative size of the two specimens. Increasing the size of the iron relative to the tin increases the rate of solution of the tin and decreases the protection afforded the iron by the tin.

Table II—Effect of Relative Size of Specimens in Contact for 308 Hours in Blackberries

Area of Specimen		Total Loss		Loss per Sq. Cm.	
Fe	Sn	Fe	Sn	Fe	Sn
Sq. cm.[a]	*Sq. cm.*[a]	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0.0	38.7	0.0	5.6	0.000	0.145
1.6	38.7	0.0	8.5	0.000	0.220
19.4	38.7	0.9	19.4	0.046	0.501
38.7	38.7	5.0	30.9	0.129	0.799
38.7	19.4	8.7	22.1	0.225	1.14
38.7	1.6	15.8	5.2	0.408	3.25
38.7	0.0	15.9	0.0	0.411	0.00

[a] Specimens of 1.6, 19.4, and 38.7 sq. cm. area were, respectively, 1/2 by 1/4 inch, 1 by 1 1/2 inches, and 1 by 3 inches in dimension.

The electrolytic potential measurements which can be reported at this time are only preliminary. They are in harmony with the corrosion data given above. It has been found that electrical measurements are very erratic immediately after the experiment is started. In some cases various reversals occur for several hours. It is not always possible to duplicate the first results with the same products. In some cases the first measurements indicated that iron was momentarily cathodic but very quickly reversed to become anodic, and later another reversal occurred and the iron remained cathodic. In general, however, the iron is anodic at the beginning, but becomes cathodic within a short period and remains so. It is possible to make either the tin or the base plate cathodic at will by gently bubbling air around the electrode.

As a result of a number of determinations, the average potentials of iron and tin in strawberries were found to be −0.039 and −0.081 volt, respectively. In rhubarb the potential of iron was −0.038 volt and of tin −0.141 volt.

Discussion

It is generally accepted that the relative positions of the metals in the electrochemical series do not necessarily indicate their potentials in various mediums. There is no doubt, however, that the discussion of this series in most textbooks gives the impression that the electrolytic potential is largely an intrinsic property of the metal rather than that of a system. The static potentials of two metals in a given medium do not necessarily show the relative rates at which they corrode, as corrosion is a dynamic process. The influence of overvoltage, depolarizers, and other substances, and the physical structure of the metals must also be considered.

Measurements of the solution potentials of iron and tin in strawberries, rhubarb, and other foods show that the potential of tin is more negative than that of iron. Table I, however, shows that the solution of iron is greater than that of tin when the two specimens are not in contact. Overvoltages of hydrogen evolution or of cathodic reduction on iron and tin in these solutions have not yet been determined. It has been shown that hydrogen has a higher overvoltage on tin than on iron.[4] Under these conditions the high overvoltage on tin might prevent its solution when alone, despite its greater solution pressure. However, the electrical contact with a metal of lower hydrogen overvoltage—in this case, iron—would break down the protection afforded by the high overvoltage.

The experiments described in this paper clearly show that under certain conditions iron may be cathodic to tin. The experience of the canning industry further confirms this view,

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[4] Caspari, *Z. physik. Chem.*, **30**, 89 (1889); Knobel, *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923); Newberry, *Mem. Proc. Manchester Lit. Phil. Soc.*, **61**, No. 9 (1917).

for, as previously mentioned, a heavier coating of tin reduces corrosion in the can as measured by its tendency to perforate. Increasing the tin coating decreases the area of the cathodic iron relative to the anodic tin and, in accordance with the electrochemical theory, corrosion of the iron is reduced. Again, commercial experience shows that enameled cans perforate sooner than plain cans. The enamel covers a larger area of tin than of iron, thus reducing the area of the tin relative to that of the iron. This follows from the fact that at points where relatively more iron is exposed owing to forming and closing of the can the enamel is also least continuous. On the basis of the electrochemical theory, corrosion of the anode should increase as the relative area of the cathode increases. The mechanism of corrosion as indicated by these results is in harmony with the corrosion encountered in commercial experience.

An Inexpensive Cell for the Purification of Colloids by Electrodialysis[1]

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Among the greatest impediments to progress in colloidal chemistry have been the difficulties involved in obtaining pure, reproducible products. Nearly all colloids, synthetic or natural, contain variable quantities of ordinary electrolytes which are either neglected or only partially removed by ordinary dialysis. The purification of colloidal electrolytes in which one ion is of colloidal, the other of crystalloidal, dimensions is even more difficult to accomplish, but no less important for an understanding of the behavior of the sol. The classical dialysis of Thomas Graham is extremely slow and tedious. It has long been known that the rate of purification could be greatly accelerated by the application of an electrical current to electrodes placed outside the dialyzing membrane containing the colloid. But not until recently has this method of purification, now commonly termed "electrodialysis," received the attention it seems to deserve. Freundlich[2] has found that in the case of serum a degree of purification that would require a week by ordinary dialysis can be accomplished in 10 to 40 minutes by electrodialysis. Dhéré,[3] Pauli,[4] Bechold,[5] and numerous others have also called attention to the advantages and limitations of the process.

In spite of this increased interest in the subject, so far as the author is aware, there is no apparatus on the American market for this purpose. For that reason a description is given herein of a very simple, inexpensive cell which can be easily made from an old rubber storage battery case. Cells of this type have been used in the author's laboratory for three years and are still giving satisfaction.

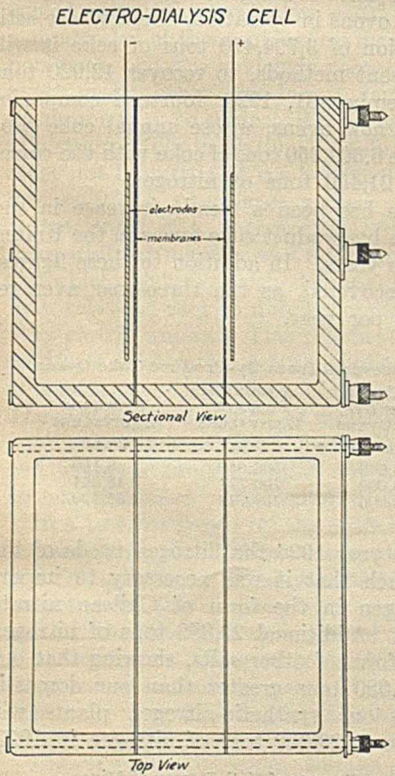

Figure 1—Rubber Cell Made from Storage Battery Case

Description of Cell

The construction of the cell is shown in Figure 1. The battery jar is sawed into three sections, the outside sections about the width desired in the finished cell. The width of the resulting center section will vary with the type of cell used, but it can be sawed again into any desired size. The following dimensions have been found to be satisfactory for routine work: width of each section, 4.0 cm., depth, 14 to 15 cm., length, 14 to 15 cm. Such a cell will have a working capacity of about 700 cc. in each compartment. The edges of each section are carefully smoothed and squared so that water-tight joints may be obtained without the use of gaskets. The three sections of the cell are held together by seven brass rods, three of which are regularly spaced on each side of the cell, and one in the middle of the cell bottom. These rods pass through holes drilled in the cell itself, as shown by the dotted lines in Figure 1. This arrangement holds the membranes tightly in place and prevents warping of the different sections of the cell. Brass strips about 2 cm. wide and the same length as the cell, with holes drilled to correspond with those in the cell proper, serve as washers and hold each rod in place. If the edges of the cell have been properly squared, water-tight junctions can be obtained by merely tightening the thumb screws on each rod.

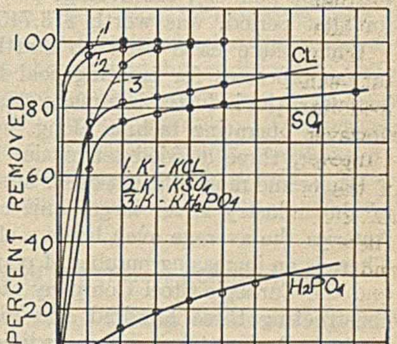

Figure 2—Rate of Electrodialysis of Different Ions when Placed between Parchment Membranes

Any type of dialyzing membrane can be used. A good grade of parchment paper is satisfactory for most purposes. The cathode may be made of nickel or copper gauze, the anode of platinum, gold, gold-plated gauze, or carbon. For greatest efficiency the electrodes should have approximately the same dimensions as the dialyzing membranes. The cell can be used for continuous electrodialysis by allowing a continuous stream of distilled water to enter at the bottom

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[1] Received August 20, 1927.

[2] Bogue, "Colloidal Behavior," p. 300, McGraw-Hill Book Co., 1924.

[3] *Kolloid-Z.*, **41**, 243 (1927).

[4] *Biochem. Z.*, **152**, 355 (1924).

[5] Alexander, "Colloid Chemistry," p. 834, Chemical Catalog Co., 1926.

and flow out through an exit tube at the top, or it may be drained periodically and fresh distilled water added.

The most suitable voltage to apply at the electrodes will vary with the nature of the sol being electrodialyzed, and with its content of electrolyte. It is generally best to keep the current under one ampere in order to avoid too much heating. This can be done by controlling the line voltage or, more conveniently, by using an adjustable rheostat connected in series with the cell. A line voltage of 100 to 220 volts is commonly used.

Rate of Electrodialysis

The comparative rate of electrodialysis of different ions through parchment membranes is shown in Figure 2. Ten-cubic centimeter samples of solutions of KCl, K_2SO_4, and KH_2PO_4, all normal in potassium content, were placed in 500 cc. of water in the middle chamber of the electrodialysis cell and 100 volts d. c. applied at the electrodes. The anolyte and catholyte were siphoned off every 10 minutes and titrated with standard acid or base. In every case the cation is removed much more quickly than the anion. The rate of removal of the cation is influenced by the nature of the anion with which it is combined, while the rate of removal of the anions is in the order $Cl > SO_4 > H_2PO_4$. In every case the cation is removed quantitatively within 20 to 40 minutes. The anion can also be removed quantitatively, but the time required is greater, especially in the case of the phosphate ion. The rate of removal of anions should be facilitated by the substitution of a positive membrane for the negative parchment membrane on the anode side. A satisfactory positive membrane has not yet been found, although the chromated gelatin membrane[2] has proved helpful in certain cases.

Present Status of Coal By-Product Nitrogen[1]

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Within the last fifteen years coal has been a very influential factor in wresting the world nitrogen monopoly from Chilean nitrate. Power for the manufacture of fertilizers is obtained from coal; 85 to 90 per cent of the hydrogen required for the synthetic fixation of nitrogen will be produced in 1927 through coal, either from water gas or by-product coke-oven gas; and Aikman, Ltd. (London), estimates that of the world consumption of 1,315,000 tons of nitrogen in the year ending June 30, 1927, 24 per cent, or 310,000 tons, were produced as a distillation product of coal. This figure of 310,000 tons of nitrogen from by-product ammonium sulfate shows an increase over the figures of 300,000 and 275,000 tons for the two previous years and on the basis of $50.40 per ton (2000 pounds), the average price of ammonium sulfate for that period, was worth $73,745,280.

While there have been no startling new developments in the processes for treating coal by-products within the last year, the industry has made steady progress and developed its operating technic along lines already established. However, three decided tendencies have become apparent.

Bigger and more efficient ovens are being built. The trend of the industry is for larger unit coke-oven capacity. In America the average oven holds a charge of 12 tons of coal. There is an increasing number of plants having 16-ton ovens and the Carnegie Steel Company at Clairton, Pa., is now constructing three hundred and forty-eight ovens of the Koppers-Becker type, whose individual capacities will be 19.13 tons of coal per charge. It is estimated that this new group of ovens will produce 2,721,000 tons of coke annually, so that this new plant alone will potentially be able to recover 45,000 tons of ammonium sulfate per year.

The city gas companies are becoming more closely allied to the by-product coke-oven interests. In the United States five of the eleven companies which placed new by-product coke ovens in operation in 1926 were connected with public utilities companies and will market their surplus gas through these systems. City gas works thus owned 27 per cent of the new ovens opened up in the past year, and these ovens will manufacture 22 per cent of the additional estimated annual coke output.

Furthermore, the keen competition due to the increased production of synthetic nitrogen is forcing the by-product companies to convert their ammonia liquor to sulfate. More and more industries needing highly pure ammonia are looking to the synthetic plants to supply their wants and the output of the coal industries will be converted into fertilizer materials.

A study of the statistics[2] for the United States for the year ending June 30, 1927, will give an accurate picture of the condition of the industry. On that date there were seventy-seven active by-product coke-oven plants and one idle one, and these plants were producing slightly more than 82 per cent of their capacity. These plants had about 12,000 ovens in actual use. During the year eleven companies placed 679 new ovens in operation,[3] from whose estimated annual production of 3,794,470 tons of coke it will be possible, using present methods, to recover 12,920 tons of nitrogen. On December 31, 1926, fourteen companies were constructing 945 new ovens, whose annual coke production capacity will be 6,304,250 tons of coke with the corresponding recovery of 21,450 tons of nitrogen.

Table I shows there has been a steady increase in the nitrogen produced from by-product coke ovens in the United States in the last three years. In addition to these figures, the gas works have recovered, as the three-year average, 5300 tons of nitrogen per year.

Table I—Nitrogen Recovered from By-Product Coke Ovens

YEAR ENDING JUNE 30	COAL CONSUMED IN BY-PRODUCT OVENS	AMMONIUM SULFATE EQUIVALENT	NITROGEN EQUIVALENT
	Tons	*Tons*	*Tons*
1925	51,525,000	595,050	126,150
1926	60,653,000	700,774	148,564
1927	63,963,000	738,772	156,620

During the calendar year 1926 the nitrogen needs of the United States were such that it was necessary to import 155,200 tons of nitrogen in the form of Chilean nitrate valued at $42,781,400. Additional 22,880 tons of nitrogen were imported in the form of other salts, showing that our consumption was 178,080 tons greater than our domestic production. Although our synthetic-nitrogen plants will probably produce at least 23,000 tons of nitrogen in 1927,

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[1] Received October 13, 1927.

[2] Taken from Weekly Coal Reports of U. S. Bureau of Mines.

[3] *Blast Furnace Steel Plant*, **15**, 41 (1927).

as compared with about 12,800 tons in 1926, and although their output will be further increased in the next five years, the nitrogen demand of the United States will be so great that the coke industries will have no difficulty in disposing of all of their nitrogen by-products.

Owing to the growth of the by-product coke industry caused by the increased demand for both coke and gas, and also to the adoption of new processes, such as the Bergius process for the hydrogenation of coal (which recovers 50 per cent of the coal's nitrogen by conversion into ammonia as compared with less than 20 per cent recovery by present practices), the nitrogen derived from coal is bound to remain an important factor in the nitrogen situation of the United States. Thus, in spite of the probability of a lower selling price resulting from the competition of the direct synthetic processes, the quantity of by-product ammonium sulfate produced in this country is likely to increase in the next decade.

Brittleness Tests for Rubber and Gutta-Percha Compounds[1]

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An insulating material compounded of rubber, gutta-percha, or of similar substances becomes brittle at a temperature characteristic of the material, below which it may not be used if liable to mechanical stress. An apparatus has been designed for determining this temperature by giving the sample a sharp bend through a fixed angle. The highest temperature at which fracture occurs in this test (the brittle temperature) has been found to be nearly independent of the bending angle and the sample's dimensions provided the rate of bending is maintained at a nearly constant (high) rate. A modified form of the apparatus is also described with which the brittle temperature may be determined when the material is under high hydrostatic pressure. The constancy of the brittle temperature when determined under different conditions suggests that it marks a change in the structure of the material.

A SELDOM mentioned property of rubber and gutta-percha compounds, which is yet of considerable importance in their use for insulating purposes, is the temperature at which they become hard and brittle. Raw rubber, when quickly removed from a bath of liquid air in which it has been held for a minute or so, and struck with a hammer, will shatter like glass. The same effect may be observed at any temperature up to about −60° C. A similar behavior is shown by gutta-percha compounds cooled to temperatures below −30° C. Insulating materials compounded of these substances may be brittle at higher temperatures, and it is obviously necessary that this brittle temperature be below the lowest temperature to which the insulation may be subject, if it is likely in use to come under any strain. The insulation of a submarine cable, for instance, must not be brittle at sea-bottom temperature, which is as low as 0° C. over large areas.

Brittleness is a phenomenon which can only be defined in an arbitrary manner, as it refers to a combination of properties which produce a fairly definite practical effect, but whose inter-relations vary in different materials and are in no case very clearly known. This practical effect is fracture under moderate deformation quickly applied. The simplest method of measurement is in terms of the sudden bending of a strip. The shattering of a sheet of material under a hammer blow, another common condition under which brittleness is apparent, involves similar strains along the radii of the circle struck, combined with compressive strains.

In a test developed by the authors the bending of a strip is used, and the highest temperature at which the strip will fracture under fixed conditions determined. The dependence of this temperature on the sample dimensions and on the rate and character of the deformation will be discussed below. The other factor in the design is that of temperature control and measurement. To provide for these, and at the same time to avoid having the mechanism subject to the varying resistance of the viscous bath liquid, the sample is held on a sliding vertical support, which normally holds the sample in the temperature bath. To test, this support is raised sharply and, as it brings the sample from the bath, automatically trips a hammer which bends the sample through a fixed angle (about 45 degrees).

Apparatus

A photograph of the apparatus is shown in Figure 1. *S* is the sample held against the movable support *A* by the clamp *C*. The hammer *H*, operated by the spring *B*, is shown in the tripped position, in which it has bent the sample as shown. When the hammer is locked by means of the catch *D*, the sample and support can be lowered into the Dewar flask *F*, in which is a temperature bath of ethyl alcohol. The temperature is adjusted by means of a small heating coil (not shown) and by additions of liquid air. The bath is stirred mechanically by a glass stirrer (dismounted, to simplify the photograph). Temperatures are measured by means of potentiometer readings on a thermocouple, the fixed junction of which is held in steam, thus giving readings conveniently over any range below 100° C.

Determination of Brittleness Temperature

The sample in the form of a strip approximately 0.050 inch (1.3 mm.) and 0.3 inch (7.6 mm.) wide is inserted beneath the clamp *C* in such a way as to project beyond the end of the support *A* far enough to be struck by the toe of the hammer when the latter is tripped. The support is then lowered into the bath and held there for about 2 minutes to allow the sample to reach the bath temperature. The support *A* is then sharply raised, tripping the hammer, and the sample examined for signs of fracture. If the sample breaks the operation is repeated at a higher temperature, if it does not break, at a lower; and this is repeated until the highest temperature at which the sample will fracture has been located, as can generally be done, within 2° C. The determination first made is checked by repeating the procedure, starting with a temperature slightly higher than the brittle temperature found in the first determination, and changing the temperature in the opposite direction.

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[1] Received September 27, 1927.

For purposes of comparison, typical results are given in the accompanying table.

Brittleness Temperatures of Rubber and Gutta-Percha Compounds

	° C.
Raw rubber:	
Pale crepe	−58
Smoked sheet	−57
Pure rubber hydrocarbon	−55
Pahang gutta-percha	−28
Vulcanized rubber	−53
Balata	−44

Precise descriptions of the stocks listed are not included as the results given in the table are fairly typical. Compounded materials are generally brittle at higher temperatures, and for these the change is often not so sharp as for the materials listed.

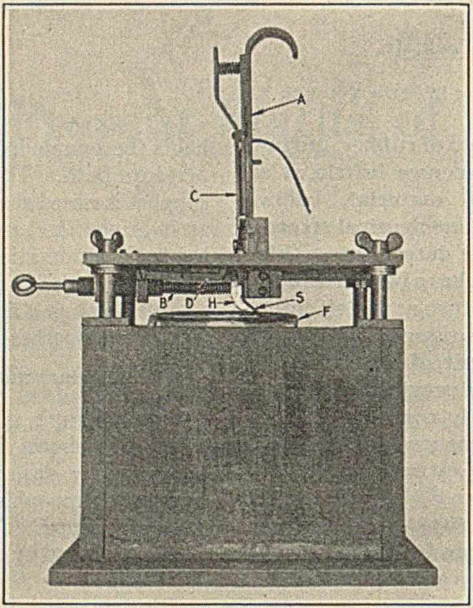

Figure 1—Apparatus for Testing Brittleness of Rubber and Gutta-Percha Compounds

The test dimensions are purely arbitrary, and if the brittle temperature were very sensitive to changes in them it would be of very doubtful significance. This has been found, however, not to be the case. Brittleness determinations were made on gutta-percha samples using the hammer shown, which bends the sample through an angle of about 45 degrees, and with two other hammers of similar shape which bend the sample through angles of 15 and of nearly 90 degrees, respectively. The brittle temperatures determined with the three hammers were the same within 2° C., which is about the limit of reproducibility in any case. Tests were made on samples of gutta-percha both 50 and 70 mils thick, and the results from the latter were from 5° to 10° C. higher than those from the former, indicating a comparatively slight difference in brittle temperature corresponding to the considerable increase in strain intensity involved in bending the thicker sample through the same angle. A similar test on samples of a rubber insulating compound indicated that its brittle temperature was the same for samples of these two thicknesses (50 and 70 mils).

When the spring tension used is light, the results are not so reproducible as when it is heavy. In the first case a stiff sample will be deformed more slowly than a soft one, and the test does not then afford a good comparison. Accordingly, the spring tension is maintained at a high value, so that the resistance of the sample is small compared with the frictional and inertia resistance of the hammer and the spring. The rate of movement of the hammer is thus very high, and nearly independent of the material tested. Under these conditions highly reproducible results are obtained. The spring actually used is under a tension of 12 pounds when held by the catch, and under a tension of 6 pounds when the hammer is resting against the sample holder. These approximate figures were obtained with a spring balance.

Apparatus for Material under High Pressure

A modified form of the apparatus, shown in Figure 2, has been employed to determine brittle temperatures under high pressure. The sample, as a short strip, is held in a horizontal position below the lower plate, *C*, and is bent through an angle of about 60 degrees by the plunger *A*, which is shown in the released position. This apparatus is placed in a high-pressure bomb, in which pressures up to 20,000 pounds per square inch can be generated by screwing down on a piston. When the bomb has been brought to the required temperature and pressure, the hammer plunger is released by the action of a screw acting through the wall of the bomb on the smaller plunger, *B*, of which the upper part projects above the rest of the apparatus (Figure 2). This smaller plunger is beveled at its upper bearing, and in being forced down presses a small spring hinge to one side: this hinge is forced from a horizontal groove in the hammer plunger, and thus releases the plunger.

Temperatures may be measured in the refrigerator in which the bomb is held for about 12 hours before each test. The slowness of the operation, the difficulties of temperature control, and the uncertain effect of the viscous resistance of the compressed cooling liquid on the plunger action have made it difficult to obtain precise results. It was found, however, that the brittle temperature of gutta-percha and similar compounds thus determined, even at pressures up to 18,000 pounds per square inch, showed a difference of only 2° to 3° C. from the results obtained in the other apparatus at atmospheric pressures.

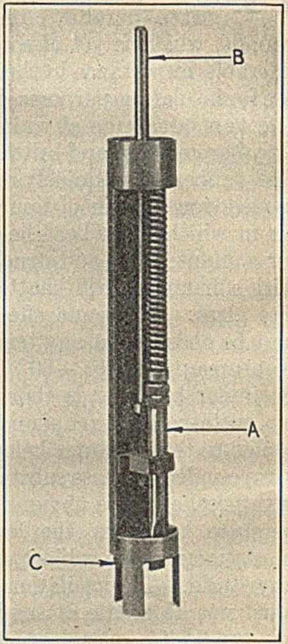

Figure 2—Apparatus for Material under High Pressure

Marks Change in Structure of Material

It is evident from the sharpness of the brittle temperature, and its independence of precise test dimensions, that it represents a temperature range in which the physical properties of the material change very abruptly, if it does not represent an actual change of phase. The existence of this temperature has been noted previously. Park[2] included it in the series of changes which he showed to take place in balata, gutta-percha, and rubber over different temperature ranges. Like other investigators, he determined the temperature by a hand test. Owing to the sharpness of the change, this procedure would not be very inaccurate were it not for the difficulty of determining the temperature of the material at the actual moment of test.

[2] *India Rubber J.*, **69**, 421 (1925); *Ind. Eng. Chem.*, **17**, 152 (1925).

Hock[3] observed that rubber stretched at a low temperature and struck with a hammer broke into bundles of fibers parallel to the direction of stretch, and that rubber, stretched and frozen, must be warmed to a definite temperature (about 17° C.) before retraction will take place. Reference may also be made to the work of Le Blanc and Kröger,[4] who determined the stress-strain curve of rubber at low temperatures and showed it to change greatly in character. That the rubber will submit to considerable elongations at low temperatures is not inconsistent with the results noted here, as the rate of deformation in the tensile test is of a much lower order than that employed to determine brittleness.

[3] *Rubber Age*, **19**, 141 (1926); *Gummi-Ztg.*, **39**, 1740 (1925).

[4] *Kolloid-Z.*, **37**, 205 (1925).

The Estimation of Nitrogen in Petroleum and Bitumens[1]

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Suggestions of procedure are offered for the estimation of nitrogen in petroleum products and bitumens by the Dumas and Kjeldahl methods. The analytical data presented make it doubtful whether any California petroleum contains as much as 1 per cent nitrogen or any Texas Gulf Coastal oil as much as 0.1 per cent nitrogen. Analyses show certain Mexican, Venezuelan, and Colombian petroleums to approach California crudes in their abnormally high nitrogen content. Proof is furnished that (1) the nitrogen compounds in crude petroleum are not always in basic form, and (2) chemical changes occur in the nitrogen compounds on distillation of petroleum.

IT IS quite evident that the Kjeldahl method in some one of its modifications would be preferred to the Dumas method in estimating nitrogen in a product like petroleum, provided a complete conversion of the nitrogen to ammonia could be realized. Where applicable, the Kjeldahl method can be relied on for greater accuracy, it is more convenient in many respects, and where a number of analyses are involved it is not so time-consuming. Another consideration favoring the Kjeldahl procedure is the low amount of nitrogen in petroleum, the amount varying from 0.00 to 0.80 per cent.

Mabery and co-workers,[5] after trying out the Kjeldahl and Dumas methods of estimating nitrogen on sixteen samples of California crudes, decided in favor of the combustion method with the claim that "the Kjeldahl method evolves only a part of the nitrogen as ammonia." Furthermore, Engler and Höfer,[6] with Takano as their authority, state in connection with a discussion of the "nitrogen content of petroleum" that "in relation to nitrogen content Japanese petroleum lies between that of California and Ohio; the nitrogen determinations were made by the volumetric method (Dumas), since the Kjeldahl method cannot be used with Japanese petroleum."

When it is considered that the American Society for Testing Materials recommends the Kjeldahl-Gunning method for the estimation of nitrogen in coal,[7] it would seem that sulfuric acid digestion of petroleum with the addition of the common catalysts and accelerators would prove effective when applied to petroleum. As a matter of fact, the Kjeldahl method of estimating nitrogen in petroleum is now in general use. However, directions sometimes given for effecting the process need revision, e. g., Hamor and Padgett[8] recommend the use of only 25 cc. of sulfuric acid in the digestion, an amount we find entirely inadequate in view of the fact that "the weight of the sample may be as much as 5 grams for crude oils low in nitrogen."

Note—Fleischner ["Die Stickstoffbestimmung in Kohle und Koks," p. 39 (1919)] claims the combustion method to be the only one that can be relied on in an accurate determination of nitrogen in coal: "Through determinations made on anthracite brown coal and coke I have definitely determined that the Kjeldahl-Gunning and the Jodbauer methods do not convert all the nitrogen in coal to ammonia. The total nitrogen in coal can be determined only by the Dumas method." Fieldner and Taylor, however, in a series of coal analyses [*Ind. Eng. Chem.*, **7**, 106 (1915)] obtained a mean difference of only 0.05 per cent in nitrogen per cents determined by both the Dumas and Kjeldahl methods.

Using the following procedure we have obtained quite satisfactory results in estimating nitrogen in crude oil, distillates, petroleum asphalt, petroleum coke, and natural bitumens.

Procedure

One to 5 grams of the sample are digested with 150 cc. of sulfuric acid, 50 grams of potassium sulfate, 2.5 grams of mercuric oxide, and 2.5 grams of copper sulfate. It will be found advantageous to radiate the heat downward onto the upper layer of the acid mixture by placing a strip of thin asbestos paper just above the bowl of the flask. Depending on the nature and weight of the sample, 30 minutes to 2 hours are required for the appearance of the clear, dark green color when the heating is continued 5 hours.

The remaining procedure is in line with common laboratory practice, although in the ammonia distillation 1 gram of granulated zinc is added just preceding the introduction of the caustic solution. Furthermore, we have observed that the neutralization of the large amount of sulfuric acid used in kjeldahling petroleum gives rise to foaming and "sucking back" troubles when the ammonia distillation is conducted in the ordinary way. To overcome these difficulties the following technic has been developed: (1) The caustic solution is introduced above the surface of the acid through a dropping funnel with the lower end of the outlet tube bent

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[1] Received August 8, 1927. This paper contains preliminary results obtained at the Chemical Laboratory, University of Texas, in an investigation on "The Nitrogen Compounds in Petroleum," listed as Project 20 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] *J. Soc. Chem. Ind.*, **19**, 502 (1900).

[6] "Das Erdöl," Vol. I, p. 479 (1913).

[7] Stanton and Fieldner, *Bur. Mines, Tech. Paper* **8** (1913); Fieldner and Taylor, *Ibid.*, **64** (1915); A. S. T. M. Standards, p. 570 (1916).

[8] "The Examination of Petroleum," p. 9 (1920).

upward. (2) The titration flask is provided with a two-hole rubber stopper; through one hole passes the condenser tube and through the other connection is made with a mercury seal 1 cm. deep. The distillation of the ammonia in a closed system also obviates the introduction of laboratory gases that might affect the titration.

Table I—Analyses from the Texas Laboratory of California Crudes

Sample No.	Description	Nitrogen by Kjeldahl	Nitrogen by Combustion
		Per cent	*Per cent*
A.O.X.			
1	Ventura crude (sample from Pipeline)	0.429–0.420	0.477
2	Midway crude (sample from Pipeline)	0.424–0.432–0.425	0.475
S.O.X.			
1	Ventura crude (sample from Pipeline)	0.381–0.395	0.382–0.399
2	Coalinga crude (sample from Pipeline)	0.358	0.406–0.426
3	Ventura crude (sample from Pipeline)	0.448	0.491–0.490
U.O.X.			
1	Timber Canyon Well No. 1	0.320	0.318
2	Kentucky Well No. 11	0.401	0.430
3	Crane Well No. 3	0.600	0.549
4	Moherb Oil Co. Well No. 4	0.426	0.485
5	Torrey Well No. 15	0.479	0.530
6	Ojai Lease Well No. 4	0.802–0.803	0.815
7	Newhall Lease Well No. 14	0.488	0.451
8	Snyder Well No. 1	0.442	0.513
9	Torrey Well No. 59	0.497	0.478
10	Torrey Well No. 58	0.503	0.548
11	C. D. L. D. Lease Well No. 1	0.696–0.685	0.749
12	Lincoln Oil and Gas Co. Well No. 1	0.323	0.421
13	Grimes Lease No. 4	0.619	0.531
14	Crane Well No. 2	0.451	0.403
15	C. D. L. B. Well No. 3	0.437	0.486
16	Robertson Lease Well No. 4	0.572–0.561	0.458
17	Pyramid Oil Co. Well No. 1	0.396	0.441
18	W. H. Cochrane Lease Well No. 4	0.379	0.387
G. P. C.			
1	Tonner No. 1 Brea Olinda Field	0.515	
2	Standard Oil Co., Vickers No. 1	0.559	
3	Belridge No. 3, Belridge Field	0.475	
4	Santa Fe Well No. 3, Santa Fe Springs	0.254	
5	Bell and Wrightman	0.102–0.14	
6	Marine Oil Co. Benwell No. 19	0.510	
7	Barnard No. 1, Ventura Field	0.507	
8	Oscar Howard No. 3, Bardsdale Field	0.484	
9	Shell Oil Co., Ridge No. 3	0.502	
10	Native Oil Co., No. 2	0.560	
11	Stern No. 1, Yorba Linda Field	0.550	
12	Clock No. 3, Signal Hill	0.507	
13	Obispo No. 6, Obispo Oil Co.	0.590	
14	Marine Oil Co., Amick No. 37	0.520	

A. O. X. refers to Associated Oil Company; S. O. X. to Shell Oil Company; U. O. X. to Union Oil Company; G. P. C. to General Petroleum Corporation—all of California.

Unless certain precautions are taken, the Dumas method of estimating nitrogen when applied to petroleum will, even in the hands of an experienced analyst, give results too high. Errors here arise principally from two sources: First, owing to the small nitrogen percentage unusually large samples must be employed; and in the second place, what is more important, volatile hydrocarbons can escape combustion, thus increasing the gas volume in the azometer. The second difficulty is overcome by employing two combustion furnaces in series. Two quartz tubes are used, the one in the furnace next to the azometer being heated to dull redness before the one next to the carbon dioxide generator, and carrying the sample, is swept out. A continuous carbon dioxide generator of a form designated by Young and Caudwell[9] is employed, and at the start this is exhausted with an oil pump. As a further refinement all rubber connections except the stoppers in the combustion tubes are eliminated, the usual rubber-tube connections being displaced by glass tubing and mercury seals.

Analytical Data

Using the Dumas method, Mabery found a minimum of 0.91 per cent, a maximum of 2.39 per cent, and an average of 1.66 per cent nitrogen in the California oils analyzed. Our California samples showed a minimum of 0.102 per cent, a maximum of 0.815 per cent, and an average of 0.473 per cent nitrogen (Table I). From these figures it is evident that the nitrogen content of California petroleum, as determined in Mabery's laboratory, is on the average 3.5 times that found in the Texas laboratory.

In connection with an investigation of natural bitumens, Bardwell, Berryman, Brighton, and Kuhre carried out nitrogen determinations by the Kjeldahl method.[10] Later, in a criticism of their paper, Richardson[11] stated, "They do not seem to be aware that the nitrogen in bitumens cannot be determined by a modified Kjeldahl method."

Through the courtesy of Professor Brighton we have obtained samples of the bitumens investigated in the Utah laboratory. As in the case of petroleum nitrogen, we find that the determinations of bitumen nitrogen by the Kjeldahl method agree on all samples investigated with determinations by the Dumas method. Furthermore, as shown in Table II, our analyses are in close accord with those made in the Utah laboratory, although we are not acquainted with the procedure followed by Professor Brighton and co-workers.

Table II—Analyses from Texas Laboratory of Natural Bitumens

Sample No.	Description	Nitrogen by Combustion	Nitrogen by Kjeldahl	Nitrogen Reported from Univ. of Utah as Detd. by Kjeldahl
		Per cent	*Per cent*	*Per cent*
U. U. X.				
1	Gilsonite ordinary	2.13(2.32)	2.18(2.37)	2.21
2	Gilsonite special	2.80(2.80)	2.8(2.86)	
3	Tobbyite	2.29(2.35)	2.26(2.32)	2.10
4	Wurtzilite	2.10(2.38)	2.14(2.43)	2.10
B. A. X.				
1	Trinidad Lake asphalt	0.78(1.12)	0.70(1.01)	0.66
2	Bermudez Lake asphalt	0.93(0.96)	0.88(0.91)	0.89
3	Gilsonite (selects)	2.28(2.28)	2.26(2.26)	
U. A. X.				
1	Uvalde asphalt with pyrite	0.66(0.67)	0.63(0.64)	
U. O. X.				
19	Asphalt from Brea, Los Angeles, Calif.	1.22(2.38)	1.14(2.23)	

U. U. X. refers to University of Utah; B. A. X. to Barber Asphalt Company; U. A. X. to Uvalde Asphalt Company; and U. O. X. to Union Oil Company.

The nitrogen figures outside of parentheses refer to the crude samples as received, and those within parentheses are figured on an ash-free basis.

Attention should be directed to the fact that since his publication of nitrogen determinations on California crudes, Mabery[12] has described a modification of the Dumas method which gives concordant results with the Kjeldahl method of estimating nitrogen in petroleum. Unfortunately, however, as is evident from the following quotation, he did not seem to suspect the need of revision of his earlier nitrogen work on California oils, which has been universally accepted in petroleum literature as authoritative:

> That nitrogen bases are generally present in Japan petroleum was shown by Mabery and Takano,[5] who found in many samples from different fields percentages of nitrogen varying from 0.35 to 1.5 per cent. The wide distribution of these bodies in California petroleum appeared in the analysis of sixteen samples from as many different fields that gave amounts from 1.0 to 2.55 per cent.

In our work, which comprises a very extensive survey of the nitrogen content of petroleum from practically all producing fields in the United States, as well as certain fields in Mexico, Venezuela, Peru, and Colombia, no sample has been analyzed with a nitrogen content higher than 0.815 per cent. Data on certain Mexican, Colombian, and Venezuelan crudes that approach the average California oil in nitrogen content, are given in Table III.

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[9] *J. Soc. Chem. Ind.*, **26**, 184 (1907).

[10] *Ind. Eng. Chem.*, **5**, 973 (1913).

[11] *Ibid.*, **6**, 865 (1914).

[12] *J. Am. Chem. Soc.*, **41**, 1690 (1919).

Table III—Analyses of Mexican, Colombian, and Venezuelan Crude

Sample No.	Description	Nitrogen *Per cent*
R. O. X. 2	Heavy Mexican crude	0.358
R. O. X. 3	Light Mexican crude	0.326
G. R. X. 10	Mexican heavy crude-mixed type	0.354
R. O. X. 4	Colombian crude	0.226
G. R. X. 12	Venezuelan crude-mixed type	0.231

R. O. X. refers to Standard Oil Company of New York, and G. R. X. to Gulf Refining Company of Texas.

In the case of Texas oils attention is directed to the following analyses cited by Day:[13]

> Jefferson County, Lucas Well—more than 1 per cent nitrogen [Mabery, *Proc. Am. Acad. Arts. Sci.*, **23**, 265 (1901)]. Beaumont Field—0.92 per cent oxygen and nitrogen [Richardson, *J. Franklin Inst.*, **162**, 113 (1906)].

Our analyses of thirty-four crude oils from the Texas gulf coastal region indicate that no petroleum from this section will be found to run as high as 0.10 per cent nitrogen. Samples investigated in the Texas laboratory from Brazoria, Chambers, Galveston, Harris, and Wharton Counties conform in their nitrogen content to approximately 0.02–0.04 per cent; whereas specimens from Jefferson, Liberty, and Orange Counties were in the main within the limits of 0.055 to 0.075 per cent nitrogen.

Form of Nitrogen Compounds Present in Petroleum

It may not be out of place to note that, contrary to statements often found in petroleum literature,[8,14] we find, at least as far as California petroleum is concerned, that very little of the nitrogen can be extracted from crude oil with dilute mineral acids. Our observation is in line with Day's claim[15] that "none of the investigators has accounted for the total nitrogen in various oils by the amount of pyridine bases extracted."

That there is nothing inherent in crude petroleum to interfere with the extraction of bases, were they present, can be demonstrated by the addition of a small amount of an organic base, such as quinoline. Our experiments show that quinoline admixed with petroleum can be regained by dilute acid extraction. Of course it is possible that the nitrogen in certain types of petroleum is entirely in basic form, but such oils have not come under our observation.

Through the coöperation of R. E. Haylett and T. F. Ott, of the Union Oil Company of California, there have been examined in this laboratory nineteen products from the Oleum refinery. One of these samples, "asphalt crude," represents the crude oil from the McKittrick district of California, and from this are produced the various crude distillates, refined products, and residual asphalt included in the remaining eighteen samples. In an experiment where equal volumes of the asphalt crude (containing 0.64 per cent nitrogen) and 16 per cent sulfuric acid were employed it was found that practically none of the nitrogen was removed from the oil. In all distillates a part of the nitrogen was in dilute acid-soluble form, but as a rule nitrogen in non-basic form predominated. From these observations the conclusion follows that in crude oil the nitrogen compounds are in the main not basic, but in distillates bases appear along with non-basic nitrogen compounds of unknown structure. At this time it will suffice merely to emphasize the fact that in the case of neither petroleum nor distillates can the nitrogen compounds be quantitatively extracted with dilute mineral acids, and a method of estimation of nitrogen in these products be developed from this initial procedure.

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[13] Handbook of the Petroleum Industry, Vol. I, p. 530 (1922).

[14] Redwood, "Petroleum and Its Products," Vol. I, p. 204 (1896); Engler, *Chem.-Ztg.*, **30**, 713 (1906).

[15] *Op. cit.*, p. 529.

Analysis of Mixtures of Similar Organic Compounds[1]

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ONE of the most difficult types of problems in analytical chemistry is the determination of the individual components of a mixture of homologous or isomeric organic compounds. The substances present in such mixtures usually resemble each other so closely that they cannot be separated quantitatively by chemical means. Most of the methods which have been suggested are based upon the relationships which exist between the composition and the physical properties of the mixtures—as, for example, the boiling points, melting points, densities, or refractive indices. Such methods are frequently unsatisfactory and are more or less limited in their application. Frequently the rate of change of physical properties with change in composition is so slight that physical methods of analysis are subject to very considerable error. Furthermore, such methods are applicable only to the analysis of mixtures in which the number of components is small and the identity of each component is known.

Method

In a great many cases the amount of a particular substance present in a mixture of similar organic compounds can be calculated from the results obtained by determining, by the cryoscopic method, the apparent average molecular weight of the mixture in two different solvents, one of which is not a component of the mixture while the other is identical with the particular component being determined. When the solvent used in the determination of the average molecular weight is a substance which is not present in the mixture, each component in the mixture dissolves in the solvent and exerts its normal influence in lowering the freezing point, so that the result is the true average molecular weight of the sample. When the solvent used is a substance which is itself a component of the mixture, that amount of that substance which is present in the sample taken for the determination acts simply to increase the amount of the solvent. The other substances dissolve in the solvent and lower its freezing point, the magnitude of the depression of the freezing point depending upon the molal concentration of these other components in the total amount of solvent. From the two sets of results thus obtained the concentration of that particular component in the mixture can be calculated.

The equation for calculating the percentage of an individual component from the results of the two determinations of apparent molecular weight may be developed as follows:

Let M_a = molecular weight of a specific component, A

m = average molecular weight of the mixture, as determined by cryoscopic methods using as a solvent

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[1] Received June 18, 1927.

a substance which is not a component of the mixture

w = weight of sample of mixture taken in cryoscopic determination of apparent molecular weight in pure A as solvent

N = total number of gram-molecules in w

N_a = number of gram-molecules of A in N

N_x = number of gram molecules of substances other than A in N

W = weight, in grams, of pure A taken as a solvent in determination of apparent molecular weight

W_1 = total weight, in grams, of A present in solution of w grams of mixture in W grams of pure A

K = freezing-point constant of pure A—i. e., depression of freezing point produced when 1 gram-molecule of solute is dissolved in 1000 grams of A

dT = observed depression of freezing point when w grams of mixture are dissolved in W grams of A

x = percentage by weight of A in mixture

Then

$$N = N_a + N_x$$

$$N_a = N - N_x$$

$$W_1 = W + N_aM_a$$

$$dT = 10^3 \frac{KN_x}{W_1}$$

$$= 10^3 \frac{K\,(N - N_a)}{W + N_aM_a}$$

$$N_a = \frac{10^3\,KN - dTW}{10^3\,K + M_adT}$$

Since

$$N = \frac{w}{m}$$

we have

$$N_a = \frac{10^3\,Kw - dT\,Wm}{10^3\,Km - M_a\,mdT}$$

Also

$$x = 100\,\frac{N_aM_a}{w}$$

Therefore

$$x = \frac{100\,M_a}{w} \cdot \frac{10^3\,Kw - dT\,Wm}{10^3\,Km + M_amdT}$$

Extent of Application

This method of analysis should be of extensive application, athough not all mixtures of organic compounds can be analyzed in this way. It cannot be used when the substances present are ionized or polymerized, nor is it applicable when chemical compounds are formed between the various components. Furthermore, the method can be applied conveniently only to the determination of substances which have freezing points within the range of temperatures covered by the ordinary Beckman thermometer. It so happens, however, that a great many common organic compounds—as, for example, many of the components of ordinary coal tar—do fulfil these requirements. For the analysis of such mixtures this method should prove of considerable value. The method is applicable to the determination of a given component in the presence of any number of other substances, even when the identities of these other substances are not known.

Analysis of Mixtures

A number of synthetic mixtures of organic compounds were analyzed by this method. The components of these mixtures were naphthalene, diphenyl, α-nitronaphthalene, dinitronaphthalene, and heavy coal-tar oil. The naphthalene, diphenyl, and α-nitronaphthalene were purified before use. The dinitronaphthalene was from a purchased supply of supposedly pure material. The heavy coal-tar oil was a naphthalene-free fraction obtained by the careful fractional distillation of creosote oil. It had a specific gravity of 1.030, distilled completely between 239° and 303° C., and consisted principally of a mixture of methylnaphthalenes, diphenyl, and acenaphthene.

In making the cryoscopic determinations precautions were taken to secure uniformity of conditions and to minimize supercooling. A fairly large quantity (13 to 27 grams) of the solvent was weighed into a large test tube (2.5 cm. diameter) and a weighed quantity of the sample to be analyzed was added. The amount of sample added was usually sufficient to depress the melting point of the solvent about 0.6° to 1.2° C. The tube containing the solution was provided with a Beckman thermometer and with a ring stirrer of nichrome wire, and was surrounded by a second tube so as to leave an air jacket approximately 2.5 cm. thick between the sample and the cooling bath. In order further to minimize supercooling, the bath was maintained 1° C. below the freezing point of the sample. In each case the solution was cooled slowly and with regular stirring until freezing began and the reading on the Beckman thermometer became constant. The solution was then warmed slightly until the crystals disappeared and again cooled and the freezing point again noted. The average of the concordant results of a series of determinations made with the same sample was taken as the true freezing point of the sample. The freezing-point constants for the solvents used were not taken from the data appearing in the literature, but were determined experimentally with the same lots of material, the same apparatus, and the same procedure that were used in determining the average molecular weights.

In each case the average molecular weight of the mixture was first determined, using as a solvent a substance which was not a component of the mixture. This solvent was usually benzene, but because of the very slight solubility of dinitronaphthalene in benzene, the solvent used for the mixture containing this component was diphenyl. The freezing-point constants of benzene, diphenyl, and α-nitronaphthalene were determined experimentally, using pure naphthalene as a solute. In the determination of the freezing-point constant of the naphthalene, diphenyl was taken as the solute. The results are given in Table I.

Table I—Freezing-Point Constants of Components
(Depression produced by 1 mol solute in 1000 grams solvent)

SOLVENT	° C.
Benzene	5.25
Naphthalene	7.04
Diphenyl	7.71
α-Nitronaphthalene	9.02

Table II—Analysis of Synthetic Mixtures of Organic Compounds

MIXTURE[a]	m	w	W	dT	PER CENT Found	PER CENT Taken
Naphthalene Oil	155.9	0.3930	17.3837	0.962	4.66	4.64
Naphthalene Oil	148.2	0.7162	19.3619	1.274	23.25	23.71
Naphthalene Oil	147.2	0.5213	24.0356	0.634	33.45	33.90
α-Nitronaphthalene Naphthalene	134.2	0.5193	13.3562	2.384	10.88	11.56
α-Nitronaphthalene Dinitronaphthalene	217.7	1.0044	21.4653	1.722	8.60	8.78
Diphenyl Naphthalene	140.9	0.5625	27.1955	0.609	49.93	49.54
Naphthalene Diphenyl α-Nitronaphthalene	152.4	0.6941	25.0459	0.825	29.45	29.84
Diphenyl Naphthalene α-Nitronaphthalene	152.4	0.6012	20.4169	0.887	40.20	40.65

[a] In each mixture the component which was determined separately and of which the percentage is given is listed first.

In the analysis of a number of synthetic mixtures by the method described above, the results in Table II were obtained. In each case the result given is that of a single determination, although the values taken for the lowering of the freezing point were obtained by averaging a series of concordant results obtained with the same solution.

The first attempts to analyze mixtures of α-nitronaphthalene and dinitronaphthalene gave results which indicated a much higher content of mononitronaphthalene than was actually taken. Upon examination the dinitronaphthalene, which was supposed to be pure, was found to contain considerable amounts of mononitronaphthalene. The dinitronaphthalene was then purified by repeated extraction with benzene. The analysis of mixtures of the purified material with known amounts of mononitronaphthalene gave satisfactory results.

Measurement of Hydrogen-Ion Concentration in the Control of Pulp and Paper Manufacture[1]

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Since many industries have found the measurement of hydrogen ions very useful in the control of factory practice, some studies of its possible uses in the manufacture of pulp and paper were undertaken. The results allow the following conclusions to be made:

(1) The hydrogen electrode gives valuable information about many pulp mill liquors, but in sulfite solutions with a pH less than 7.0 the readings cannot be taken as true pH values.

(2) The quinhydrone electrode is untrustworthy in the presence of sulfites or other oxidizing or reducing compounds. It is questionable on water, unless the latter is acid.

(3) The most generally useful electrode in the pulp and paper mill is antimony. The best type is the ordinary pure stick preparation, of a radially crystalline structure. The antimony electrode has the following advantages: (a) it requires no hydrogen; (b) it is inert toward sulfites; (c) it is mechanically sturdy; (d) it gives a fairly quick response when placed in solutions; (e) it is cheap and easy to secure; (f) it is admirably suited for continuous reading on recording instruments.

(4) The measurement of pH should prove especially useful in the control of the preparation of cooking liquors, the addition of alum and size to the beaters, in water purification and possibly in determining the end of the cooking process.

WHEN the present investigations were begun almost no use was being made of hydrogen-ion measurements in the control of pulp and paper manufacture. Since then, however, Shaw[22,*] has pointed out that there is an optimum hydrogen-ion concentration, at least during a part of the time of the beating of the pulp. This beating is generally carried out in an acid medium. The pH is also important when the stock is delivered to the paper machine. He has also shown that a maximum precipitation of aluminum occurs at pH 5.0 to 5.5. A great reduction in consumption of alum has resulted by maintaining this pH. It has been shown that any excess of alum beyond this pH value has no favorable effect upon the sizing quality of the paper.

Taylor[23,24] states that indicators are not feasible for pH measurements in the pulping process. They are of value, however, in showing the thoroughness of the washing process, and in indicating the extent of bleaching and washing of the bleached stock. He questions the use of such measurements in the beating operation, but confirms Shaw's work on sizing. In coloring or dyeing of pulp, the adsorption, fastness, and hue of dyes are dependent upon the pH of the dye bath. This may explain the difficulties some manufacturers have in matching colors. In the coating operation the pH of the coating mixture (composed of clay, glue, casein, starch, and other materials) is important. Here one is dealing with materials in the colloidal state which we know are profoundly influenced by the hydrogen-ion concentration.

In dyeing, Briggs and Bull,[6] Gordon and Marker,[12] and Fort[11] have found that the pH has a marked effect upon color and fastness, but more than this, that it is one of the important factors in the adsorption of dyes.

Miller, Swanson, and Soderquist[15] have studied the pulping process using various acids which differ in hydrogen-ion concentration, but they do not suggest hydrogen-ion control as a technical procedure.

Roschier[20] has found that the retention of China clay is dependent upon a definite percentage of alum and a pH of 5.5 to 5.7.

Experimental Method

The electrometric method for determining the H-ion concentration was chosen because of the probable limitations of colorimetric methods, such as (1) the color or turbidity of the solution itself, as in the cooking and in the dyeing solutions; (2) the presence of active chemicals, such as sulfurous acid and chlorine solutions; and (3) the high salt content of the solutions under investigation.

Four types of electrodes were used—viz., the Bailey, bubbling hydrogen, quinhydrone, and antimony. For convenience the experiments with each type will be considered separately.

A normal potassium chloride calomel cell was used in all electrometric determinations except in the case of the recording potentiometer, when a saturated potassium chloride cell was used.

Bailey Hydrogen Electrode

The first step was the determination of hydrogen-ion concentrations of solutions of the individual chemical compounds that are, or may be, present in the solutions used in the pulping processes. These measurements were made on different concentrations which covered the range found in actual practice.

Sodium carbonate solutions of 0.02 to 2.0 *M* concentrations were prepared, using the C. P. salt. The data presented in Figure 1, curves 3 to 6, show that satisfactory measurements of pH were obtained. There is practically no change in pH throughout this range in concentration.

Sodium acid carbonate solutions from 0.01 to 1.0 *M* made from U. S. P. chemical, also gave satisfactory results. (Figure 1, curves 1 and 2) There seems to be a decrease in alkalinity with increase in concentration.

Sodium sulfate solutions made from C. P. chemical in concentrations of 0.01 to 1.0 *M* gave the results in Figure 2, curves 5 and 6. The determinations in 6 were made 12 hours later than those in 5. The pH is practically the same at all concentrations. When the electrodes, after use with these solutions, were filled with buffer solutions, they gave correct results.

Sodium sulfide solutions were made from C. P. chemical. The readings were very erratic, and the electrodes would not check on buffer solutions after more than one deter-

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[1] Received August 22, 1927. Published, with the approval of the Director, as Paper No. 719, Journal Series, Minnesota Agricultural Experiment Station.

[2] The work reported in this paper was submitted by Mr. Franke to the Graduate School of the University of Minnesota as a doctor's thesis and was made possible by a fellowship granted by the Cloquet wood products companies. Thanks are due especially to The Northwest Paper Company for mill facilities.

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

mination had been made, and at times not even one determination could be secured. The data in Figure 2, curve 10, are the best determinations that could be made and are probably fairly correct. Again in these solutions there is not much change in pH with change in concentration. Hydrogen sulfide is known to poison hydrogen electrodes.[2,9] This point will be mentioned in connection with the bubbling type.

Sodium sulfite solutions were prepared from c. p. salt. The results are shown in Figure 2, curves 7, 8, and 9. Again the electrodes behaved erratically, and, after having been in the sulfite, were useless on buffer solutions until after thorough washing. Curve 9 may partly explain these results. These readings were made 24 hours after those in curve 7, and show that the sulfite became partially oxidized to sulfate; hence the readings tend to approach those in curves 5 and 6 for sodium sulfate, especially in the dilute solutions.

Sodium acid sulfite solutions made from c. p. chemical were next studied. (Figure 2, curves 1, 2, 3, and 4) The readings in curves 1 and 2 were made by starting the hydrogen-ion determinations with 0.01 M solutions, while those in curve 3 were obtained by starting with a different electrode at each end of the series of concentrations. Those in curve 4 were made by beginning with the 1.0 M solution. Extremely high apparent acidities were obtained, some of the pH values being less than zero. A logical explanation is that the free sulfur dioxide in these solutions displaces the hydrogen from the electrode and thus creates an abnormal relation between the hydrogen of the electrode and the hydrogen ions of the solutions. This will be mentioned again in connection with Figure 4. This assumption may partly explain the erratic readings obtained, at times, in the determination of hydrogen-ion concentrations in the sodium sulfite solutions. These data, unquestionably, do not represent the true hydrogen-ion concentration of these solutions.

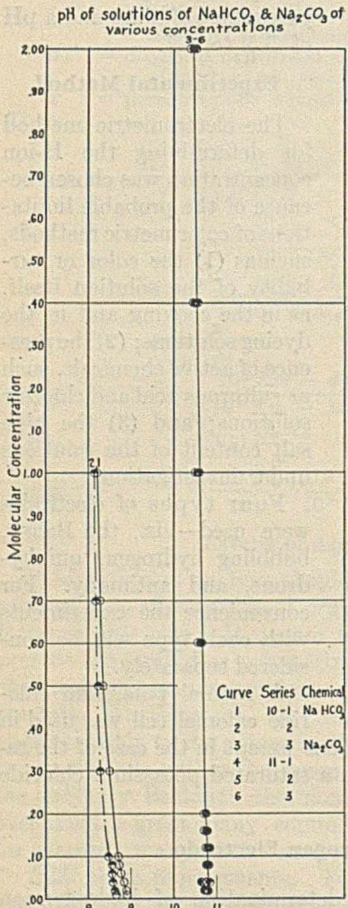

Figure 1

Bubbling Hydrogen Electrode

It was thought that a bubbling hydrogen electrode (of the Hildebrand type), in which a constant flow of hydrogen gas passed the platinum black, might prevent the apparent poisoning effect of hydrogen sulfide and the displacement of hydrogen by the sulfur dioxide. The results obtained by passing sulfur dioxide into solutions of sodium carbonate, sodium acid carbonate, sodium hydroxide, and leach liquor from the mill are shown in Figures 3 and 4.

Series 13-1, Figure 3, represents the results obtained by passing sulfur dioxide into a molar solution of sodium acid carbonate. There is a very rapid change toward the acid side just as soon as the gas is added, which is probably due to the formation of sodium acid sulfite. This was the initial experiment and was run to get some idea of controlling the flow of gas. The control of flow was made by submerging a capillary point 75 mm. beneath the surface of a saturated solution of sulfur dioxide and counting the number of bubbles formed per minute.

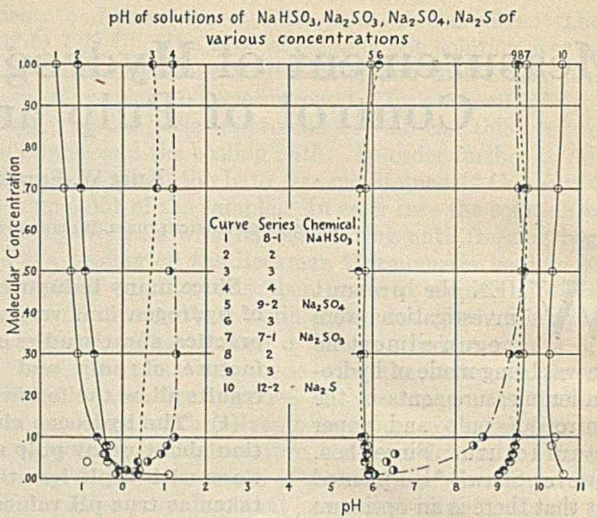

Figure 2

Series 13-2, Figure 3, of a 2 M sodium carbonate solution, shows that the sodium carbonate acts as a buffer, for there is not the rapid change toward acidity that there was in the bicarbonate solution. On account of the high concentration, crystallization occurred and prevented the completion of this experiment.

Series 14-1, Figure 3, represents the reaction during the flow of sulfur dioxide into a 0.5 M sodium carbonate solution. Owing to the low concentration of sodium carbonate the change toward acidity is fast and may again be explained by the formation of sodium acid sulfite. On stopping the flow of sulfur dioxide at the end of 30 minutes a recovery toward the alkaline side is noted, indicating a loss of free

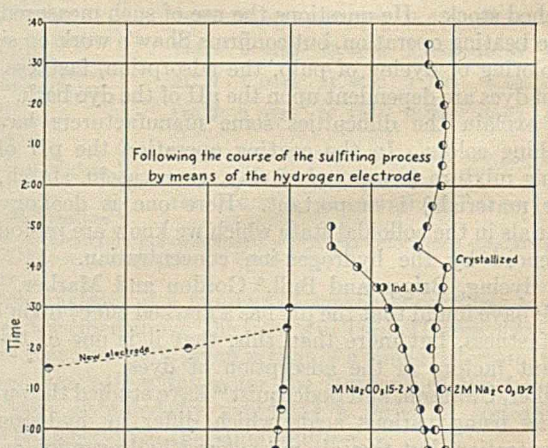

Figure 3

sulfur dioxide from the solution. When a new electrode was inserted after 75 minutes, it agreed with the old after it had attained an equilibrium. An indicator showed a pH of 8.3 when the hydrogen electrode showed 8.0.

Series 15-1, Figure 4, involving a 1 *M* sodium carbonate solution, shows the same buffering action as 15-2 to a pH of 8.3. Curve 15-1, having been carried further, showed a higher acidity with a recovery, shown in curve 14-1, as soon as the flow of sulfur dioxide was stopped.

Series 15-2, Figure 3, with a 1 *M* sodium carbonate solution, shows again the buffer action. An indicator control determination gave a pH of 8.3 when the hydrogen electrode gave a pH of 8.132. This conforms with a like test made in curve 14-1, and noted thereon.

Series 16-1, Figure 4, shows the course of sulfitation of a 1 *M* sodium hydroxide solution. There is a sudden shift toward the acid side as soon as any sodium acid sulfite is formed. Indicators showed higher pH values, probably indicating a displacement of hydrogen from the electrode by the sulfur dioxide, with a consequent abnormal reading.

Series 17-2, Figure 4, of a 1 *M* sodium hydroxide solution which was run under better control of gas flow, shows the same features as the above.

Series 27-1, Figure 4, of a 1 *M* sodium hydroxide solution, shows the same features as 16-1 and 17-2 from the fact that the curves correspond in the main features. It seems possible that the hydrogen electrode might be used for the control of the manufacture of cooking liquors, at least in the neutral sulfite cook, where sulfitation should not be carried beyond neutrality. The fact that the readings produce very smooth curves would indicate that there is an equilibrium between the sulfur dioxide of the solution and that of the electrode. The accuracy seems to be good until after pH 7.0 is passed, or at least until all the sodium ions present have been converted into sodium sulfite and before the probable appearance of free sulfurous acid. Brewster and Raines[5] state that the hydrogen electrode is useless in the presence of free sulfur dioxide and it therefore cannot be employed for the control of sulfitation in the sugar industry.

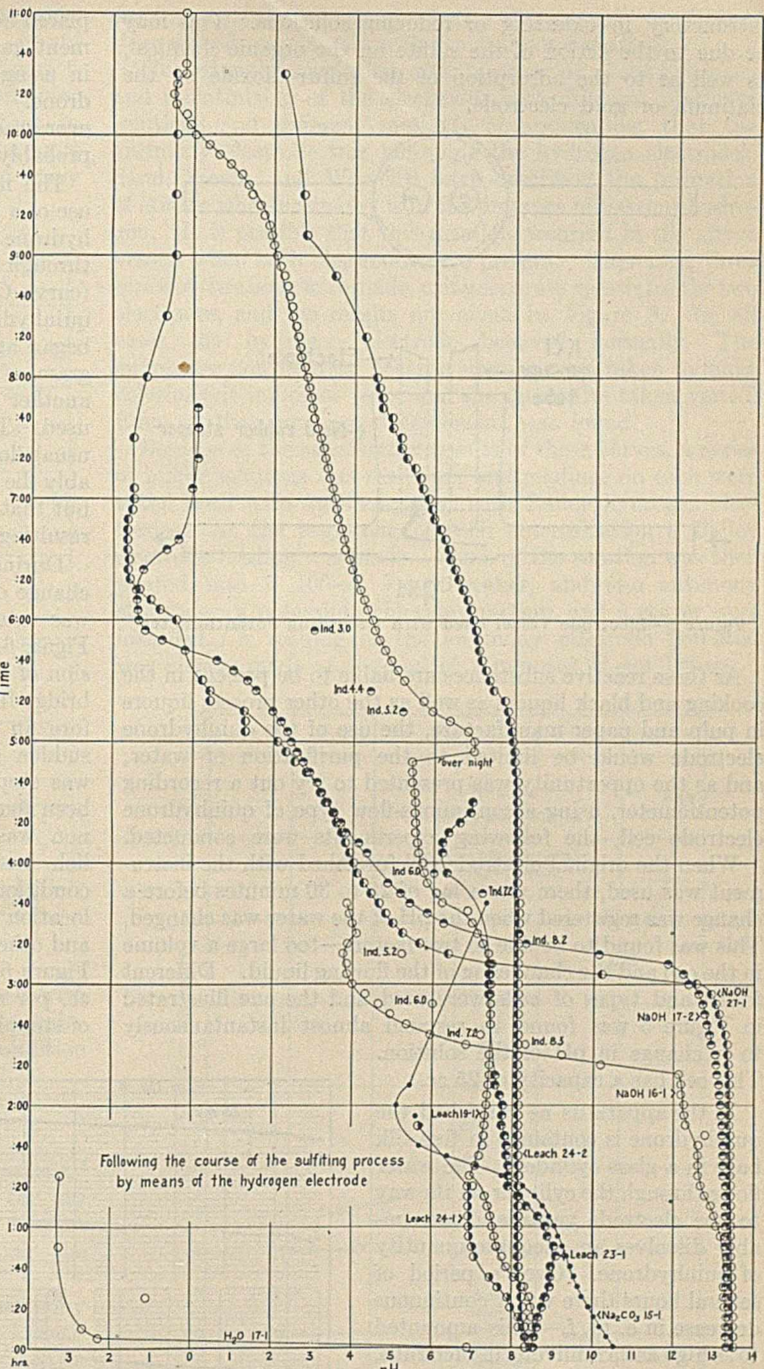

Figure 4

Series 19-1, 23-1, 24-1, and 24-2, Figure 4, show the results obtained when paper-mill leach liquor (diluted one-half) is treated with sulfur dioxide. This liquor is obtained by leaching the crude ash recovered by incinerating the previous spent cooking liquors, and consists largely of sodium carbonate. The color of these solutions did not permit the use of indicators. Since the odor of hydrogen sulfide was noticed during the course of runs 19-1 and 23-1, tests were made during the run of 24-2, and it was found that evolution of the gas began at about pH 8.3 and ended at about pH 7.2. In these experiments the electrodes did not give abnormal readings while hydrogen sulfide was being evolved. This may be due to the continuous flow of hydrogen around the electrode.

Series 17-1, Figure 4, shows the results obtained when distilled water is treated with sulfur dioxide. The same characteristics regarding the possible substitution of hydrogen by sulfur dioxide are indicated, except that it is far more aggravated. pH values of −3.26 were obtained when the quantity of acid present represented only a small fraction of the concentration of H-ion required by this value.

Quinhydrone Electrode

The quinhydrone (benzoquinhydrone) electrode has the advantage of requiring neither a platinized electrode nor gaseous hydrogen; it comes to equilibrium very rapidly, and the bright electrode of platinum or gold is less affected by outside influences than a platinized one. It has one disadvantage—its limited pH range of 0 to 8.0.[1,2,3,9]

In the attempt to use quinhydrone with solutions of sodium sulfite and acid sulfite a constant drift in e. m. f. was observed. This was also noted by Dawson,[9] who states that solutions containing free sulfur dioxide give very erratic results. Others have stated that the quinhydrone electrode is not satisfactory in oxidizing or reducing solutions. This may be due to the action of the sulfite on the organic chemical, as well as to the adsorption of the sulfur dioxide by the platinum or gold electrode.

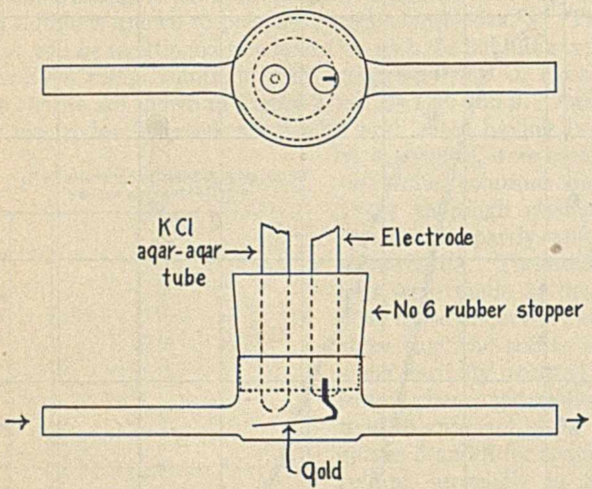

Figure 5—Electrode Vessel Used with Recording Potentiometer

As these reactive substances are liable to be present in the cooking and black liquors as well as the other process liquors in pulp and paper manufacture, the use of the quinhydrone electrode would be limited to the purification of water; and as the opportunity was presented to try out a recording potentiometer, using a continuous-flow type of quinhydrone electrode cell, the following experiments were conducted.

When the original electrode cell furnished with the instrument was used, there was a lag of 25 to 30 minutes before a change was registered when the pH of the water was changed. This was found to be due to two factors—too large a volume in the cell and the channeling of the flowing liquid. Different forms and types of cells were used and the one illustrated in Figure 5 was found to respond almost instantaneously to a change in pH of the solution. This cell has a capacity of 25 cc.

In the apparatus as furnished the quinhydrone is contained in five silk bags in a glass cylinder. The water flows through the cylinder on its way to the electrode vessel and presumably dissolves an adequate quantity of quinhydrone. Over a period of several hours there was a continuous decrease in e. m. f. This amounted to as high as 25 millivolts in such runs. One of these shifts is shown in curve *A*, Figure 6. Apparently the quinhydrone was not properly saturating the solution. A new bag of quinhydrone was added before each run, but in a very short time a coating formed on the surface of the bags, which might prevent proper saturation.

A buffer solution was made from monopotassium phosphate and disodium phosphate in order to have the same pH as the city water, and the above experiments were repeated by passing this buffer solution through the cylinder of bags. Similar results were obtained, as shown in curve *B*, Figure 6. To overcome this decreasing e. m. f. the quinhydrone was placed between layers of glass wool in a tube. This arrangement gave very good results, indicating that the question in using the bags is one of concentration of the quinhydrone. The consumption of quinhydrone in this case, however, was about 2 grams per hour, and its high cost would probably prevent its use in a filtration plant.

The next step was the elimination of the bags and the use of a buffer solution to which were added 2 grams of quinhydrone per 18 liters of solution. When this was passed through the system a similar decrease of e. m. f. was noted (curve *C*, Figure 6). On the addition of 1 gram more of quinhydrone a recovery was noted (curve *D*), but a decrease began again almost immediately. The addition of another gram of quinhydrone had a similar effect (curve *E*). In another case twice the initial quantity of quinhydrone was used. This gave the same initial voltage followed by the usual downward shift. It is therefore concluded that probably the quantity of quinhydrone is not the only explanation, but that there is a constant decomposition of the substance, resulting in the shifts as shown.

During these experiments it was noted that a very sharp change of e. m. f. would occur when the flow of the liquid was interrupted, as noted at *n* in the curve *C* and in *F*, Figure 6. It was thought that this might be due to the diffusion of potassium chloride from the porous cup used as the bridge from the electrode vessel to the calomel cell. Therefore an agar-agar bridge was substituted. Still this same sudden change of potential was obtained when the flow was stopped. So far no explanation for this behavior has been found. As will be mentioned later, the same phenomenon was observed with an antimony electrode. Freundlich has described a flowing potential, but none of the conditions required for its manifestation, such as capillarity, location of electrodes, and hydrostatic pressure, which he and others have specified, are found in this cell. Curve *G*, Figure 6, shows that the change of rate from 100 cc. to 200 cc. per minute flow has no appreciable effect, but the effect of stopping the flow of solution is illustrated again here.

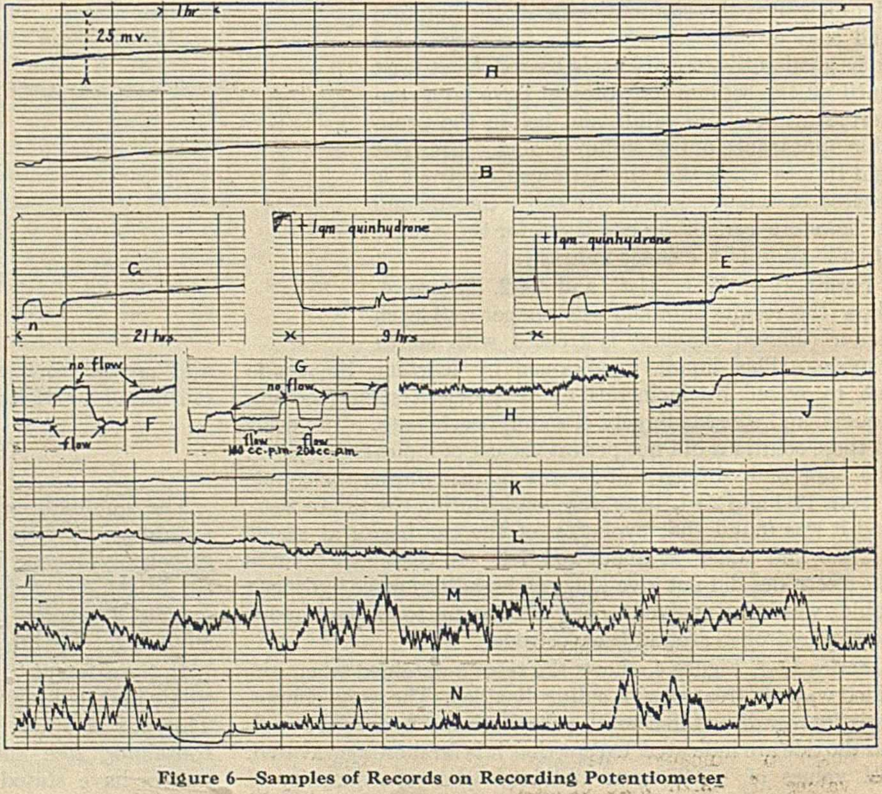

Figure 6—Samples of Records on Recording Potentiometer

On the other hand, excellent results were at times secured for short intervals with the quinhydrone in bags, charts usually of the types shown in curves *H* and *J* in Figure 6 being obtained. No explanation of the irregular behavior has been found. The water was apparently constant in its pH value, and the various parts of the apparatus have been gone over many times in the attempt to find stray currents and other causes of trouble.

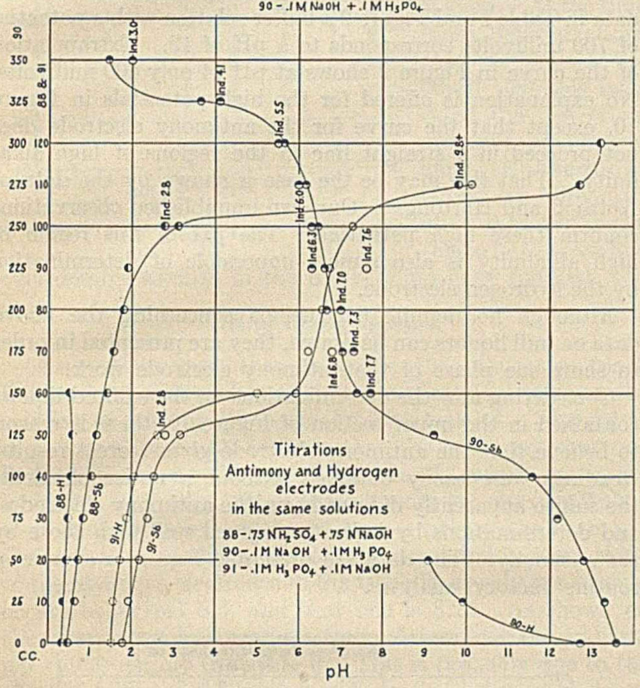

Figure 7

It is possible that better results would be obtained with more acid water, as it is generally considered that the quinhydrone electrode works better under a more acid condition than that of the water used, which was 6.8 to 7.2.

Stick Antimony Electrodes

Uhl and Kestranek[25] in 1923, and Kolthoff and Hartong[15] in 1925, published the results of investigations on the use of antimony electrodes in measuring hydrogen-ion concentration. No hydrogen is required, thus simplifying the electrometric method.

An extensive series of trials of various types of antimony electrodes was carried out. The ordinary pure stick antimony proved to be the best type. Since this was used in securing the fundamental data for converting the antimony potentials into pH values, and since these conversions are required in the discussion of all the other types, the experiments with this stick antimony are presented first, although most of the other types were actually used first.

These sticks were about 7 mm. in diameter and about 40 to 50 mm. long. They were smoothed with a file and then with emery, until a fairly smooth surface was secured.

The attempt was made to titrate with the antimony and bubbling hydrogen electrodes in the same vessel. The data are in Figure 7. In Series 88, 100 cc. of 0.75 *M* sulfuric acid were titrated with 0.75 *M* sodium hydroxide. In Series 90, 100 cc. of 0.1 *M* sodium hydroxide were titrated with 0.1 *M* phosphoric acid. In Series 91, 50 cc. of 0.1 *M* phosphoric acid were titrated with 0.1 *M* sodium hydroxide. The antimony potentials were converted to pH value by the data in Table I. In these titrations it was soon found impossible to get satisfactory readings with the hydrogen electrode, since no equilibrium was reached. Colorimetric determinations agreed very closely with the antimony readings.

This led to the conclusion, after purification of the hydrogen and replatinizing of the electrodes with different platinum solutions and different methods of application, that the antimony electrode was poisoning the hydrogen electrodes. Sand, Weeks, and Worrell[21] have described the formation of stibine when antimony is in the presence of nascent hydrogen. It is possible that this reaction occurred in the above vessels when both electrodes were present. Therefore, three series of titrations were made, using separate vessels for the two electrodes, and the results are given in Figure 8. In all cases the hydrogen electrode behaved normally. The curves are not identical because samples were taken to make colorimetric indicator tests, and the quantities taken varied. Even at that, very good agreement was found.

Because of the satisfactory results of these curves, a series of buffer solutions was made up, and readings on each were taken both with antimony and with Bailey hydrogen electrodes. At the beginning of each determination a Bailey electrode reading was made. Some of the solution was then poured into a 100-cc. Pyrex beaker, and two antimony electrodes, a potassium chloride junction, and a stirrer were installed. A reading of the antimony electrode potential was always made at the end of 2 minutes, if not before.

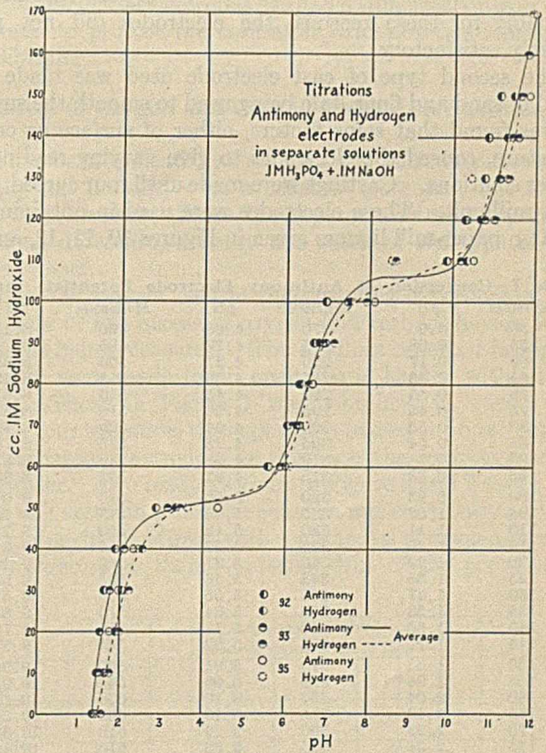

Figure 8

This method was used in determining the values given in Figure 9. This chart was used in compiling the data contained in Table I, which then became the reference table for converting all antimony electrode potentials into pH values.

The antimony curve in Figure 9 corresponds to the following equation:

$$E = 0.050 + 0.054 \text{ pH, at } 25^\circ \text{ C.}$$

In comparison with this, the equations offered by Kolthoff and Hartong[15] might be given:

$$E = 0.0415 + 0.0485 \text{ pH, at } 14^\circ \text{ C. (from pH 1 to 5)}$$
$$E = 0.009 + 0.0536 \text{ pH, at } 14^\circ \text{ C. (above pH 9)}$$

After plotting the data of these workers, the writers fail to see how they obtain the number 0.009 since any probable lines drawn among their points cut the axis at about 40 to 50 millivolts, and not at 9. Two lines are also required for their data, whereas in the present work one sufficed, which corresponds to the theory as discussed by Kolthoff and Hartong. These investigators used ten different buffer substances, while the present data were secured by means of readings on a series of solutions prepared from hydrochloric acid, phosphoric acid, and sodium hydroxide.

Cast Antimony Electrodes

When it was decided to try out the antimony electrode on some paper-mill liquors, no stick antimony as described above was available. Therefore an electrode was made by melting lump metal and pouring it into a mold made by boring a hole in a piece of charcoal. This electrode had a rough surface, contained many small pits, and probably was not of uniform crystal formation. Probably for these reasons, the electrodes did not prove entirely satisfactory.

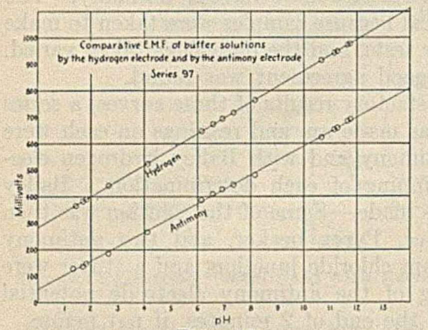

Figure 9

The second type of cast electrode used was made in a mold of sand and flour, talc being used to smooth the surface. It was found that some factors, either of surface or crystal structure, caused the electrodes to give varying readings on buffer solutions. Castings were made until four agreed within 1 millivolt. These electrodes were used in obtaining the data on paper-mill liquors given in Figures 10, 11, 12, and 13.

Table I—Conversion of Antimony Electrode Potentials into pH

Millivolts	*pH*	*Millivolts*	*pH*	*Millivolts*	*pH*
50	0.0	270	4.08	490	8.18
55	0.08	275	4.17	495	8.23
60	0.17	280	4.27	500	8.32
65	0.26	285	4.36	505	8.42
70	0.36	290	4.45	510	8.51
75	0.45	295	4.55	515	8.60
80	0.55	300	4.64	520	8.69
85	0.64	305	4.73	525	8.78
90	0.74	310	4.82	530	8.87
95	0.83	315	4.91	535	8.95
100	0.93	320	5.00	540	9.04
105	1.02	325	5.09	545	9.13
110	1.11	330	5.18	550	9.22
115	1.20	335	5.27	555	9.31
120	1.29	340	5.37	560	9.40
125	1.38	345	5.46	565	9.50
130	1.47	350	5.55	570	9.59
135	1.56	355	5.64	575	9.68
140	1.66	360	5.73	580	9.78
145	1.75	365	5.82	585	9.87
150	1.85	370	5.91	590	9.96
155	1.94	375	6.00	595	10.05
160	2.04	380	6.10	600	10.15
165	2.13	385	6.19	605	10.24
170	2.22	390	6.29	610	10.34
175	2.31	395	6.38	615	10.44
180	2.40	400	6.48	620	10.53
185	2.50	405	6.57	625	10.62
190	2.59	410	6.67	630	10.72
195	2.68	415	6.76	635	10.81
200	2.78	420	6.86	640	10.90
205	2.87	425	6.95	645	10.99
210	2.97	430	7.04	650	11.08
215	3.06	435	7.13	655	11.18
220	3.15	440	7.21	660	11.27
225	3.24	445	7.30	665	11.36
230	3.33	450	7.40	670	11.45
235	3.42	455	7.49	675	11.54
240	3.51	460	7.58	680	11.63
245	3.61	465	7.67	685	11.72
250	3.70	470	7.77	690	11.81
255	3.79	475	7.86	695	11.90
260	3.89	480	7.96	700	12.00
265	3.98	485	8.05		

A series of observations was made on paper-mill liquors. The first step in preparing the cooking liquors is the leaching of the crude ash. This "leach liquor" is largely sodium carbonate, but contains also some sulfate, sulfite, thiosulfate, and sodium hydroxide. It is causticized with calcium hydroxide and the product is then called "causticized liquor." This is diluted to the proper concentration and becomes the "caustic cooking liquor." The lower section of Figure 10 contains the determinations of these liquors with the cast antimony electrodes.

The conspicuous fact in these data is the very high potentials obtained—1000 millivolts in many solutions. In the data in Table I and Figure 9 a buffer solution with a potential of 700 millivolts corresponds to a pH of 12. Extrapolation of the curve in Figure 9 shows at pH 14 only 800 millivolts. No explanation is offered for the high potentials in Figure 10, except that the curve for the antimony electrode does not proceed in a straight line in the regions of high alkalinity. That this may be the case is shown by the data of Kolthoff and Hartong.[15] Our own unpublished observations confirm these high potentials. The pH in this region of high alkalinity is also almost impossible of determination by the hydrogen electrode.

Although no definite conclusions concerning the above data on mill liquors can be drawn, they are presented in order to show one phase of the antimony electrode work.

Considering now the determinations on the sulfited liquors contained in the upper section of Figure 10, there is reason to believe that the antimony electrode gives correct results. Readings were easily obtained without a noticeable drift; the sulfite apparently did not harm the antimony electrodes; and determinations by indicators agreed well with those by the antimony. The data are presented here as a sample of routine factory analyses.

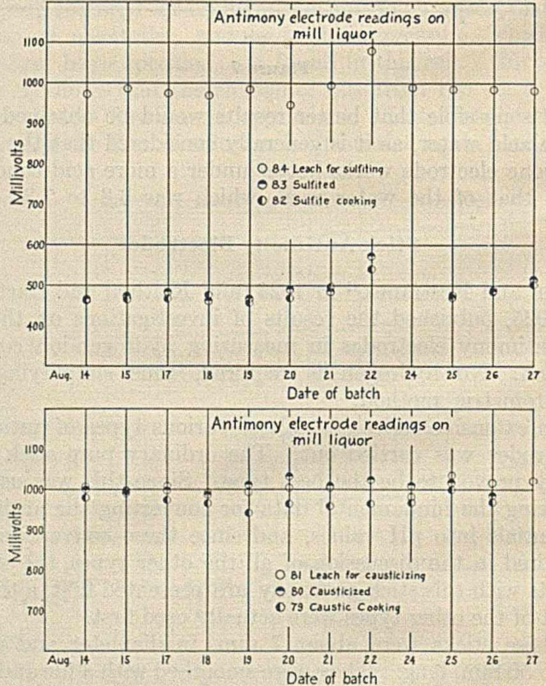

Figure 10

Another series was run on a mill caustic solution during the process of sulfiting. Analyses for sodium sulfite were made in parallel. The data are presented in Figure 11, and indicate that the electrode could be used to follow the sulfiting process.

Figure 12 shows the application of the antimony electrode as a control method in beater operation. Series 86-1 and 86-2 are on book-paper stock. Since the readings taken after the addition of size do not change, the amount of acidity present must have been more than sufficient to neutralize the alkali added in the size. Series 87-1 and 87-2 represent envelope stock. In this case the addition of the stock (fiber) and the rosin size decreased the acidity, but it was increased again by the addition of alum. At the time these determinations were made it was believed that this indicated the use of an excessive amount of alum. Subsequent work by the mill chemists has shown this to be the case and considerable savings in the use of alum have resulted.

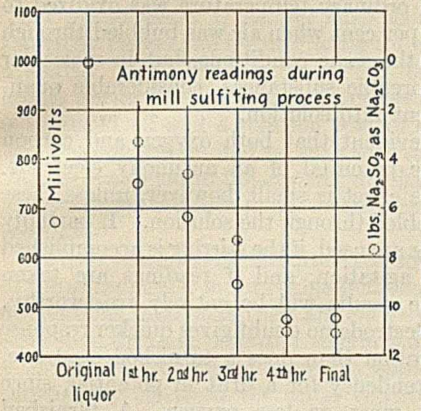

Figure 11

pH of Black Liquors

Observations were then taken on 128 batches of black liquors from mill cooks—that is, the spent liquors from the cooking of pulp by the neutral sulfite method. The determinations (Figure 13) indicate that the antimony electrode is not affected by the sulfur compounds present as is the hydrogen electrode. Since these liquors are always alkaline to phenolphthalein, and hence have a pH greater than 8.3, the antimony readings correspond more closely than those of the hydrogen electrodes to the true pH, as only one reading occurs below pH 8.3, and that one is 8.25. As shown on the chart, the hydrogen-electrode determinations indicate pH values mainly from 6 to 8. This is probably due to the effect of sulfite on the hydrogen electrode, as discussed above. The data for the original cooking liquors corresponding to some of these black liquors are taken from Figure 10 and are indicated in the chart by crosses.

There is also considerable variation from day to day in the alkalinity of both the fresh cooking liquor and the spent liquor. Since it is reasonable to suppose that there is a certain optimum alkalinity for the cooking of pulp, it is believed that the antimony electrode could well be used to find this optimum, by means of experimental cooks, and then that the electrode could be used as a mill control method in preparing the cooking liquors.

Faults in the Cast Electrode

The data on the pH of the black liquor, caustic liquor, and sulfited liquors of the mill, besides those shown in the titration curves and the curves on buffer solutions, all seemed to warrant further consideration of the factors which might influence the accuracy of the antimony electrode.

The first factor to be determined was whether or not the surface and crystal structure of the antimony electrode might affect its accuracy. This was considered a possible explanation of the difficulty mentioned above in securing cast electrodes which would give the same potentials.

Those electrodes which appeared erratic showed, when broken up, great heterogeneity in crystal structure. As the size of the crystals varied, it was thought that this might cause the observed drifts in potential. Furthermore, an irregular surface might act as an adsorption medium, so that, when an electrode was changed from an acid to an alkaline solution, with intermediate washing with distilled water, a drift would occur towards the alkaline side for a considerable period of time.

Castings were therefore made, the object being to have as even crystallization as possible, and also a smooth surface. The success in this varied, owing especially to the formation of small pits or blow holes. The best castings were obtained by pouring the antimony into a Pyrex tube, sealed at one end and imbedded in a heated sand bath. Others were cast by heating the tubes directly.

But even these electrodes would give slight drifts which, as a rule, were toward a lower e. m. f., indicating that the castings were not yet perfect.

Plated Antimony Electrodes

The next step was to examine the possibilities of electroplating antimony, for by this process even structure and perfect surfaces might be expected. Various methods were tried out, such as those given by Blum and Hogaboom,[4] Chaney,[7] Classen and Hall,[8] Foerster,[10] Langbein and Branut,[16] and Watt and Phillips.[26]

Platings on platinum, gold, carbon, copper, brass, and various alloys were tried. In general the results were not very satisfactory, especially where the plating bath contained sulfides or chlorides, as occlusion of these salts in the plated metal was noted and the platings peeled. The most common fault was the thinness of the plating. When thicker ones were attempted, sluffing and peeling occurred. An oxidized coating forms on all electrodes, and up to the present none of the plated electrodes has had a sufficiently heavy layer of metal to protect the core after oxidation has reached an equilibrium.

Effect of Oxygen and Carbon Dioxide on Antimony

It has been indicated above that the antimony electrodes usually did not arrive at a constant potential, but tended to drift somewhat. Since the type of electrode apparently made no difference, a study was made of the type of electrode vessel.

In all the vessels used in the foregoing experiments there was more or less access of oxygen and carbon dioxide to the solutions being measured. The readings reported in Figures 10 to 13 were made in an open Pyrex beaker without agitation. Those in Figure 7 were obtained in vessels containing four tubulures through which passed the bubbling and the antimony electrodes; in this case the hydrogen served as agitator. The readings given in Figure 8 and Table I were made in a vessel in which the solution was constantly agitated by a motor-driven stirrer, with some access of oxygen possible. In all these cases there was some drift of the potential.

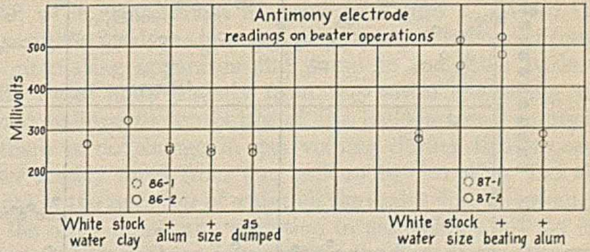

Figure 12

Kolthoff and Hartong[15] claimed that in neutralization reactions with the antimony electrode there was no difference between agitating with a mechanical stirrer or with an inert gas such as hydrogen and nitrogen. Kolthoff and Furman[14] stated that these gases should be employed, but gave no reason. Uhl and Kestranek[25] found that carbon dioxide affected results adversely; they therefore washed the air used in agitation.

Apparatus as described by Uhl and Kestranek was therefore set up, the solution being stirred with washed air. The same tendency to drift was observed, however. The same apparatus was used to determine the temperature effect. Determinations were made which showed a decrease in e. m. f. with decrease in temperature, but it was found on plotting the results that the curves varied in slope, which could not be explained by any temperature factor. Nevertheless, the electrode chamber was placed in a constant-temperature water bath. A series of determinations was then made, using, as a means of agitation, the flow of the solution to be tested. Much better results were obtained, although very small drifts were still noticed, a change of 2 millivolts occurring in runs of from 1 to 4 hours' duration in some cases. There were indications that the factor influencing the drifts had not yet been found.

As Uhl and Kestranek had stated that carbon dioxide affected the results adversely, this gas was passed into the solution in the vessels mentioned above. In alkaline solution and in water a drop in potential occurred, as was to be expected. But in the case of acid phosphate solutions an increased potential of 25 millivolts was noted. This is an anomalous behavior, and cannot be explained by the usual acid properties of carbon dioxide in solution. No reasonable explanation has yet been found.

Table II—Effect of Oxygen on Potentials of Various Solutions

TIME	$NaOH^a$	$H_3PO_4{}^a$	NaOH AND $H_3PO_4{}^a$	KF^b	KI^b	KCl^b	KBr^b	$Al_2(SO_4)_3{}^a$
Min.	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*	*Volt*
00	0.821	0.145	0.261	0.438	0.397	0.392	0.327	0.232
15	0.746	0.125	0.246	0.409	0.354	0.347	0.304	0.189
30	0.754	0.122	0.241	0.411	0.353	0.350	0.297	0.189
45	0.751	0.121	0.236	0.413	0.350	0.354	0.294	0.189
60	0.749	0.120	0.233	0.413	0.349	0.353	0.292	0.189

[a] 0.1 *M* solution. [b] 0.05 *M* solution.

The next experiment was the passing of oxygen into the electrode chambers to provide agitation. The results given in Table II were obtained in numerous trials made on various solutions. The figures given indicate successive readings on the same solutions, with no factor introduced other than the bubbling of oxygen.

It is seen that oxygen or air will affect the e. m. f. of an antimony electrode, especially during the first few minutes of agitation. Milbauer and Slemr[17] found that powdered antimony in water of ordinary temperature was oxidized to the extent of about 8 per cent when air was bubbled through the mixture. Under the same conditions, but in molecular solutions of various organic substances, considerable quantities of antimony went into solution.

The conclusion is evident that both oxygen and carbon dioxide can affect the potential of an antimony electrode. The magnitude of the effect is small, however, unless these gases are actually bubbled through the solution. If partially closed electrode vessels are used, if the stirring is accomplished without unnecessary agitation, and if readings are taken within 2 minutes, the results will be entirely trustworthy.

Although a bright electrode no doubt gives quicker response when placed in a solution than does a tarnished electrode, there is much more tendency for a drift in potential, since all solutions contain more or less oxygen. A tarnished electrode is much more stable and dependable, and is advocated for all purposes.

Experiments with Recording Potentiometer

As mentioned during the discussion of the quinhydrone electrode, the antimony electrode was also tried out on the recording potentiometer. The only change made in the cell as illustrated in Figure 5 is that the gold electrode was replaced by an antimony stick electrode. The results are given in Figure 6. Curve *K* shows very consistent and satisfactory results with the potentiometer on phosphate buffer solution. Curves *L*, *M*, and *N* were obtained while city water was running through the cell at a rate of 100 cc. per minute.

Out of many yards of such records obtained, the four sections reproduced in the figure were chosen because they represent different types of records obtained. Only the first three will be discussed. In the left half of *L* we have a wavy curve with only slight total variations. In the middle is a period of about 3 hours during which the record is essentially a ruled straight line. This is followed by the wavy type again. In *M* there is a wavy type with relatively larger total fluctuations. *M* and *N* are continuous. Beginning at the right end of *M* and continuing at intervals

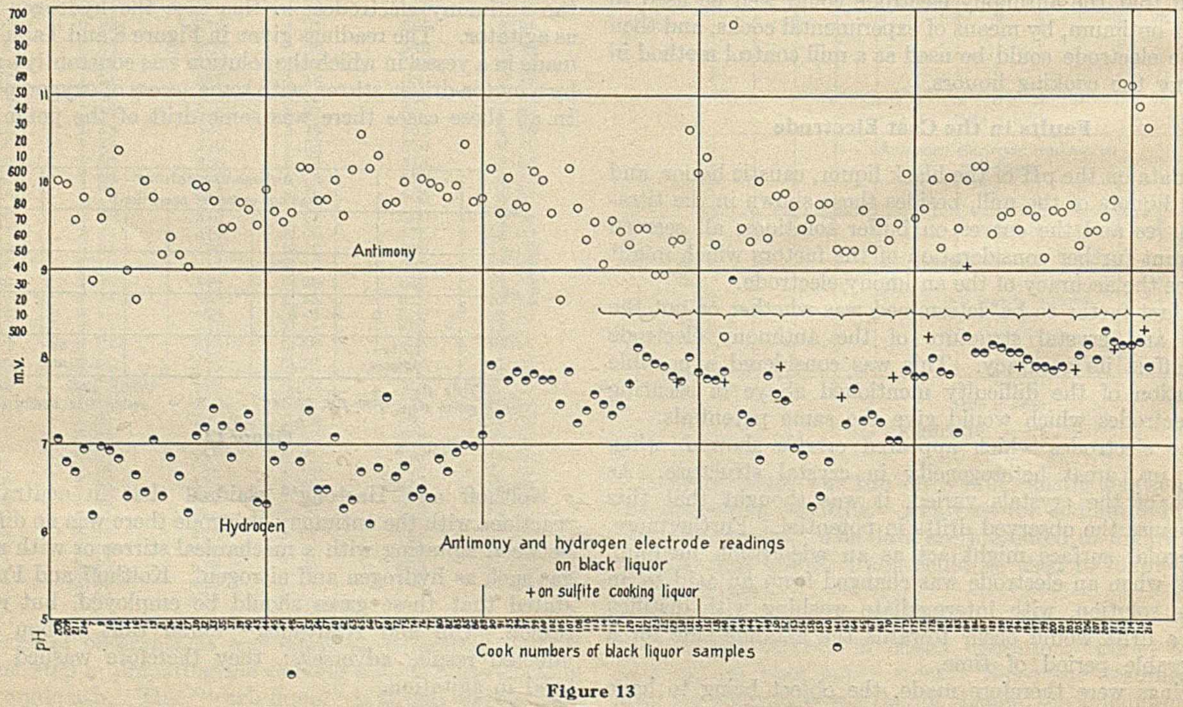

Figure 13

throughout *N*, the wavy record apparently hits a "dead line," beyond which it cannot go, except for short periods. This phenomenon is as yet unexplained. On the charts shown by Parker and Greer,[19] using the same type of recorder, a similar "dead line" is noted, but they explain that this occurs during the one-minute intervals in which the recorder is switched off and a solution control device is switched on. The present writers had no such interruption. If an outside voltage is applied to the system, the dead line will be crossed immediately, indicating no mechanical interference in the recorder.

On comparing the quinhydrone records in general with those of the antimony, it is noticeable that the latter give no greater fluctuations, and that they are entirely free from the long-continued drifts in potential seen in the quinhydrone records. From this standpoint the antimony appears to be a much more satisfactory electrode for water control, although it is not known whether the fluctuations are actually due to changes in the pH of the water. Because of the unbuffered nature of the water it is almost impossible to check the pH's with indicators or with a hydrogen electrode. It is quite probable that this lack of buffers is responsible for the fluctuations seen in the antimony records.

Antimony in Strong Alkali

It was indicated above that in the case of the leach and other mill liquors potentials of 1000 millivolts were obtained, although values of such magnitude were inconsistent with the data shown in Table I and Figure 9 on buffer solutions. Since this casts doubt on the usefulness of this electrode in high OH-ion concentrations, a series of readings was attempted in solutions of sodium hydroxide up to 5 *M*. Bubbling hydrogen electrodes were tried on the same solution but in different vessels. Neither electrode would give readings which were at all reliable. Rapid shifts in the potential and disagreements between electrodes characterized both types, and unexpectedly low potentials were the rule with the hydrogen electrodes. The antimony gave the high values of from 800 to 1000 millivolts.

Grube and Schweigardt[13] have reported a study of the properties of antimony in highly alkaline solutions. In potassium hydroxide solutions of from 3 to 15 *M* they detected at least three different reactions, each of which would give rise to a potential between metallic antimony and the antimony compounds in the solution. This no doubt explains the high potentials found with the antimony electrodes in strongly alkaline solutions. The writers believe that a pH of 12 is about the upper limit for the antimony electrode.

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Apparatus for Storing and Circulating Gases[1,2]

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The study of gas reactions often requires equipment for circulating and storing gases. The weight and expense of mercury makes this liquid objectionable as a containing liquid when volumes of more than a few hundred cubic centimeters are to be used. The apparatus described herein, which uses only small volumes of mercury, has proved itself useful where contact with rubber is permissible and the contact does not have to be prolonged more than a few hours.

The gas-storage system consists of two rubber basket-ball balloons, each surrounded by water and contained in a large inverted bottle. The gas balloons are connected with each other through the pump and gas-circulating system, and the water bottles are connected with each other and with a reservoir of water carried on a small platform scale. The arrangement is shown in Figure 1. When this apparatus is used, gas is transferred from one balloon through the circulating apparatus and pump to the other balloon, while water flows directly from the bottle containing the second balloon to the bottle of the balloon being emptied. If there is no change in gas volume during this process, water merely flows from one balloon to the other and the weight of the reservoir of water on the scales does not change. On the other hand, any variation in gas volume will be detected at once without interrupting the flow of gas, through the change in weight of the water reservoir. The corrected volume of gas is computed from the weight of water and the temperature and barometric pressure. The error in reading a volume of 1 liter should not be over ±0.3 per cent. The connections between the balloons and the pump are detailed in Figure 2. Gas from the circulating system enters through the three-way cock, *A*, and passes to either balloon 1 or 2. Gas from the other balloon passes to the inlet side of the pump through the three-way cock, *B*. A by-press, not shown in the drawing, permits the gas to be

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[1] Presented before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

[2] This paper forms part of the dissertation of Frank W. Hightower submitted in partial fulfilment of the requirements for the Ph.D. degree at the University of Michigan.

transferred from one balloon to another. Fused glass connections are not needed. If glass tubes are cut so that plane surfaces will be in close contact, a joint with good rubber tubing may be made gas-tight by wiring the rubber tube and then smearing it with liquid glue, which is allowed to dry in the air until it loses its first stickiness and is then brushed with molten paraffin.

A general diagram of the whole equipment as applied to a study of the synthesis of methane from blue water gas is given in Figure 3. When the first balloon was empty the gas flow was interrupted by stopping the pump; measurements of gas volume in the system were then taken and samples withdrawn for analysis. Where recirculation of the gases was desired, the positions of the two balloons in the order of flow could be exchanged in a few seconds by changing cocks and without interrupting the circulation of gas. The change was usually made at the instant the manometer of one balloon showed it to be empty.

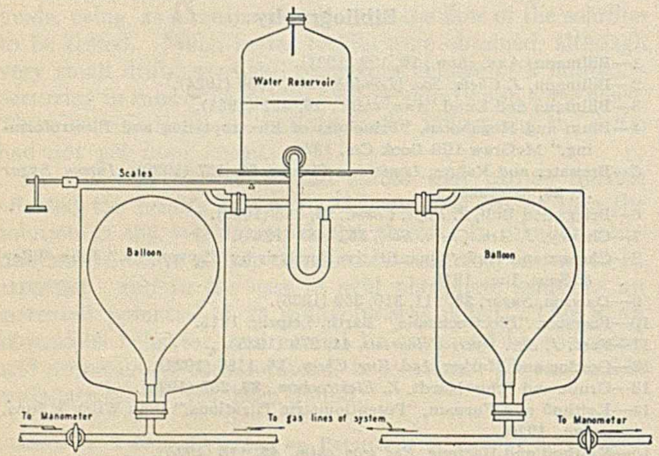

Figure 1—General Arrangement of Balloons and Scales

The gas-circulation pump is based upon the unit described by Chatterji and Finch,[3] who used a mercury piston actuated by a direct-driven plunger. The apparatus shown in Figure 4 utilized a standard bicycle pump to compress air whose pulsations actuated the mercury piston of the gas-circulation pump. The pump was connected by rubber tubing to the open side of the U-tube which contained the mercury piston. The plunger shaft was fitted with a piston head of two soft leather disks slightly larger than the inner cross section of the pump tube, and so placed as to act as a packing on both the suction and compression strokes. Positive seal at the piston head in the pump was insured by wetting the leather disks with a little olive oil at intervals of several weeks. One end of this rod was screwed into the end of the hollow shaft, forming a rigid extension of the shaft, the other end was fitted with a pin at right angles to its length. A reduction gear, driven by a motor and eccentrically connected, operated the piston. A series of holes at intervals along one radius of the reduction-gear wheel, into which the pin on the shaft fitted, allowed the stroke of the piston to be varied from 1 inch to 7 inches (2.5 to 17.5 cm.). With the shortest stroke a volume of about 8 liters per hour was pumped. The maximum volume which could be pumped without throwing mercury out of the tube was about 60 liters per hour with this particular equipment, which had a mercury piston slightly less in diameter than the piston of the pump.

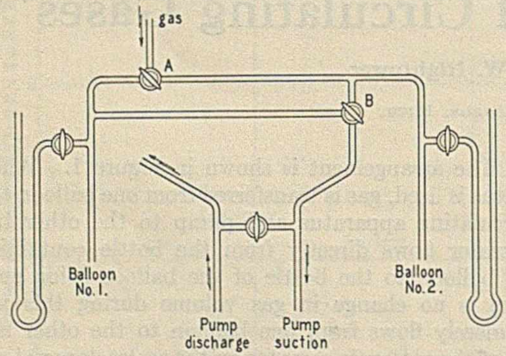

Figure 2—Detail of Connections in Gas-Circulation Apparatus

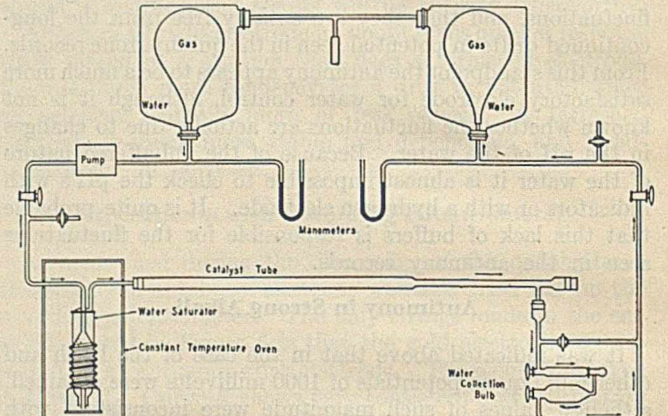

Figure 3—Apparatus as Used for Synthesis of Methane

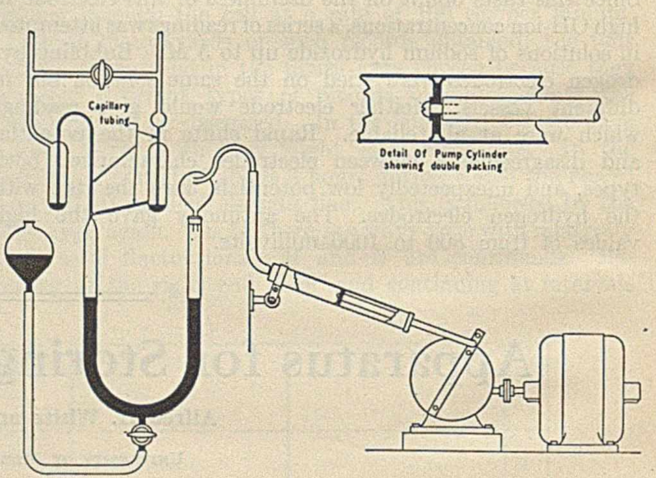

Figure 4—Details of Circulation Pump with Mercury Piston

The pump may be mounted where convenient and connected by rubber tubing to the U-tube containing the mercury piston. On the compression stroke of the pump the mercury is depressed in the right-hand arm and raised in the left-hand arm of the U, compressing the gas above it. The compressed gas has two paths open to it, through the left-hand and right-hand traps. The outlet to the right-hand trap is, however, sealed by the mercury in the bottom, which is forced back into the capillary inlet tube. The gas therefore must bubble through the shallow mercury seal of the left-hand trap. On the suction stroke it is the left-hand trap which is sealed while the gas flows with relatively little resistance into the pump chamber through the right-hand trap. The pump is effective for heads of less than 50 mm. of mercury and might readily be designed to work against higher pressures.

The only material error which may arise from the use of this equipment comes from solubility of the gases in the rubber balloons or from diffusion through the rubber. A

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[3] *J. Chem. Soc. (London)*, **127**, 2464 (1925).

gas mixture which initially contained 25.8 per cent carbon dioxide contained only 24.8 per cent after 12 hours and 23.7 per cent after 22 hours. After the water in the bottle surrounding the balloon had come into equilibrium with the gas content by standing 113 hours, further standing for 200 hours failed to show any measurable change in volume. Carbon dioxide diffused through rubber about eight times as fast as any of the other gases tested. Hydrogen, methane, and carbon monoxide diffused at the rate of about 1 per cent a day.

Elimination of Antimony in the Refining of Arsenic Trioxide[1]

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ARSENIC trioxide is recovered principally as a by-product of the smelting of pyrite and sulfide ores of nonferrous metals, most of which contain arsenic. The flue dusts usually contain from 15 to 30 per cent arsenic, largely as arsenic trioxide. "White arsenic," which is 99 per cent trioxide, is produced from this material in two stages. In the first stage the arsenical dust is roasted and the arsenic trioxide volatilizes and is condensed and collected in flues as black dust. This black dust contains from 85 to 97 per cent arsenic trioxide. White arsenic is separated from black dust in one operation if the volatile impurities are not present in excessive amount by sublimation in a coke- or oil-fired reverberatory furnace. The volatilized portion passes into a series of settling chambers or kitchens, where it condenses. When these kitchens become full, they are sampled and the condensates produced, containing the highest quality of arsenic trioxide, are so mixed as to obtain the largest possible yield of 99 per cent arsenic trioxide. The lower grade material is resublimed.

The black dusts, which cannot be refined effectively in one operation, usually contain antimony, which is probably the most difficult impurity to eliminate in the refining process. About half the antimony volatilizes in the refining furnace and condenses with the arsenic trioxide. Under these conditions it is not possible to refine black dust of high antimony content in one operation and at the same time secure a high recovery of white arsenic. Under normal conditions when the antimony content of the black dust is under 1.5 per cent, about 75 per cent of the arsenic charged into the refining furnace is recovered as white arsenic. As the antimony content of the black dust increases above this figure, the yield of white arsenic is correspondingly decreased and the yield of lower grade arsenic trioxide, which must be recharged to the refining furnace, increases. The object of this investigation was to discover a method of treating black dust or by-products, relatively high in antimony, to make possible a high recovery of white arsenic in one refining operation.

Preliminary Work

Experiments undertaken to discover a method of preventing the volatilization of antimony from the refining furnace charge by forming compounds of antimony less volatile than the trioxide met with little success. Efforts were then directed toward the separation of antimony oxide from arsenic trioxide while they were in the vapor phase.

At its melting point, 251° C., arsenic trioxide[2] has a vapor pressure of 11 mm., which corresponds to a content of 16 pounds in 1000 cubic feet of saturated vapor. On extrapolating the data of Welch and Duschak to 550° C. it is apparent that at this temperature 1000 cubic feet of saturated vapor should contain 325 pounds of arsenic trioxide. No data were found on the vapor pressure of antimony trioxide. However, when it is heated slowly in the air within these temperature limits, it is oxidized to a higher oxide, little if any material is volatilized, and an increase in weight is obtained. If the antimony trioxide is mixed with arsenic trioxide in the ratio found in black dust and the mixture heated as above, all of the antimony may be volatilized.

The higher oxides of antimony may be present in black dust, but they are usually considered to be much less volatile than the trioxide. The material used in these experiments contained so small a quantity as to be negligible and none was detected in any of the volatilized products.

It was thought that by passing the vapors of the oxides through a heated tube, the temperature of which was such that the vapor pressure of arsenic trioxide would be high enough to prevent its condensation, antimony trioxide could be condensed and a separation could be obtained.

Procedure—Two electric tube furnaces were placed end to end and a 2.5-cm. (1-inch) Pyrex glass tube was placed in them so that it extended 15 or 20 cm. (6 or 8 inches) beyond the outside ends of the furnaces. The temperatures of the furnaces were maintained at 500° C. and 400° C., respectively. The end of the glass tube projecting from the cooler furnace was connected to the vacuum line. The other end of the tube was fitted with a loose plug of asbestos. A porcelain boat filled with black dust which contained 6 per cent antimony was placed in the hottest section of the tube, the plug was inserted, and the suction was so regulated that just enough air was passing through the tube to carry the fumes from the boat into the cooler section of the tube. As the volatilization progressed it seemed apparent that all the volatilized material was condensing in large crystals in that portion of the tube just beyond the cooler furnace. When the fumes ceased to come from the boat, the furnaces were cooled. In the section in which none of the fumes had apparently condensed, a thin, transparent deposit had formed. Both the vitreous deposit and the crystals were removed for analysis. The vitreous deposit was found to contain 25 per cent antimony. The crystals were arsenic trioxide, containing only 0.25 per cent antimony.

In this experiment there were three factors that might be varied—the temperature of volatilization, the temperature of formation of the vitreous deposit, and the amount of air passed through the system. In order to determine the effect of each of these variables and gather quantitative data, the first series of experiments was run.

Small-Scale Experiments

Apparatus—The volatilization apparatus (Figure 1) consisted of a 20-cm. (8-inch) section of 2.5-cm. (1-inch) Pyrex

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[1] Received August 25, 1927.

[2] Welch and Duschak, *Bur. Mines, Tech. Paper* 81 (1915).

glass tubing constricted at one end to which was fused a 60-cm. (24-inch) section of 8-mm. ($^5/_{16}$-inch) glass tubing to serve as a condensing flue or tube. The open end of the large glass tube was closed with an asbestos plug, which was traversed by tubes for the admission of air and a thermocouple. An aspirating device for drawing air through the apparatus and measuring it was connected to the open end of the small tube. The large section of Pyrex tubing constituted the volatilization chamber and was heated by an electric tube furnace as in the previous experiment. The 12-inch section of the small tube next to the volatilization chamber was heated by a second electric tube furnace set end to end with the first one. The black dust was placed in a porcelain boat in the volatilization chamber and its temperature was measured by means of a thermocouple, the junction of which was immediately above the boat. The junction of a second thermocouple was placed just below the condensing tube about midway of the second electric furnace.

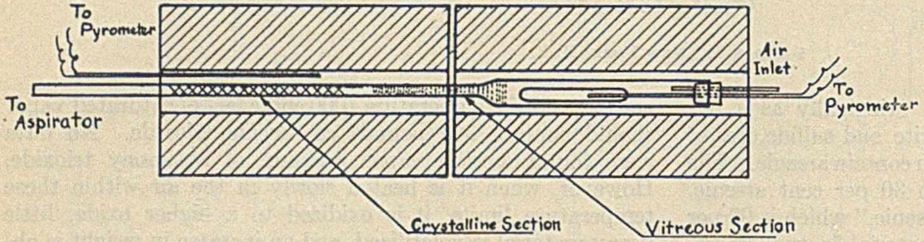


Figure 1—Volatilization Apparatus

Procedure—The volatilization and condensing tubes were first brought to the desired temperatures. The aspirating device was attached to the end of the condensing tube and a flow of air started through the apparatus. The porcelain boat, containing 5 grams of black dust, was then introduced into the volatilization chamber and the asbestos plug inserted. The volatilization chamber and the condensing tube were held at the desired temperatures and the air current was drawn through the apparatus at the desired rate of flow for a given time. At the end of that time the volatilization chamber and the condensing tube were removed from the furnaces and broken apart at their junction and the condensing tube was cut up into several sections to facilitate the segregation of the condensation products. These products were then weighed and analyzed.

Experimental Data—The black dust used in these experiments had the following analysis: total antimony, 6.07; trivalent antimony, 6.00; arsenic, 68.3 per cent.

Using this material and not more than four times the amount of air theoretically required to absorb all the arsenic trioxide at the temperature of the volatilization chamber, there were two zones in the condensing tube. The first, next to the volatilization chamber, contained vitreous arsenic trioxide, which contained the major portion of the antimony volatilized; its antimony content varied from 10 to 30 per cent in the different experiments. The second contained arsenic trioxide crystals of high purity. There was a very distinct division line between the two zones, which seemed to correspond to a definite temperature, approximately 300° C.

Six sets of experiments, each set consisting of four individual experiments, were completed with this apparatus. The condensing tube was held at four different temperatures in the four experiments of each set, while the temperatures of the volatilization chamber and the volume of air used were approximately the same.

In two sets the temperature of the volatilization chamber was maintained at 450° C.; this was too low for complete volatilization of the arsenic trioxide in a reasonable time. In one of these sets 2 liters of air were used in each experiment, and in the other 4 liters were used. The use of smaller quantities of air was not feasible because of the slow rate of volatilization of the arsenic trioxide.

In three sets of experiments the temperature of the volatilization chamber was held at 500° C., and the volumes of air used were 1, 2, and 4 liters, respectively. In a sixth set the temperature of the volatilization chamber was 550° C. and the volume of air used in each experiment was 1 liter.

The experimental data are given in Table I.

With the aspirating device used in these experiments it was not possible to regulate closely the rate of flow of air through the apparatus, although the total volume of air

Table I—Small-Scale Experiments
(Weight of sample, 5 grams)

Expt.	Time Required	Volatilization Temperature	Condensation Temperature	Air Used	Vitreous Deposit		Refined Arsenic Trioxide		
					Weight	Sb content	Weight	Sb content	As_2O_3 recovery
	Min.	° *C.*	° *C.*	*Cc.*	*Grams*	%	*Grams*	%	%
SET 1									
1	56	430	255	2900	0.31	25.0	1.68	0.70	37.3
2	60	450	285	2100	0.54	21.3	2.10	1.41	46.5
3	60	450	335	2400	0.27	23.0	1.75	0.67	38.0
4	60	450	385	2100	0.72	22.0	2.98	0.87	66.3
SET 2									
1	45	460	255	4000	0.11	29.5	1.20	1.17	26.6
2	45	455	280	4500	0.23	26.0	1.43	0.89	31.8
3	45	450	340	3700	0.63	24.8	3.07	0.73	68.1
4	40	450	385	4000	0.42	27.4	2.58	1.63	57.2
SET 3									
1	40	500	220	850	0.88	15.0	2.78	0.31	61.8
2	50	495	285	1000	1.25	16.5	3.36	0.22	74.6
3	41	515	310	980	0.99	9.6	3.10	0.10	68.7
4	39	500	350	830	0.69	12.3	2.62	0.09	58.0
SET 4									
1	40	500	225	2100	0.99	20.8	3.66	0.90	81.4
2	40	500	280	2400	1.04	19.9	3.62	0.45	80.5
3	40	495	315	2000	1.15	17.6	3.48	0.26	77.3
4	35	495	355	1700	1.12	16.8	3.18	0.33	70.9
SET 5									
1	45	505	220	4000	1.04	19.2	3.38	0.59	75.1
2	40	490	260	3700	0.69	20.1	3.28	0.32	72.9
3	40	500	320	4000	0.98	20.1	3.21	0.27	72.6
4	40	490	350	3500	1.06	22.2	3.33	0.82	74.0
SET 6									
1	35	540	210	1000	0.85	19.0	3.68	0.63	82.2
2	40	540	290	1100	1.06	16.5	3.55	0.80	78.9
3	30	550	350	900	1.30	13.2	3.51	0.27	73.6

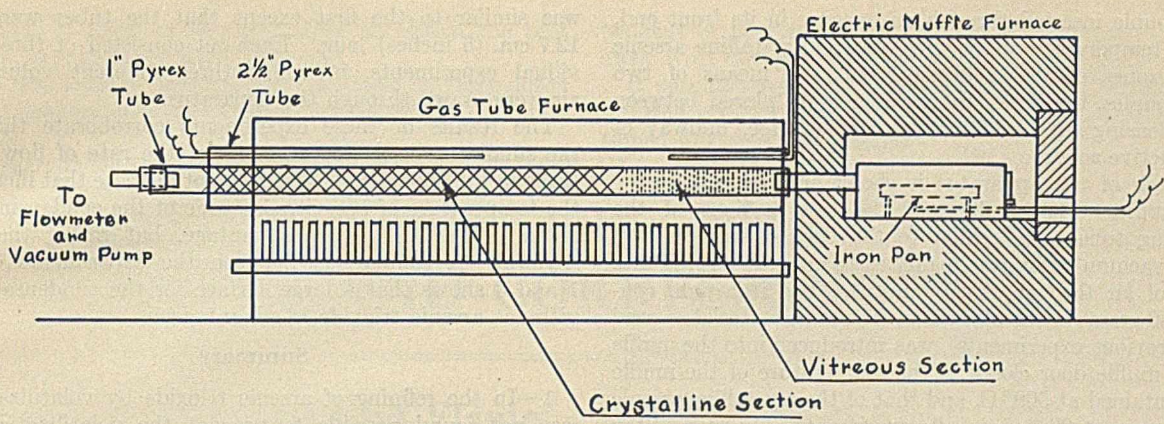


Figure 2—Apparatus for Large-Scale Experiments

used in the experiment could be controlled fairly well. The variations in rate of flow were especially marked at the beginning of an experiment, when the arsenic trioxide was being volatilized more rapidly. This fact made it impossible to obtain as consistent results as could have been obtained otherwise. Steps were taken to correct this fault in the apparatus used in the second series of experiments.

Conclusions—Although the data obtained from these experiments are not so consistent as could be desired, they point to the following conclusions:

1—The antimony content and the yield of crystalline arsenic trioxide decrease as the temperature of that portion of the tube where the vitreous deposit is formed is increased.

2—The antimony content of the crystalline arsenic trioxide increases as the volume of air drawn through the volatilization and condensing system is increased.

3—The temperature of the volatilization chamber has very little effect, except in the rate of volatilization of the charge, for most of the antimony is volatilized, even with small volumes of air, at temperatures sufficient to volatilize the arsenic trioxide in a reasonable length of time.

4—Under properly controlled conditions it is possible to recover 70 to 80 per cent of the arsenic, from black dust containing 6 per cent antimony, as crystalline arsenic trioxide containing less than 0.70 per cent antimony.

Large-Scale Experiments

In order to extend the data obtained from the preceding series of experiments and to determine if the results could be duplicated on a somewhat larger scale, a second series was carried out.

Apparatus—In this series it was desired to use 50 grams of black dust per charge. It was necessary to heat the volatilization chamber to one temperature, the portion of the condensing tube in which the vitreous deposit was to be formed at a somewhat lower temperature, and that portion in which the crystalline arsenic trioxide was to be condensed to 150–200° C.

A small electric muffle furnace was used to heat the volatilization chamber. An iron muffle 20 cm. (8 inches) long, 11.4 cm. (4.5 inches) wide, and 7.6 cm. (3 inches) high, was built to fit this furnace. At its rear end it was fitted with an iron pipe about an inch (2.5 cm.) in diameter which projected through a hole in the back of the furnace. The front end of the muffle was fitted with a hole for a thermocouple and a sliding door just large enough to admit an iron pan 12.7 cm. (5 inches) long by 6.4 cm. (2.5 inches) wide by 2 cm. (3/4 inch) deep. A Pyrex glass tube 91 cm. (36 inches) long and 2.5 cm. (1 inch) in diameter, to serve as the condensing chamber, was fitted over the iron pipe at the back of the muffle; the junction was made tight with asbestos packing. The other end of the glass tube was connected, through a flowmeter, to the vacuum pump. The apparatus was air-tight except for the door at the front of the muffle, which allowed the entrance of enough air to maintain a proper current of air through the apparatus.

A 76-cm. (30-inch) gas-combustion furnace was used to heat the vitreous and crystalline zones of the glass condensing tube. To obtain a uniform temperature in the condensing tube it was necessary to place it inside another glass tube 6.4 cm. (2.5 inches) in diameter to serve as a sort of muffle. The space between the two tubes was packed with asbestos at the point of transition between the vitreous section and the crystalline zone, to make it possible to maintain the two zones at different temperatures. This arrangement permitted fairly satisfactory temperature control.

In the first experiments with this apparatus very small amounts of the vitreous deposit were obtained and the antimony content of the crystalline arsenic trioxide was high. To duplicate the results obtained on a smaller scale in the previous experiments it was necessary to provide more surface for the condensation of the vitreous deposit; this was accomplished by filling the portion of the condensing tube next to the muffle with small glass tubes.

The temperature of the iron muffle was measured by a

Table II—Large-Scale Experiments

(Volatilization temperature, 500° C.; weight of sample, 50 grams)

Expt.	Condensation Temperature	Air Used		Tubes			Vitreous Deposit			Refined Arsenic Trioxide		
		Volume	× Theoretical	No.	Length		Weight	Sb content		Weight	Sb content	As_2O_3 recovery
	° C.	Liters			Cm.	Inches	Grams	%	Grams	Grams	%	%
SET 1												
1	350	37.8	7.7	9	25.4	10	6.0	18.6	1.11	33.0	1.55	73.1
2	350	24.5	5.0	9	25.4	10	9.0	11.8	1.06	32.0	0.40	71.0
3	350	14.7	3.1	9	25.4	10	16.0	8.1	1.30	28.0	0.25	65.0
SET 2												
1	385	24.6	5.0	9	25.4	10	5.0	19.4	0.97	35.0	1.55	78.5
2	385	15.7	3.2	9	25.4	10	8.0	20.9	1.67	42.0	1.70	93.0
3	385	9.8	2.0	9	25.4	10	6.0	17.5	1.05	37.0	1.42	82.0
SET 3												
1	350	25.5	5.2	9	12.7	5	7.0	16.4	1.15	39.0	1.82	86.5
2	350	19.7	4.0	9	12.7	5	12.0	10.4	1.24	33.0	0.50	73.1
3	350	9.9	2.0	9	12.7	5	10.0	17.8	0.62	37.0	0.62	82.0

thermocouple inserted through an opening in its front end, and the temperature of the vitreous and crystalline arsenic trioxide zones of the condensing tube by means of two thermocouples, the junctions of which were placed between the condensing tube and the outer glass tube, midway of the respective zones.

A sketch of the apparatus is shown in Figure 2.

Procedure—The muffle and the two sections of the condensing tube were heated to the desired temperatures and the vacuum pump was regulated to give the desired rate of flow of air through the apparatus. The iron pan, containing 50 grams of the black dust (the same material as used in the previous experiments), was introduced into the muffle and the muffle door closed. The temperature of the muffle was maintained at 500° C. and that of the crystalline arsenic trioxide zone at 200° C. in all experiments. As soon as the volatilization of the arsenic trioxide had stopped, which was in about an hour in all cases, the pan was removed and the different condensation products were removed, weighed, and analyzed.

Experimental Data—The data are given in Table II. There were three variables—the temperature of the zone of the condensing tube in which the vitreous deposit was condensed, the volume of air used, and the number and length of tubes in the vitreous zone of the condensing tube (surface available for the condensation of the vitreous deposit). The temperature of the vitreous zone was 350° C. in the first set of experiments and 385° C. in the second set; an attempt was also made to carry out some experiments at 325° C., but there was so much condensation at the connection between the muffle and the condensing tube that it became clogged. In the first and second sets of experiments nine small glass tubes 25.4 cm. (10 inches) long (sufficient to fill a 10-inch section of the condensing tube) were placed in the vitreous zone of the condensing tube. The third set was similar to the first except that the tubes were only 12.7 cm. (5 inches) long. Each set consisted of three individual experiments, in which three different volumes of air were drawn through the apparatus.

The results of these experiments corroborate those on the smaller scale as to the effect of the rate of flow of air through the apparatus. They do not indicate that increasing the temperature of the vitreous zone of the condensing tube above 350° C. is of any advantage, but rather that it is harmful. A comparison between the experiments of sets 1 and 3 shows that a large surface for the condensation of vitreous arsenic trioxide is advantageous.

Summary

1—In the refining of arsenic trioxide by volatilization it was not found possible to prevent the volatilization of a large portion of antimony present in the material being refined. It was possible, however, to concentrate the major portion of the volatilized antimony in a small amount of arsenic trioxide (10 to 30 per cent Sb) in that portion of the flue (condensing tube) nearest the furnace. Seventy to eighty per cent of the arsenic in the black dust was obtained as a pure arsenic trioxide further along the flue.

2—Segregation of the antimony in a small part of the arsenic trioxide was accomplished by careful control of the temperatures of the furnace and flue, and regulation of the volume of air drawn through them.

3—For the best results the temperature of the flue near the refining furnace should be about 350° C., as much surface as possible should be provided for the condensation of the vitreous deposit, and the volume of air drawn through the system should be as small as possible.

4—The temperature of the furnace is apparently not so important except in so far as it affects the temperature of the flue.

A Rotary Filter Stand[1]

W. M. Shaw

The University of Tennessee Agricultural Experiment Station, Knoxville, Tenn.

ROUTINE analysis filtrations often have to be carried out in large numbers. A long 12-unit funnel rack is usually available for such work, and the operator is dependent upon overhead shelves to furnish sufficient head for wash solutions. In many laboratories where several analysts have to be accommodated the space available for such operations is very limited. With the object of insuring greater facility in laboratories of limited space and independence of built-in equipment, the accompanying filtration stand was designed.

The filter stand consists of the following parts as illustrated:

(1) A cast-iron base 8 inches in diameter and 2 inches high, with a perpendicular rod $^1/_2$ by 36 inches.

(2) A metal tube which slips over the iron rod, rests upon a thrust ball-bearing within the cast-iron base, and extends about two-thirds the height of the rod.

(3) A bottom shelf 24 inches in diameter which carries two sets of twelve beakers in concentric arrangement.

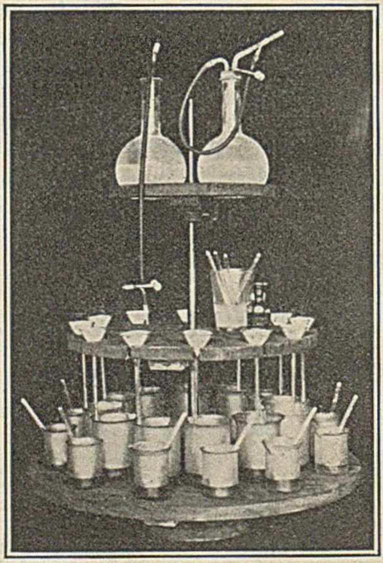
(4) A middle shelf 18 inches in diameter with two 12-unit sets of holes on the periphery which carry twelve filter funnels each.

(5) A top shelf 12 inches in diameter provided with two large holes for holding two wash bottles.

The first two shelves are fastened by means of set screws to the slip-over tube, and revolve as a unit. The third shelf is fastened to the rod in the same manner and is adjustable. The middle shelf is also adjustable as to height over the slip-over tube length.

Advantages—It occupies about one-third of the bench space required by the ordinary rack of same capacity, and may be set upon an ordinary laboratory stool.

It consists of one unit assembly for twelve precipitates, twelve receivers, and twelve funnels together with wash solutions, and it may be easily transported



Rotary Filter Stand

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[1] Received October 20, 1927.

POLITECHNI ŚLĄSKIEJ

from place to place in the laboratory to obtain the best condition of light, heat, and ventilation.

When not in use it furnishes shelving space for three dozen assorted beakers and twenty-four funnels ready for immediate use.

The reservoir shelf makes the washing of precipitates independent of permanent shelving for gravity flow, and does away with the ordinary wash bottle.

It permits easy access to all parts from a sitting posture, insuring comfort for the manipulation in case of long-continued filtration and washing.

NOTES AND CORRESPONDENCE

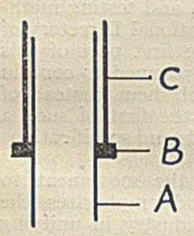
Device for Maintaining Flame Height in Sulfur Determinations

Editor of Industrial and Engineering Chemistry:

In the recently published Report of Committee D-2 of the A. S. T. M. the members of Sub-Committee VII on Sulfur Determination and Differentiation call attention to the difficulty of maintaining the flame at the prescribed height.

The writer has found the device described by Squire [*J. Soc. Chem. Ind.*, 45, 466T (1926)] to be of great value where accurate flame-height adjustment is required during sulfur determinations, especially in a study of the effect of rate of burning, etc., on the accuracy of such determinations.

The device is briefly as follows: By filling the wick tube with glass wool and having trimmed the wick flush with the top of the tube, any flame from 2 cm. in height to a mere flicker can be obtained with natural gas gasoline in the lamp. The novel feature is that the flame can be kept at a definite height from the beginning of a burning, without interruption of the test, by raising or lowering the small length of tubing which rests on the rubber ring.



A = wick tube
B = rubber ring
C = 13-mm. length of closely fitting tubing

C. I. Kelly

Anglo American Oil Co., Ltd.
Purfleet, Essex, England
October 22, 1927

Formation of Petroleum

Editor of Industrial and Engineering Chemistry:

Apropos of the instructive résumé by D. H. Killeffer, "A Year's Progress in Chemistry," in the October, 1927, number of *Industrial and Engineering Chemistry,* in which he states that Fischer and Tropsch have advanced a theory that petroleum is formed by reaction similar to that involved in their preparation, at low pressures, of high-melting, high-molecular weight hydrocarbons comparable to those present in paraffin waxes melting as high as 120° C., and that their said theory is the only one so far advanced by which it can be supposed that petroleum is still being formed in nature; it may be interesting to suggest that Mendelejeff advanced the theory that water acting on carbides (perhaps iron carbide) in the deep layers of the earth's crust was responsible for the formation of petroleum.

Sabatier and Senderens went much farther and actually created appreciable amounts of oil corresponding exactly with Pennsylvania crude in gravity, color effects, odor, and all physical and chemical properties tested, at atmospheric pressure (if I remember aright) by simply bringing acetylene and hydrogen together in the presence of finely divided nickel at temperatures of 200° C. and less. By varying the temperature and catalyst they also produced other specific crude petroleums. Consequently they advanced the extremely plausible theory that water in contact with carbides in the earth's deep or comparatively deep crust-layers generated the requisite acetylene and, also, acting on alkali metals or compounds, such as could most reasonably be inferred to exist in quantity at different levels, was decomposed, the two reactions thus furnishing the requisite hydrogen and acetylene.

Geologically speaking, the water could get down to the carbide and alkalies through fissures made by faulting and the oils generated could ride back up the same way on water, being trapped at intervals under water pressure by further intermittent slippings of the measures along the fault cracks and by the sealing of the vents by impervious top, bottom, and side formations, while the uncombined or otherwise combined gases could also ascend with pressure incident to their creation or with water pressure.

As tending to account, at least in part, for the fate of the oxygen released, the interesting fact may be mentioned that within the last year or so a great oil well has been brought in in Colorado at a depth of about 4000 feet in which the gas accompanying the oil was not, as usually, a hydrocarbon, but was carbon dioxide in enormous quantities and under enormous pressure.

S. A. Hobson

Amory, Miss.
October 24, 1927

Corrections

In our article entitled "Polarized Platinum Electrode in Neutralization Reactions," *Ind. Eng. Chem.*, 19, 749 (1927), in the second sentence under Apparatus and Procedure the polarizing current should be 0.43 ampere $\times 10^{-5}$ instead of 2.3 $\times 10^{-5}$ amperes.

A. H. Wright and F. H. Gibson

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In "Use of Quinhydrone Electrode for Following Changes of pH in Swiss Cheese," *Ind. Eng. Chem.*, 19, 1272 (1927), the gages for the gold and platinum wire given on page 1272 should be interchanged.

Paul D. Watson

New Books

Index to Proceedings, Volumes 21–25 (1921–1925). 224 pp. American Society for Testing Materials, Philadelphia. Price, $2.50.

Schiess- und Sprengstoffe. Band XVI. Technische Fortschrittsberichte. Ph. Naoum. 212 pp. Theodor Steinkopff, Dresden. Price, 14 marks.

Significance of the Elasticity and Thermal Expansion of Fireclays with Reference to the Spalling of the Fired Product. R. F. Geller. *Technologic Paper* 4. 14 pp. Price, 50 cents. Kilns and Fuels for Firing Refractories. W. E. Rice. *Bulletin* 15. 8 pp. Notes on the Design of Fire Clay Shapes. E. H. Van Schoick. *Bulletin* 16. 4 pp. American Refractories Institute, Pittsburgh, Pa.

BOOK REVIEWS

The Story of Chemistry. By Floyd L. Darrow. 528 pages. Bobbs-Merrill Company, Indianapolis, Ind., 1927. Price, $4.00.

This is the latest of the books written for the non-technical reader to meet the demand that has arisen from the humanizing of the science in progress these several years. It is so up to date in references and subject matter as to give the impression that presses must have been held for last-moment additions.

The author has chosen the historical form of treatment and begins with an interesting account of the alchemist, from which the reader may be left wondering whether this ancestor of the chemist is to be more condemned for his chicanery than credited with the crude beginnings which he made. The second chapter is somewhat disconnected, for a large number of actors are brought upon the stage. The stories of men are used to introduce discoveries, and vice versa. In the third chapter a brave attempt is made to make fundamental theory pertaining to atoms, electrons, and protons easily understood. In the chapters on Chemistry and Power, A Glance at Gases, Agriculture and War, Rubber, The Age of Metals, and In the Realm of Synthetics, the story swings more to the industrial side and the text is illuminated with occasional diagrams reminiscent of industrial chemistry. These subjects are presented from the most modern point of view. The chapter on Agriculture and War contains a straight-forward discussion of chemical warfare, which should do much to correct any false impressions with respect to this method of defense. An interesting chapter is devoted to American progress in chemistry, in which reference is made to chemical organization, industry, and research, and this is followed by one on chemistry in the day's work. The book concludes with a strong plea for the support of fundamental research and a dozen pages of bibliography keyed to the various chapters.

We find an occasional use of an unconfirmed news item, but this is not serious. The book is written in good style. The weight of paper and the dimensions selected make it convenient to handle, and the illustrations are both interesting and instructive. Frequently a wish has been expressed for something in popular form in which a little more of the science could be found than has characterized earlier books issued when the first consideration was to gain public interest. "The Story of Chemistry" may be the first of this new group of popular accounts.

Chemical Patents Index (U. S. 1915–1924). Volume One. By Edward C. Worden. 904 pages. The Chemical Catalog Company, Inc., New York, 1927. Price, 5-volume set, $100.00; $25.00 payable on receipt of first volume.

This is the first of a set of five volumes constituting a subject matter index to the United States patents for chemical inventions granted between 1915 and 1924. This first volume contains a list of names of inventors for the whole ten-year period and the index of subjects beginning with the letters A and B.

The items refer to the numbers of the patents and there are, for each patent, as many items as are needed to refer to each separate piece of information. If one patent, for example, refers to or describes twenty-five alloys, there are as many separate, concise, condensed (and occasionally puzzling) items. Not only are the constituent metals named, but in many cases the percentage composition is given. Limited as it is to the patents granted in these ten years, it is doubtful whether there is in any other one publication such a useful compendium of information on this subject. Not only the patents for chemical processes and products, but also the uses to which these products are put, are indexed.

It is often difficult to decide from the cryptic, sometimes almost fantastic, headings in the Patent Office classification where to start a search. This index will at once give the necessary clue. There is no royal road to this or any other kind of learning, but this index not only puts the searcher on the road but takes him a long way on his journey.

Its price is relatively high, and necessarily so; but when it is realized that in a few minutes there can be obtained information which it might take hours, or even days, to get otherwise, and perhaps not so completely, its price is low. It will be a boon to the chemical searcher, whether he be scientist, manufacturer, or patent solicitor.

Doctor Worden and his co-workers are entitled to great credit for the completion of this monumental work, covering as it does more than 23,000 United States chemical patents issued during this ten-year period. It is hoped that the work will be extended to cover the period from 1790 to 1914 and that it will be supplemented by other volumes as the passage of time requires.

J. H. Brickenstein

Standards and Specifications in the Wood-Using Industries. Nationally Recognized Standards and Specifications for Wood and Manufactures Thereof, Including Paper and Paper Products. *Miscellaneous Publication* 79, National Bureau of Standards. 349 pages. Superintendent of Documents, Government Printing Office, Washington, D. C. Price, $1.50.

This volume represents the first attempt on the part of the Department of Commerce to collect and publish the substance of the standard specifications in wood-using industries formulated by the national technical societies, the trade associations having national recognition, or other organizations which speak for industry or with the authority of the Federal Government as a whole.

In 1923 the Secretary of Commerce outlined plans for a review of the standard specifications, simplifications, and testing methods in use in this country, and in 1925 the National Directory of Commodity Specifications was issued as the first part of this review. The second part of the review was planned to contain copies of actual specifications or abstracts of them, instead of mere titles, and the present compilation is the first of such a series of publications dealing with the standards and specifications in various industries.

This book shows the present status of the movement to standardize lumber and wood products and emphasizes the degree of success already attained by the industry in unifying its grading rules and conforming to the dimensional standards set up within the industry. An attempt has been made to include directly or by adequate reference the substance of all standards and specifications of the wood-using industries. The same decimal system of classification which is employed in the National Directory of Commodity Specifications is used. The major divisions are: timber and other unmanufactured or partly manufactured wood; lumber for building and factory use; manufactures of wood (except furniture); furniture; paper; books and other printed matter; miscellaneous wood and paper products; and finally a list of technical societies, trade associations, and other organizations issuing standards and specifications in the wood-using industries.

Guide to the Literature of Chemistry. By E. J. Crane and Austin M. Patterson. 438 pages. John Wiley & Sons, Inc., New York, 1927. Price, $5.00.

When we consider the tremendous literature of chemistry, both as regards books and periodicals, it is not surprising that we need a guide to show us the correct path to take in our particular search, especially in the hurry and rush of our present generation. While many brief magazine articles have appeared from time to time, the book by Crane and Patterson is the first serious attempt to cover the entire field. Both authors, being closely associated with *Chemical Abstracts*, approach their task with a very practical viewpoint.

Chapter I discusses the purposes of searches and obstacles. "We sometimes think that there is not so much need of hurry about the making of more experiments as there is of a fuller understanding of the meaning and significance of the data already accumulated." Chapter II discusses books, listing the most important encyclopedic works, handbooks, formula lexicons, and general books and sources of information regarding them. Appendix 8 gives a very carefully chosen list of 1685 books, selected and evaluated by 154 men, classified according to the sections in *Chemical Abstracts*. Chapter III is devoted to periodicals; there is a brief discussion of current journals of greatest chemical interest, classified according to subjects or fields, and secondarily according to countries, while appendix 6 gives a list of 1263 current periodicals and 626 which have ceased publication. The information is similar to that contained in the List of Periodicals Abstracted by *Chemical Abstracts*, but without the library data. Appendix 4 gives a bibliography of lists of periodicals. Abstract journals naturally are fully discussed and a list of such journals for special subjects is given. Chapter IV discusses the nature and scope of patent literature, sources of patent information, official patent publications, scientific and technical journals containing patent abstracts, patent digests and lists, and procedure in making patent searches. Chapter V discusses other sources of information such as bulletins, theses, reviews, addresses and lectures, bibliographies, trade literature, information services, etc. Chapter VI covers the very important subject of indexes, the methods of preparation and their use, and concludes with a list of existing indexes. Chapter VII discusses the method of using libraries, while appendix 3 gives a list of American libraries of interest to chemists. The last chapter discusses the procedure of literature searching and gives the experiences of others.

This brief summary of the contents of this book shows that there has been assembled here a large amount of information of great value to the one who would unearth a single fact from the mass of now existing chemical literature or to him who would search out the present state of any art. It would seem that the work would be especially valuable as the basis of a seminar course in our graduate schools of chemistry.

C. J. West

The Metallurgist's Manual. By T. G. Bamford and H. Harris. 266 + x pages. D. Van Nostrand Company, Inc., New York, 1927. Price, $5.00.

A book with this title, written by lecturers in metallurgy at the University of Birmingham, was expected to be a notable addition to metallurgical literature. It was a disappointment to find that it contains almost nothing of interest to the metallurgist, as that profession is usually defined in this country. Information on the hot- and cold-working of metals, mechanical testing, and heat treatment is conspicuous by its absence. The iron-carbon diagram appears, with a few comments on heat treatment of steel, but the reader gets no hint that heat-treatable aluminum alloys exist.

Some elementary information is given on pyrometry, metallography, and phase-rule diagrams, which is available in many other places, as are the tables of properties which are included. These sections and a short one on slags seem thrown in for good measure, though they take up half the book, for the manual is primarily a compilation of works methods for analysis and assaying of metallurgical materials. As such it has no greater value than it has in respect to physical metallurgy. The methods are sketchily described, are again all available in other books, and very often fail to take into account the presence of interfering elements. Although only works, rather than precision, methods are given, many of them are ancient and cumbersome. In half a dozen instances the name of another writer, with perhaps the title of a textbook, is cited as authority for some statement, and the reviewer has found two references to journal articles, one published in 1886 and one in 1891. Otherwise the existence of metallurgical and chemical literature is ignored. The manual is distinctly below the average of the other books in its field.

H. W. Gillett

Principles of Chemical Engineering. By William H. Walker, Warren K. Lewis, and William H. McAdams. 2nd edition. 770 pages. McGraw-Hill Book Co., Inc., New York, 1927. Price, $5.50.

Concerning the second edition of this famous textbook very little can be added to what has been said repeatedly.

This edition contains considerable data which have been acquired since 1923 by various investigators. The addition of up-to-date methods has distinctly improved the chapters on flow of fluids and heat transfer. These chapters are extremely well written even in the first edition and they could probably only be improved by the use of large, rather than small, charts. Students and engineers using this book would appreciate the incorporation of charts that could be easily read and the curves readily interpolated.

The reviewer notes with pleasure that the authors have changed from mathematical to graphical methods in their determination of the number of plates in a fractionating column. He notes with even more pleasure that they refuse to admit that their mathematical methods were incorrect. In brief, it is their "story" and they will stick to it.

The most noteworthy additions to the book are the chapters on diffusion and on absorption and extraction. From the academic standpoint the addition of problems to be solved is a noteworthy new feature. Without doubt many of our college professors would appreciate even more problems and, most of all, having the correct answers supplied with the questions.

It is interesting to note that the English Institute of Chemical Engineers in their public examination of June, 1926, asked a great many questions which could be only answered by one who had a thorough knowledge of the Walker, Lewis, and McAdams textbook.

It is the reviewer's opinion that this book has done more to raise the standard of chemical engineering education in our universities than any other factor in all time. The real, immediate value of this book, however, is not in training future chemical engineers, but in educating prominent chemical engineers of today whose lack of appreciation of the fundamentals of chemical engineering has cost our industries vast sums of money.

D. B. Keyes

Boiler Feed Water Purification. By Sheppard T. Powell. 363 pages. McGraw-Hill Book Co., Inc., New York, 1927. Price, $4.00.

A comprehensive modern work on boiler feed-water has been needed for a long time. In the present book the author has met this need and has accomplished the purpose set forth in the preface: "to present such basic facts concerning feed-water treatment as may assist the designing engineer in the selection of the appropriate type of treatment and may aid the operating engineer, upon whom is placed the responsibility, in controlling the system most efficiently. So far as it has been possible, ultra-technical discussions have been avoided.***A number of chapters are included in the text which may not deal with purification processes, rigidly defined. Their subject matter, however, is so closely related to that of feed-water treatment that they should not be omitted."

Valuable features are: the excellent illustrations, actual and diagrammatic, of commercial apparatus for different kinds of water treatment; operating results and cost figures from the author's experience with some of the processes; the bibliography at the end of each chapter; the summaries of advantages and disadvantages of many of the processes; the appendix of 31 pages of useful tables and collateral information such as definitions of terms and specifications for chemicals for water purification.

The book should be available to every one interested in boiler feed-water.

W. D. Collins

The Microscopy of Drinking Water. By George Chandler Whipple, revised by Gordon M. Fair and Melville C. Whipple. 4th edition, rewritten and enlarged. 585 pages. John Wiley & Sons, Inc., New York; Chapman and Hall, Ltd., London, 1927. Price, $7.00.

"The Microscopy of Drinking Water," by George Chandler Whipple, is probably in every water laboratory. If not, it should be, as there is no book of such practical value for determination of microscopic organisms and interpretation of their presence in water supply. The function of the book is unique as it has no rival. The ground covered seems to be complete, including every phase possibly connected with these minute forms of life which are of such supreme importance from the esthetic point of view. The life history of organisms so far as known is thoroughly covered in the chapter on limnology from the physical, chemical, and biological aspects. Thorough consideration is given to the control of organisms by all known methods, particularly copper sulfate and chlorination treatment, with the associated control of taste and odor.

The new edition is absolutely up to date, containing the latest data on superchlorination. The treatment of the entire subject is very broad and practical, presenting data gathered from numerous sources the world over. Whipple's viewpoint was always sensible and his judgment sound. No author was ever more adept at gathering data from many sources and weaving them into a helpful unity.

It is impossible to cover the new material adequately. The following may be briefly indicated: the relationship and effect of microscopic organisms upon the sanitary analysis and interpretation; the effect of chlorination in producing taste and odor as well as controlling by superchlorination; comparison of old and new methods of enumeration of organisms; copious additions to the subject of limnology, including a new chapter on rheology or stream life; the self-purification of streams; latest methods of control of microscopic organisms; relation of microscopic organisms to filter-plant operation; large additions to the classification and description of organisms; a new chapter classifying the organisms according to their environment—i. e., pure water, sewage, etc. Many additional references from modern sources are appended to each chapter. The book is a fund of useful, practical information.

Frank E. Hale

City Water Supplies of Arkansas. By Harrison Hale. University of Arkansas Engineering Experiment Station, *Bulletin* 2. 100 pages. November, 1926.

Mineral analyses of 95 samples from 82 public water supplies are given, with results of bacteriological examination of samples from many of the supplies. The descriptions of the waterworks systems include depths of wells, methods of treatment, capacities of reservoirs, pumping equipment, consumption, and rates. The report concludes with summaries of the chemical and engineering features of the supplies.

W. D. Collins

Noxious Gases and the Principles of Respiration Influencing Their Action. By Yandell Henderson and Howard W. Haggard. A. C. S. Monograph Series, No. 35. The Chemical Catalog Company, Inc., New York, 1927. Price, $4.50.

The purpose of this monograph is to render any general knowledge available upon the subjects of noxious gases in a readable form, intelligible to those whose activities may be along a different line.

The book, in dealing with the physiology of respiration, makes a special feature of toxic action dependent upon volatility. The mode of classification is practical rather than strictly logical. It brings out the fact that immensely valuable measures of protection against industrial gases have resulted from the study of war-gas defense, and in Chapter VIII references are given to works dealing with chemical warfare. A full description of the function of respiration is included, which goes far beyond any current textbooks in presenting a vital function as a mechanism. The medicine of volatile poison, written especially for chemists and engineers rather than for medical men, is also featured.

The laws of gases are taken up from the standpoint of their relation to respiration, the relation of volume to temperature and pressure, and the law of partial pressures. The solubility of gases, as discussed, shows the important part they play in the absorption, distribution, and elimination of volatile substances through the lungs in the body, and in this connection the process of absorption and elimination of non-reactive gases is fully discussed and a mathematical explanation given.

The table of noxious gases, listed in Chapter VI according to their chemical compositions and classified according to their actions, is of great importance and help for reference work and is unusually complete.

The concise, clear, and expressive statements add to the importance and interest of the book, not only to the technician but also to the layman who is interested in this special field of research work, and the monograph is highly recommended both for study and for reference.

Harry L. Gilchrist

Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases. 3rd edition. 187 pages. Carnegie Steel Company, Pittsburgh, 1927. Price, $2.00.

The mere fact that a book has reached the dignity of a third edition shows that it has an honorable history and is of recognized worth. The committee which prepared the text consisted of six chief chemists of the United States Steel Corporation and a representative of the Bureau of Inspection. This committee spent a year in the collection of data and details before undertaking a revision of the earlier edition, and as suggestions were made they tested carefully all details of apparatus and methods before adopting them in their final form.

The book was compiled to be used as a standard handbook in the laboratories of the Steel Corporation. The directions are therefore carefully standardized and details are prescribed with more minuteness than in texts which aim to give general principles applicable to various commercial types of equipment.

The most important deviation from the usual practice is in the standard conditions for measuring gases. The directions for determining heating value of gases are abbreviated in the text, it being stated on page 132 that the procedure given in certain publications of the Bureau of Standards is followed closely. The Steel Corporation, however, reduces gases to the standard condition of dry gas at 60° F. instead of gas saturated with moisture at that temperature. The tables for reduction of gases to standard conditions given in their book are of the same general form as those which are used for gases saturated with moisture, and unless the reader notes the heading carefully he may use the tables from the Steel Corporation's book, thinking that they are the same as usually given. The differences may be shown by the following illustration: The correction for a gas 80° F. and 29.5 inches barometer is 0.9469 in the Steel Corporation's tables, and 0.930 in the usual tables.

The book includes methods of sampling and analysis of all the usual industrial gases, as well as a number of special methods including hydrogen sulfide, organic sulfur, light oil, naphthalene, tar in mineral solids, and moisture in gases. The last chapter gives a careful discussion of methods of measuring and calculating volumes of gases under varying conditions.

The book is to be commended highly for its careful and accurate presentation of a subject where all too frequently slipshod methods still prevail.

Alfred H. White

Ceramics—Clay Technology. By Hewitt Wilson. 1st edition. 6 by $9^{1}/_{4}$ inches. 296 pages. McGraw-Hill Book Co., Inc., New York, 1927. Price, $4.00.

The author is well and favorably known in ceramic circles, an associate professor of ceramic engineering at the University of Washington, Seattle.

This book is the first general text on ceramic problems from recent physical-chemical viewpoints and as such is a valuable contribution to ceramic literature. The subject matter is logically arranged. The book is well printed and illustrated with a large number of graphs and a few halftones.

The author first properly defines the scope of ceramics, giving complete tabular outlines of the classification and description of ceramic products. The second chapter briefly deals with the formation of clay, showing their geophysical-chemical relationships. The characteristics of clay in the original condition is the third general subject, and under this heading he gives a classification chart, condensed from Orton's original work, of the principal types of clays as well as a description of types and the compositions of clays. From pages 55 to 120 he describes the characteristics of clay in the plastic and dry condition, primarily from the physical-chemical standpoint. Chapter 5 deals with the drying of clay wares. Naturally after drying comes the effect of heat on clays, which is taken up under two general headings—namely, Vitrification and Melting, and Crystallization of Silicates. These two chapters, because of their importance, take nearly one-half the text.

At the end of each section is a large number of references which will be very valuable to the users of the book. The book has a comprehensive table of contents as well as a good author's index and a very usable subject index.

It is a book which will be of great value to those interested in ceramic problems and one which every ceramic man will be glad to have on his desk for ready and repeated reference.

L. I. Shaw

A Dictionary of Applied Chemistry. Vol. VII. Thalenite—Z, with Index to Complete Work. By Sir Edward Thorpe, completed by H. Forster Morley. Revised and enlarged edition. 765 pages. Longmans, Green & Co., New York and London, 1927. Price, $20.00.

With the death of Sir Edward Thorpe in 1925, much concern was felt relative to the last two volumes of the famous Dictionary of Applied Chemistry, parts of which have appeared from time to time under his authorship and with the assistance of many eminent contributors. It was found, however, that so much progress had been made upon the last two volumes of his dictionary that it could be completed and this valuable reference work made available in its entirety.

As in the other volumes of the dictionary, so many individual and important subjects are treated that a critical review is practically impossible. Fortunately, the preceding six volumes have so well established this valuable aid to chemistry that no detailed review is either needed or expected. The volume completes a work which has for some time proved a very useful tool.

Handbook of Ore Dressing. By Arthur F. Taggart. 1679 pages, illustrated. John Wiley & Sons, Inc., New York, 1927. Price, $10.00.

Recent developments in froth flotation and fine grinding, as well as the less radical changes in other lines, have created the need for a modern handbook of ore dressing. Professor Taggart has met this need with a work which ranks as a classic. It is at once an encyclopedic compilation of data and processes and a comprehensive text on theory and practice.

The title is hardly indicative of the broad scope of the book. After an introductory definition of terms, the author devotes a large section to the ores, properties, uses, production, selling, and treatment of minerals and metals in the preparation of which the methods of ore dressing are used. This is followed by a detailed study of basic operations and equipment, such as crushers, fine grinding, crushing efficiency, sizing, classification, washing, jigging, shaking tables, vanners, flotation, differential flotation, magnetic separation, miscellaneous processes of concentration, dewatering, filtration, drying, storage, and testing. R. C. Canby has contributed a section on Hydrometallurgy, H. A. Behre on Transport of Materials and on Sampling, J. M. Callow on Design and Construction of Ore-Treatment Plants, P. F. Smith on Mathematics, W. R. Longley on Theoretical Mechanics, and C. T. Porter on Applied Mechanics.

The form of presentation is outstanding in several particulars. Under clearly classified headings, the important material is set in the usual type while numerical data and secondary material are presented in the text in smaller type. The text is fully interspersed with references to the patent, periodical, and book literature, with the scope of a complete bibliography. Extensive scientific, production, and cost data which have been culled from questionnaires, trade catalogs, and technical literature are presented.

This book should prove a most valuable reference for chemists and engineers in the mining and metallurgical fields. In its treatment of some of the basic operations, an abundance of cost and operating data not otherwise easily available are given. It is therefore a valuable addition to the literature of chemical engineering and is an example for further publications.

LINCOLN T. WORK

The Nature of Matter, Gravitation, and Light. By Albert P. Mathews. 218 pages. [illegible]7 illustrations. William Wood and Company, New York, 1927. Price, $3.50.

In pursuing his studies of living matter, the author, a biochemist and biologist, was led into the realm of physics by following such trails as cohesion and surface tension which play an important part in the production of vital phenomena. Certainly vital phenomena are associated with matter just as physical phenomena are; therefore, the author has as much right in this field as the physicist. Whatever the reactions of physicists who read this book, at least they will respect it as a serious attempt to penetrate the unknown.

Although the author was led into the field through a desire to explain the vital aspects of matter, the book for the most part deals with properties commonly termed "physical." This is natural because the goal seems to have been to correlate the aspects under which the universe appears to us, such as geometrical, mechanical, electromagnetic, and psychical. By reducing the dimensions of all physical phenomena to those of four-dimensional space, the author expresses everything geometrically. By inventing a unit of ether—the etherion—he correlates the electrical and the magnetic with their mechanical and geometrical equivalents. By assuming that one of the coördinates of space-time is a psychical coördinate and that one of the components of motion in the vortex is the psychical component, the electrons being psychrons, the author attempts to connect the psychical with its material equivalent.

The author begins with the ratio of the masses of the positive and the negative electrons and maintains lines of communication with the known by interweaving such constants with two fundamental postulates. From these two the properties of the immaterial are calculated, and from this the nature of electrostatic, gravitational, and cohesional attraction is deduced.

He recognizes three kinds of matter—ordinary matter, electricity, and radiant energy. These appear to have several kinds of properties—mechanical, electromagnetic, extent in space and time, and, finally, properties of vitality. In the last-named are embraced all the psychical phenomena of our own lives.

No one can safely predict the consequences of the theories developed in this book. Some will say that they are merely speculative. Others, who have buried the ether, will not relish its resurrection. Still others will wonder and begin to think along new lines. At least here is an interesting work, not alone for the biologist, who studies vital phenomena, it should be read by the physicist.

M. LUCKIESH

Oil Analysis. By A. H. Gill. 11th edition. 287 pages. J. B. Lippincott Company, Philadelphia, 1927. Price, $4.00.

This book is what it claims to be—a short handbook of the analysis of oils. It is intended as a concise manual primarily for beginners; therefore it is an excellent textbook for chemical engineering students. It also enables engineers to acquire a practical knowledge, to make specifications, and to test and distinguish ordinary oils. For these purposes this book is entirely satisfactory: it is clear, simple, practical, and explicit; it gives tables and formulas and refers to the original sources.

In limiting this concise handbook to the practical testing of ordinary mineral, animal, and vegetable oils according to official methods, the author has properly omitted all that is theoretical, technological, or contentious. Shale oil, casinghead gasoline, and antiknock gasoline are also omitted. The consideration of fuel oil is given on page 58, and not where indicated in the table of contents and in the index.

In general, the book is needed, it fulfils that need, it is attractively presented, and it is practical.

RESTON STEVENSON

Technical Methods of Ore Analysis. By Albert H. Low. 10th edition. 348 pages. John Wiley & Sons, Inc., New York, 1927. Price, $3.50.

The tenth edition, making the total of fifteen thousand copies printed, sufficiently shows the practical value of Doctor Low's well-known book. It is popular because it meets the needs of many who desire information about methods in common use in mine and smelter laboratories, without much chemical theory.

Well-selected methods are described in detail to the easy comprehension of those familiar with laboratory language. Methods for analysis of steel, some nonferrous alloys, fuel, boiler water, and other things not included under the title are also given.

The author "aims to give instructions that will produce good technical results if carefully followed, without embodying too large a mass of alternate methods that are apt to be confusing." The instructions are more empirical than scientific, and warning is given that departure from the prescribed details may be disastrous. Many of the methods are followed by notes in smaller type, explaining the principal reactions in terms of molecules and "hard round atoms."

Although the tenth edition is described as a revision, it is practically a reprint of the ninth so far as analytical methods are concerned. A new section, including 10 pages of Instructions to Students, 4 pages on Calculations, and 6 pages on Standard Solutions, replaces Remarks to Instructors and Outlines of Methods for Students' Use, that were in the ninth edition. The other 348 pages are substantially the same as in the ninth.

As a handy book for mine, smelter, and commercial chemists engaged in the evaluation of ores and metals, this volume is to be highly commended. One is more doubtful about its real value to students beginning quantitative inorganic analysis, even though it is supposed to be used supplementary to other instruction.

ALBERT M. SMOOT

American Lubricants. By L. B. Lockhart. 3rd edition. 408 pages. The Chemical Publishing Co., Easton, Pa., 1927. Price, $5.00.

The author is evidently a refinery man; therefore the information in his book is presented in a manner which makes it most useful to those engaged in the manufacture and testing of lubricants. Starting with a concise statement of the petroleum resources of this country, the author outlines briefly some of the standard refining processes and describes their products. The requirements of some of the most important problems in lubrication are discussed, those dealing with steam-cylinder, railway, and textile-mill lubrication being treated most fully. In the opinion of the reviewer the sections dealing with internal-combustion engine and, particularly, aircraft power-plant lubrication could be improved by being brought up to date. A large portion of the book is devoted to descriptions of the various standard specifications for lubricants and the test methods employed for their inspection, and represents an extensive compilation which should prove valuable to the lubricant manufacturer and purchaser alike.

D. P. BARNARD, 4TH

Steel and Its Heat Treatment. By D. K. Bullens. 3rd edition. 564 pages. John Wiley & Sons, Inc., New York, 1927. Price, $5.00.

If a fairly well-educated and intelligent man found himself on a desert island and in charge of a heat-treatment plant (a combination of circumstances a little hard to imagine), he would find himself well equipped if he had brought with him Bullens' "Steel and Its Heat Treatment."

This book is a thoroughly practical one and well and clearly written. It does not require any highly technical metallurgical skill to be read and used to advantage. It is divided into three parts: Section 1, covering the metallurgical phase; Section 2, the engineering phase; and Section 3, the production phase. The author has drawn upon his long practical experience and has supplemented this with material from outstanding publications and researches of others. He does not indulge in theoretical discussions or controversial points. The first section deals with underlying principles and general metallurgy. In the second many valuable data are given in regard to specific types of alloy steels, including the effects of the various alloy additions. The third section should be found particularly useful, for if it is read and understood the heat treater will not frequently have to ask forgiveness for leaving undone those things which he ought to have done and doing those things which he ought not to have done.

The book is well illustrated with excellent photomicrographs, tables, and graphs, and will prove useful both as a source of standard data in regard to the properties of engineering materials and in providing information as to how these properties may be obtained both experimentally and commercially in quantity production.

J. A. Mathews

Pyrometry. By William P. Wood and James M. Cork. 207 pages, illustrated. McGraw-Hill Book Co., Inc., New York, 1927. Price, $3.00.

The book was compiled principally as a textbook for college students. It starts off with a chapter on temperature scales followed with one on mercurial and gas thermometers. The elementary theory of thermocouples and methods of connecting them to millivoltmeters and potentiometers are well covered. Errors due to extraneous resistances are exemplified by actual problems. Cold-junction errors and many methods of compensating for same are described. In addition to indicating and recording pyrometers the authors have included automatic signaling and controlling devices and illustrated same with excellent wiring diagrams and illustrations. A chapter on refractory protecting tubes followed by many useful tables in the appendix renders the book useful not only as a textbook but as a reference book as well.

A System of Qualitative Analysis for the Rare Elements. By Arthur A. Noyes and William C. Bray. 536 pages. The Macmillan Company, New York, 1927. Price, $5.00.

When supreme authorities put the results of a lifetime of work in the form of a book, giving not only the results of their investigations but also their own critical analysis of the procedures and experimental data employed during their investigations, it seems quite unnecessary, if not impossible, to review its contents critically. However, chemists who are at all interested in the detection of the rare elements will want to know what this important book contains. The rare elements of yesterday are the commonplaces of today, and a knowledge of their properties and reactions which will enable detection and accurate separation is constantly becoming more important not only for the student but in a commercial sense.

As stated in the preface, "In this book are presented the results of an experimental investigation, carried out during the past thirty years by the authors with the aid of a large number of their associates, research assistants, and graduate students, first at the Massachusetts Institute of Technology and later at the California Institute of Technology and the University of California." The book gives "in detail a system of qualitative analysis that includes nearly all the metal-forming elements and makes possible their detection when present in quantity as small as one or two milligrams even when associated with other elements."

"This publication has three purposes in view. The first is that already indicated—to supply the chemical analyst, as is done in Part I of the book, with a system of procedure which will enable him to detect the various elements in all their combinations by as simple a process as possible.*** In Part II of the book, the numerous experimental investigations that have been carried out in developing this system of analysis" is briefly recorded. The authors state, "in these pages an amount of experimental material which, if presented in journal articles of the usual discursive type, would fill a large volume," is included. "The third purpose is to provide for students a course in advanced inorganic chemistry that will afford the man acquaintance with the chemical properties of the rarer elements, many of which have now become highly important in industry, in analytical practice, and in scientific research." Suggestions to teachers or students as to ways in which the analytical scheme may best be approached are included, and appendixes contain tables pertinent to the subject matter of the text, of which "reactions of the elements" should be specially mentioned.

The detailed methods of analyses of the various groups are supplemented by tabular outlines which enable the students to follow the procedure as a whole before studying the details of the various steps. The work is replete with explanatory footnotes and full acknowledgment and references to publications are also given.

The book has an excellent index and its mechanical structure leaves little to be desired.

Wm. Hoskins

Lubricating Greases. By E. N. Klemgard. 198 pages. The Chemical Catalog Company, Inc., New York, 1927. Price, $5.50.

This is a welcome summary of the chemists' contribution to the field of grease lubrication. According to the preface, the author has aimed to bring together, without any considerable expansion, a substantially greater body of facts than has been done in previous books and at the same time present this material in a manner easy to grasp. The author has been successful and has collected within a small compass a great quantity of material hitherto inaccessible. The volume contains an interesting and useful patent list, including a short abstract of each patent. A valuable feature of the book is the inclusion of practically all the latest specifications relating to lubricating greases.

Especial attention should be called to the description of sulfur-base oil in Chapter VII, which gives information found nowhere else in the technical literature.

No one can peruse the volume without being impressed by the magnitude of the task undertaken and experiencing a feeling of gratitude toward the author. *Multum in parvo* very fittingly describes this work.

Geo. H. Anderson

Industrie der Holzdestillations-Produkte. Technische Fortschrittsberichte. Fortschritte der Chem. Technologie in Einzeldarstellungen. Band XV. By G. Bugge. 206 pages. Theodor Steinkopff, Dresden and Leipzig, 1927. Price, paper, 15 marks; bound, 16.50 marks.

This book is one of the series of reports on progress in chemical technology edited by Professor Rassow. Since this is the first of the series on wood distillation, it has been found necessary to report more than recent progress in order to make a well-rounded publication, but most of the book is confined to new material published within the last ten or fifteen years.

The book is very complete and accurate in its literature references, including patents, and at least a brief notice is given of practically all the published articles and books on wood distillation or allied subjects within the period covered. The author has not hesitated to include other subjects of interest to the wood distiller, such as the distillation of sulfite and soda pulp waste liquors and the synthetic manufacture of products which were formerly made only by wood distillation. Little is said about resinous wood distillation, however, and nothing about resinous products obtained from wood by other than the destructive distillation process. There is an up-to-date list of the chemical compounds which have been identified in wood-distillation products. The literature references are, however, frequently to some later article which has simply repeated the information, rather than to the original article where the identification of the compound was first described.

Although the book is an excellent literature study, it is disappointing as an accurate record of the technological progress, since it is impossible to tell whether the new processes described have simply been worked on a laboratory scale or have been tried out on a large scale and found unsatisfactory, or whether they are really a part of technological progress with successful commercial operation as a proof. Some new commercial developments are not mentioned in the book, probably because they have not yet been described in the literature. As examples of these faults Hawley's method for refining crude wood alcohol, mentioned on page 116, has never even been tried commercially; and the Seaman process, described on page 88, has been tried commercially without success; while the artificial drying of distillation wood and the commercial distillation of hardwood tar, barely mentioned in the text, are successful commercial developments of the last ten or fifteen years.

L. F. HAWLEY

Optische Methoden der Chemie. BY FRITZ WEIGERT. 632 pages. 341 illustrations, 16 plates. Akademische Verlagsgesellschaft, m. b. H. Leipzig, 1927. Price, paper, 36 marks; bound, 38 marks.

Here is gathered in one book information regarding many instruments and their technic. The writer calls attention in the preface to the fact that many excellent instruments are available and admits that even an inexperienced person can by following directions accomplish a fair degree of success. Monographs relating to special devices also furnish particulars that enable the user of the instruments to proceed intelligently. But the reader is cautioned not to depend on a casual optical observation or measurement, for only through critical methods can accuracy be assured.

After general remarks on optical instruments and their use, the reader is introduced to the various standard recording and measuring instruments, and their operation is explained in text and by many diagrams. The chapter on light rays is very complete and the effect of various filters is graphically portrayed. Photographic methods are discussed, but the paragraph on photography in natural colors is disappointing because of its brevity. The spectroscope naturally deserves and receives exhaustive treatment, while photometry is not neglected. Colorimetry, the ultra-microscope, and various forms of refractometers are treated, and the phenomena of polarized light and its relation to the saccharimeter are explained.

To one familiar with the German language this book should be very useful. It is to be regretted that no English translation is available.

CHARLES P. TITUS

Lehrbuch der chemisch-technischen Wirtschaftslehre. BY ALBERT SULFRIAN. xi + 283 pages. 63 illustrations. Ferdinand Enke, Stuttgart, 1927. Price, paper, 16.50 marks; bound, 18.30 marks.

This book, which the author has chosen to call a textbook of chemico-technical economics, is one of the few which have appeared in this field and is of extraordinary interest. Chaplin Tyler's "Chemical Engineering Economics," published last year, was likewise a pioneer effort in bringing together and discussing some of the problems of economic choice which must be made in carrying a chemical process from the small-scale, laboratory stage to the final goal of profitable commercial operation. While having more or less the same underlying idea of economy and efficiency in chemical projects, the two books differ widely in choice of subject matter and in treatment.

The text is divided into four major parts—namely, analytical laboratory work, synthetic laboratory work, technical production laboratory work, and operation management. Under each of these headings a large number of individual items are discussed in an interesting and often illuminating manner.

In the part devoted to analytical laboratory work the discussion revolves around two themes—viz., the operation of an analytical laboratory with economy and utmost efficiency, and the operation of such a laboratory to secure its maximum effectiveness in solving the problems of economic choice which must be made in chemical projects. Perhaps in the end these two aims are identical, for analytical chemistry is but a handy and powerful tool. An idea of the topics discussed may be indicated by random choice of a few sampling standards, the effect of deleterious substances on the value of materials, analytical apparatus, economic and technical aids in analysis, cost of analytical work, care of platinum, recovery of reagents, means of securing accuracy in analytical work, calculation of analytical results.

Part II deals with the synthetic laboratory work in an unusual way. Only a few pages are devoted to methods of synthesis. Most of this section is given to discussion regarding chemical monographs and chemical journals, economic and statistical survey of chemical industries, patents, priority of discovery, and similar topics.

Part III strikes squarely into the technical and economic phases of chemical engineering, with discussions of raw materials, choice and application of energy, continuity of processes, conditions of reaction, reduction of losses, by-products, etc.

With Part IV we come to the chemical process in operation. There is first reviewed the fundamental relationships of energy in its various forms. Then follows a most interesting section on correct and incorrect practices in chemical plants, this section being taken largely from the Achema-Jahrbuch of 1925. Materials of construction, material handling, transportation, automatic control of processes, cost calculations, and a variety of related topics in plant management conclude the book.

As an effort to assemble and discuss the many economic considerations which are involved whenever the attempt is to be made to apply the science of chemistry to the problems of industry, the author is to be congratulated in what he has accomplished in this book. It is heartily recommended to all interested.

HARRY A. CURTIS

Der tönende Film. Das Triergon-Verfahren und seine Anwendungsmöglichkeiten. Tagesfragen aus dem Gebieten der Naturwissenschaften und der Technik. Heft 89. BY JO ENGL. 98 pages. Friedrich Vieweg & Sohn Aktien-Gesellschaft, Braunschweig, 1927. Price, paper, 6.50 marks.

This is a very clear summary of the author's and his coworkers' contribution to the problem of recording sound on photographic film and the general methods that are employed.

One chapter is devoted to the discussion of each of the fundamental pieces of apparatus and to the several factors involved in the process, such as the microphone, the amplifier, the glow lamp, the optical system, the camera mechanism, the acoustics of the recording studio, and the arrangement of microphones with respect to the source of sound to be recorded.

The author shows that for true reproduction of the recorded sound it is necessary that the gamma of the negative and the gamma of the print shall be of a value such that their product is unity. He points out that by overdeveloping the negative and adjusting the printing light intensity so that the proper development time for the positive print is about $4^1/_2$ minutes a linear relationship may be obtained between the variation in light produced by the negative sound record and the transmission of the positive sound record.

A short chapter is devoted to analysis of sound. The vowel sounds have a comparatively simple structure, while some of the consonant sounds have a very complex structure.

C. E. K. MEES

Latex—Sein Vorkommen, Seine Gewinnung, Eigenschaften, sowie Technische Verwendung. BY ERNEST A. HAUSER. Appendix, Patent Review, compiled by CARL BOEHM VON BOERNEGG. 243 pages. $6^1/_4 \times 9^1/_4$ inches, with 74 illustrations. Theodor Steinkopff, Dresden and Leipzig, 1927. Price, paper, 16 marks; bound, 17.50 marks.

This volume is the first to summarize the properties of one of the most important of all natural products, since latex is the basic raw material of the entire rubber industry. It is therefore very welcome to the technologists working in this growing field.

The monograph is divided into fifteen chapters, starting with a historical introduction; the next eight chapters review the production and biological and chemical properties of latex, and the remaining six chapters are devoted to the comparatively new methods for the industrial utilization of latex. Particular attention is directed to Chapter 4, in which Doctor Hauser reviews his work with the micromanipulator in the study of the precise physical condition of the latex globules. This important contribution has already received widespread attention and has greatly stimulated research with latex. The appendix, containing a bibliography of the patent literature on the subject, is very complete so far as the foreign patent literature is concerned, but is not so complete as might be desired in connection with the patents issued in the United States.

The book is very well arranged and exceptionally comprehensive. The chapters devoted to the more recent, direct industrial application of latex are very satisfactory when it is considered that the information is drawn largely from the patented art and from the scattered technical literature of all countries. An exceptional familiarity with the subject must be accredited to the author as a reward for his extensive travels and personal contact with the various technologists working on this subject.

It is hoped that this monograph will act as a stimulus for the preparation of others along this line and that Doctor Hauser himself will carry the work into new editions as rapidly as progress warrants them.

R. P. ROSE

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Annual Report of the Director of the Bureau of Foreign and Domestic Commerce to the Secretary of Commerce for the Fiscal Year Ended June 30, 1927. 57 pp. Paper, 10 cents.

Bureau of Education

Laboratory Layouts for the High-School Sciences. A. C. Monahan. *Bulletin*, 1927, 22. 31 pp. Paper, 10 cents.

Bureau of Mines

Annual Report of the Director of the Bureau of Mines to the Secretary of Commerce for the Fiscal Year Ended June 30, 1927. 48 pp. Paper, 10 cents.

Clay in 1926. Jefferson Middleton. *Mineral Resources of the United States, 1926.* Part II, pp. 151–8.

Coal-Mine Fatalities in September, 1927. W. W. Adams. *Reports of Investigations* 2835. 8 pp.

Coal-Mine Fatalities in the United States, 1926. W. W. Adams. *Bulletin* 283. 121 pp. Paper, 15 cents.

Consumption of Explosives in October, 1927. W. W. Adams. *Reports of Investigations* 2842. 9 pp.

Consumption of Explosives in September, 1927. W. W. Adams. *Reports of Investigations* 2836. 9 pp.

Development, Mining, and Handling of Ore in Folded and Faulted Areas, Red Iron Ore Mines, Birmingham District, Alabama. W. R. Crane. *Technical Paper* 407. 27 pp. Paper, 15 cents.

Development of Some Fundamentals in the Ferric Sulfate–Sulfuric Acid Process. F. S. Wartman and H. E. Keyes. *Reports of Investigations* 2839. 11 pp.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1926. Mine Report. J. P. Dunlop. *Mineral Resources of the United States, 1926.* Part I, pp. 81–6. Paper, 5 cents.

Gypsum in 1926. R. M. Santmyers and Jefferson Middleton. *Mineral Resources of the United States, 1926.* Part II, pp. 141–50. Paper, 5 cents.

Lime in 1926. A. T. Coons. *Mineral Resources of the United States, 1926.* Part II, pp. 183–93. Paper, 5 cents.

Magnetic Concentration of Iron Ores of Alabama. Oscar Lee, B. W. Gandrud, and F. D. De Vaney. *Bulletin* 278. 75 pp. Paper, 20 cents.

Manganese and Manganiferous Ores in 1926. J. W. Furness. *Mineral Resources of the United States, 1926.* Part I, pp. 141–79. Paper, 10 cents.

Natural-Gas Gasoline in 1926. G. R. Hopkins. *Mineral Resources of the United States, 1926.* Part II, pp. 159–68. Paper, 5 cents.

Natural Gas in 1926. G. R. Hopkins. *Mineral Resources of the United States, 1926.* Part II, pp. 175–82. Paper, 5 cents.

Permissible Explosives Defined. C. E. Munroe. *Circular* 6051. 2 pp.

Safe Practices at Oil Derricks. H. C. Miller. *Technical Paper* 419. 69 pp. Paper, 15 cents.

Safety Measures Save Lives in Colorado Explosion. E. H. Denny. *Reports of Investigations* 2838. 6 pp.

Silica in 1926. *Mineral Resources of the United States, 1926.* Part II, pp. 169–73. Paper, 5 cents.

Some Phases of Accident Prevention in Industry. A. L. Murray. *Circular* 6055. 4 pp.

The Carburetion of Combustible Gas with Butane and Propane-Butane Mixtures with Particular Reference to the Carburetion of Water Gas. W. W. Odell. *Reports of Investigations* 2840. 12 pp.

The Study of an Intermediate Base Crude Oil. H. M. Smith. *Reports of Investigations* 2837. 9 pp.

Bureau of Standards

Annual Report of Director of the Bureau of Standards for the Fiscal Year Ended June 30, 1927. *Miscellaneous Publication* 81. 47 pp. Paper, 10 cents.

Calibration and Adjustment of the Schopper Folding Tester. F. T. Carson and L. W. Snyder. *Technologic Paper* 357. 16 pp. Paper, 10 cents.

Certificate of Analysis of Standard Sample No. 80—Soda Lime Glass. 4 pp.

Controlling the Consistency of Enamel Slips. W. N. Harrison. *Technologic Paper* 356. 34 pp. Paper, 15 cents.

Density and Electrical Properties of the System Rubber–Sulfur. Part I—Density of Rubber-Sulfur Compounds. A. T. McPherson. Part II—Electrical Properties of Rubber-Sulfur Compounds. H. L. Curtis, A. T. McPherson, and A. H. Scott. *Scientific Paper* 560. 36 pp. Paper, 15 cents.

Density of Hot-Rolled and Heat-Treated Carbon Steels. H. C. Cross and E. E. Hill. *Scientific Paper* 562. 16 pp. Paper, 10 cents.

Manufacture of Lime. Superseding Technologic Paper 16 under same title. *Circular* 337. 104 pp. Paper, 45 cents.

Standards and Specifications in the Wood-Using Industries. Nationally Recognized Standards and Specifications for Wood and Manufactures Thereof, Including Paper and Paper Products. *Miscellaneous Publication* 79. 349 pp. Price, $1.50.

Tarnish-Resisting Silver Alloys. Louis Jordan, L. H. Grenell, and H. K. Herschman. *Technologic Paper* 348. 38 pp. Paper, 15 cents.

The Testing of Rubber Goods. *Circular* 38. 83 pp.

Department of Agriculture

An Apparatus for the Rapid Vaporization of Carbon Disulfide. C. A. Weigel, H. D. Young, and R. L. Swenson. *Circular* 7. 8 pp. Paper, 5 cents.

Chemistry in the United States Department of Agriculture. 36 pp.

Dairy By-Products and Methods of Utilizing Them. *Separate* 939 from Yearbook of Agriculture, 1926. 5 pp.

Experiments with Sodium Chlorate and Other Chemicals as Herbicides for Field Bindweed. W. L. Latshaw and J. W. Zahnley. *Journal of Agricultural Research*, 35 (October 15, 1927), 757–67.

Report of the Chief of the Bureau of Chemistry. 34 pp.

Report of the Chief of the Bureau of Soils. 8 pp.

Report of the Insecticide and Fungicide Board. 8 pp.

Report of the Secretary of Agriculture, 1927. 90 pp. Paper, 10 cents.

Skim Milk in Dry Form Has Various Uses. *Separate* 940 from Yearbook of Agriculture, 1926. 3 pp.

The Production of Certain Enzymes by ***Bacterium pruni.*** S. L. Jodidi. *Journal of Agricultural Research*, 35 (August 1, 1927), 219–21.

The Toxic Constituent of Richweed or White Snakeroot (***Eupatorium urticaefolium***). J. F. Couch. *Journal of Agricultural Research*, 35 (September 15, 1927), 547–76.

The Relative Assimilation by Dairy Cows of Clover and Alfalfa Hays and of Rations of Different Calcium and Phosphorus Content. W. A. Turner, T. S. Harding, and A. M. Hartman. *Journal of Agricultural Research*, 35 (October 1, 1927), 625–35.

Department of Commerce

Fifteenth Annual Report of the Secretary of Commerce for the Fiscal Year Ended June 30, 1927. 310 pp. Paper, 30 cents.

Geological Survey

Cephalopods from the Lower Part of the Cody Shale of Oregon Basin, Wyoming. J. B. Reeside, Jr. *Professional Paper* 150-A. 19 pp.

Laboratory Tests on Physical Properties of Water-Bearing Materials. N. D. Stearns. *Water-Supply Paper* 596-F. 56 pp.

The Cephalopods of the Eagle Sandstone and Related Formations in the Western Interior of the United States. J. B. Reeside, Jr. *Professional Paper* 151. 87 pp. Paper, 60 cents.

The Gilbert District, Nevada. H. G. Ferguson. *Bulletin* 795-F. 21 pp. Paper, 5 cents.

The Scaphites, an Upper Cretaceous Ammonite Group. J. B. Reeside, Jr. *Professional Paper* 150-B. 20 pp. Paper, 10 cents.

Upper Triassic Marine Invertebrate Faunas of North America. J. P. Smith. *Professional Paper* 141. 262 pp. Paper, $1.50.

Public Health Service

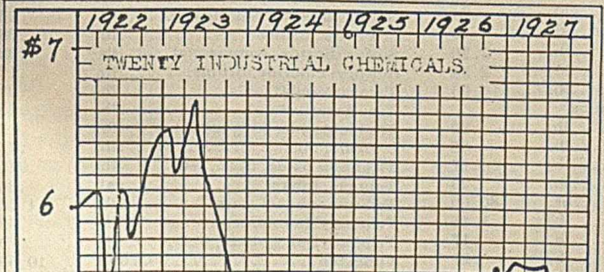
Studies on Oxidation-Reduction. XII—A Note on the Schardinger Reaction (in reply to Kodama). W. M. Clark, Barnett Cohen, and M. X. Sullivan. Supplement 66 to *Public Health Reports.* 10 pp. Paper, 5 cents.

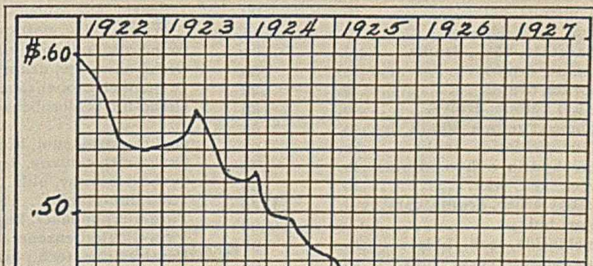
Studies of the Efficiency of Water Purification Processes. I—Results Obtained from a Preliminary Study of the Cincinnati and Louisville Municipal Filtration Plants. II and III—Results Obtained from a Collective Survey of Seventeen Municipal Filtration Plants. *Bulletin* 172. 423 pp. Paper, $1.00.

MARKET REPORT—DECEMBER, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON DECEMBER 15

Acetanilide, tech., bbls.	lb.	.21
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.12
Acetophenetidine, bbls.	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.38
56%, c/1. bbls.	100 lbs.	6.34
Glacial, c/1. bbls.	100 lbs.	11.92
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.58
Boric, bbls.	lb.	.08½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums.	lb.	.37
Cinnamic, 5-lb. cans.	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.44
Cresylic, pale, drums	gal.	.70
Formic, 85%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.57
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.36
Lactic, 22%, dark, bbls.	lb.	.05½
66%, light, bbls., wks.	lb.	.26
Mixed, tanks, wks.	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Nitric, C. P., cbys	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.08
Picramic, bbls.	lb.	.50
Picric, bbls. c/l.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.86
Salicylic, tech., bbls.	lb.	.37
Stearic, d. p., bbls. c/l.	lb.	.11¼
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.00
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.36
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	3.70
Amyl, 10%, Imp. drums.	gal.	1.40
Butyl, drums, c/l. wks.	lb.	.19¼
Cologne Spirit, bbls.	gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs	gal.	.48
No. 1, Comp. denat., drs.	gal.	.52
Isoamyl, drums	gal.	2.50
Isobutyl, ref., drums	lb.	...
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums.	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.25
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.10
Soda, bbls., wks.	100 lbs.	3.75
Aluminum, metal, N. Y.	lb.	.26
Aluminum chloride, anhyd., drums	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.23
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.75
Aminoazobenzene, 110-lb. kgs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.11
Ammonia water, 26°, drums, wks.	lb.	.03
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls	100 lbs.	5.25
Lump, casks	lb.	.11¼
Iodide, 25-lb. jars.	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs.	lb.	.35
Persulfate, cases	lb.	.27½
Phosphate, dibasic, tech., bbls	lb.	.18
Sulfate, bulk, wks.	100 lbs.	2.45
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums.	gal.	1.90
Aniline oil, drums.	lb.	.15¼
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls	lb.	.90
Antimony, metal.	lb.	.11¼
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls.	lb.	.16¼
Salt, Dom., bbls	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls	lb.	.15
Vermilion, bbls.	lb.	.37½
Tartrolactate, bbls	lb.	.45
Argols, red powder, bbls	lb.	.08
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases.	lb.	.10½
White, c/l. kegs	lb.	.04
Asbestine, bulk, c/l	ton	16.00
Barium carbonate, bbls., bags, wks	ton	47.50
Chloride, bags, wks	ton	55.00
Dioxide, bbls., wks	lb.	.13
Hydroxide, bbls	lb.	.04½
Nitrate, casks	lb.	.08
Barium sulfocyanate, 400-lb. bbls	lb.	.27
Barytes, floated, 350-lb. bbls., wks	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzene, pure, tanks, mills.	gal.	.21
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums.	lb.	.25
Beta-naphthol, bbls	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	2.00
Bismuth nitrate, 25-lb. jars.	lb.	1.85
Oxychloride, boxes.	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	2.20
Blanc fixe, dry, bbls	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.04½
Bordeaux mixture, bbls.	lb.	.11
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.47
Bromobenzene, drums.	lb.	.50





Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.55
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.05
Calcium acetate, bags	100 lbs.	3.50
Arsenate, bbls.	lb.	.07½
Carbide, drums	lb.	.05½
Chloride, drums, wks.	ton	21.00
Cyanide, 100-lb. drum	lb.	.30
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	52.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.62
Jap., cases	lb.	.60
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.63
Carbazole, bbls.	lb.	.15
Carbon, activated, drums	lb.	.05
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls.	lb.	.18
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bgs.	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine U. S. P., 5-lb. bot.	lb.	1.75
Chlorine, liq., c/l., cyl.	lb.	.04
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° sol., bbls.	lb.	.05½
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.00
Cod-liver oil, bbls.	bbl.	41.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lb.	12.90
Copper carbonate, bbls.	lb.	.16¼
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, c/l., bbls.	100 lb.	5.00
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.26½
Cyanamide, bulk, N. Y.	Ammon. unit	1.67½
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.25
Dibutyl phthalate, drums, wks.	lb.	.29½
Diethylaniline, drums	lb.	.55
Diethylene glycol, l. c. l. lots, drums	lb.	.20
Carload lots, drums	lb.	.15
Diethylphthalate, drums	lb.	.24
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.31
Diphenylamine, bbls.	lb.	.45
Diphenylguanidine, bbls.	lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.10
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.15
Ethyl acetate, 85%, drums	gal.	.90
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene dichloride, tanks	lb.	.06
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.30
Ethyl ether, drums, cars	gal.	1.79
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07½
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.09
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drs., c/l.	lb.	.17½
Glauber's salt, bbls.	100 lbs.	1.05
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.21
G salt, bbls.	lb.	.50
Hexamethylenetetramine, tech., drums	lb.	.62
Hydrogen peroxide, 25 vol., bbls.	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	110.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lb.	6.25
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls.	lb.	.14
Oxide, litharge, bbls.	lb.	.08¾
Red, bbls.	lb.	.09¾
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.09
Sulfate, bbls.	lb.	.08¼
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.45
Lithopone, bbls.	lb.	.06⅛
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	37.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.58
Mercury, flasks, 75 lbs.	flask	128.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, pure, tanks	gal.	.50
Denaturing grade, tanks	gal.	.75
Methyl acetone, drums	gal.	.88
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.05
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.10¼
Double, bbls.	lb.	.09
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.13
China wood, bbls.	lb.	.15¼
Coconut, Ceylon, tanks	lb.	.08⅝
Cod, N. F., tanks	gal.	.63
Corn, crude, tanks, mills	lb.	.09¼
Cottonseed, crude, tanks	lb.	.09¼
Lard, edible, bbls.	lb.	.16¾
Linseed, bbls.	lb.	.096
Menhaden, crude, tanks	gal.	.46
Neat's-foot, pure, bbls.	lb.	.18¼
Oleo, No. 1, bbls.	lb.	.18½
Olive oil, denat., bbls.	gal.	1.60
Foots, bbls.	lb.	.09¾
Palm, Lagos, casks	lb.	.08
Peanut, crude, tanks	lb.	.12
Perilla, bbls.	lb.	.14
Rapeseed, bbls., English	gal.	.88
Red, bbls.	lb.	.09
Soy bean, crude, bbls.	lb.	.09¾
Sperm, 38°, bbls.	gal.	.84
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.35
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.17
Ortho-toluidine, bbls.	lb.	.29
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.15
Para-dichlorbenzene	lb.	.17
Paraldehyde, tech., drums	lb.	.27
Para-formaldehyde, cases	lb.	.45
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.32
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.30
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.40
Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums	lb.	.17
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	95.00
Potash, caustic, drums	lb.	.07⅞
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅝
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.11
Permanganate, drums	lb.	.15¼
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums	gal.	1.50
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.30
Rochelle salt, bbls., U. S. P.	lb.	.23
R salt, bbls.	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.41⅞
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.10
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.42
Carbonate, sal soda, bbls.	100 lbs.	1.30
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.08¾
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.45
Nitrite, bbls.	lb.	.08½
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.12
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04¾
Stannate, drums	lb.	.48½
Sulfate, anhyd., bbls.	lb.	.02¼
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.40
Thiosulfate, reg., crys., bbls.	lb.	.02½
Tungstate, kegs	lb.	.85
Strontium carbonate, bbls.	lb.	.08
Nitrate, bbls.	lb.	.08¾
Strychnine alkaloid, 100 oz., powd.	oz.	.56
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks.	ton	19.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, commercial, cyl.	lb.	.08½
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand	lb.	.58
Tin bichloride, 50% sol., bbls.	lb.	.17¾
Oxide, bbls.	lb.	.75
Titanium oxide, bbls., wks.	lb.	.40
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.75
Tungsten	WO_3 unit	10.50
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.35
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	100 lbs.	6.40
Zinc ammonium chloride, bbls.	lb.	.05¾
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls.	lb.	.07⅜
Stearate, bbls.	lb.	.19
Zinc dust, bbls., kegs, c/l.	lb.	.09