Industrial and Engineering Chemistry

Vol. 21, No. 1

January 1, 1929

An Unpardonable Abuse

SUCCESS is always capitalized, sometimes by those who have contributed to it, but often by those who, though having no part in it, would subvert it to their own uses. The accomplishments of chemistry have made things chemical attractive to many who prey upon the gullible, and a flagrant misuse of the word "chemist" has just come to our notice.

The *Brooklyn Daily Eagle* for December 13 carried a San Francisco despatch with the information that "the United Retail Chemists Company has been formed as the result of the absorption of the Neve Drug Stores by the United Cigar Stores Company of America." Details were then given with respect to stock issues, etc.

If those responsible for the choice of the name indicated have any regard for propriety, they will immediately seek another appellation for their company, obviously organized as venders of general merchandise. If those who sell the multitude of things now found in the modern drug stores are to be allowed to call themselves "retail chemists," then certainly those who sell drugs only should be called "retail doctors," and where dentifrices and tooth brushes are handed over the counter we shall expect to find "retail dentists." The whole thing is utterly absurd, and vigorous steps must be taken to have all and sundry understand that the word "chemist" rightfully belongs to an ancient and honorable calling. To see "chemist" used as in the name of this company is a positive shock, for we have been led to believe that one of the results of the war was the opening of the eyes of the people to the necessity and importance of chemists in the defense and maintenance of the country, in the support and creation of industry, in contributions to public health and the fight against disease, and as leaders in the multiplication and preservation of our harvests. Surely these men are not retail chemists.

In England, the chemical profession has been distinctly embarrassed by the appropriation of the name "chemist" by those who are pharmacists, and has been helpless to prevent this misuse of the term. Pharmacy is a profession kindred to, but distinct from chemistry, and the American Pharmaceutical Association, which has so much to its credit, will be as incensed as we are over the misuse of the name "chemist." Here and there one occasionally finds a drug store on the windows of which is inscribed the name of some member of the staff as "chemist." This man may indeed be a chemist, but more often he is not and such a misstatement is another reprehensible practice. Even this is quite a different thing from what is involved in the term "retail chemists."

The time to stop this abuse is right now. The executives of the Neve Drug Stores and the United Cigar Stores Company of America must be made to see that common decency demands the withdrawal of the name, "The United Retail Chemists Company," and the substitution therefor of some designation that really describes what they intend to do. We must not permit a situation comparable to that in England to develop here.

Greetings from Our Newly Elected Officers

Irving Langmuir, President

S. W. Parr, President-Elect

I would like to express to the members of the American Chemical Society my appreciation of the honor they have done me by electing me to the presidency of this great scientific organization. The rapidity with which chemistry has advanced in America during recent years has exceeded the fondest hopes of our leaders of fifteen or twenty years ago. A basic factor in this progress is the fundamental chemical research which has been carried on so actively under the leadership of the American Chemical Society. Fortunately, research begets research. We can look forward to rapidly accelerating chemical growth for many years to come. It is a deep inspiration to me to feel that as President of the American Chemical Society I will be privileged to aid in this further stimulation of the research spirit.

Irving Langmuir

My greetings to the American Chemical Society for the year 1929, and congratulations on the election of Doctor Langmuir to the presidency. This choice of the Council pleases me greatly. I deeply appreciate the honor of being chosen to the newly constituted office of President-Elect.

S. W. Parr

Thanks, Northeastern Section

WITH an official communication to the SOCIETY, the Northeastern Section has transmitted a check for one thousand dollars to be added to the endowment fund of the AMERICAN CHEMICAL SOCIETY. This money is a part of the unexpended balance remaining from the funds received by the general committee at the Swampscott meeting and follows a precedent established a few years ago by the Washington Section, when it set aside a surplus from the spring meeting in the interest of a national headquarters building in Washington. Additions to the endowment fund have been made by the Philadelphia, Delaware, Richmond, and Detroit Sections where income from registration greatly exceeded expectations and generous local support was given to the national meeting.

The generous action of the Northeastern Section has been reported in the *Nucleus*. It is good news for the entire SOCIETY, the thanks of which we are glad to express.

Improved Service

WITHOUT regard to the way in which the work of chemistry may be classified or subdivided, analytical chemistry is vital to all. Its accomplishments may not be spectacular, much of it seems routine, and usually the part it contributes to the success of important work is unnoticed. The contributions of analytical chemistry may not be appreciated by the plant manager, nor by the director of the laboratory, nor the chief of the bureau, but every chemist knows to what extent we depend upon accuracy in this field of work. For a number of years the leaders in this important part of our science have stressed the need for the segregation of articles primarily of importance to the analyst, pointing out the greater ease with which they could then be made available to him and the wider utility they might be expected to have in every field of chemistry. It has not been possible heretofore to meet this need. The matter has been the subject of many conversations with those interested, and more recently we have devoted much thought to the possibilities. Several plans have been discussed with the Executive Committee of the SOCIETY and a long contemplated step has now been authorized by the Directors, who have reached their decision not alone on the basis of service to be rendered but upon financial grounds as well.

Beginning with the current year, articles on analysis which ordinarily would appear in INDUSTRIAL AND ENGINEERING CHEMISTRY will be segregated in an Analytical Edition of INDUSTRIAL AND ENGINEERING CHEMISTRY, which is to appear quarterly. This will go without charge to all those receiving INDUSTRIAL AND ENGINEERING CHEMISTRY, but it will also have a separate subscription list. This is for the purpose of making it available to the many analysts of the country who are not members of the AMERICAN CHEMICAL SOCIETY, and whose principal interest is in analytical chemistry. Teachers who may wish to do so can secure copies of the Analytical Edition for the use of students, and directors of industrial laboratories may wish to place separates in the hands of the analytical staff.

For the present the amount of space to be devoted to analytical articles will be no greater than the average in INDUSTRIAL AND ENGINEERING CHEMISTRY for the past few years. It is simply a segregation under another cover of articles dealing with analysis. While it will have its own pagination, the format will be identical with INDUSTRIAL AND ENGINEERING CHEMISTRY, so it may be bound with the industrial edition or separately as may be preferred.

With the initiation of this new service, INDUSTRIAL AND ENGINEERING CHEMISTRY still more firmly establishes itself as a unique publication. Industry and chemical technology are served by our industrial edition, which appears the first of every month. The news of chemistry reaches you through the twenty-four issues of the News Edition, and now analytical methods and improvements in analytical apparatus will come to you quarterly in the Analytical Edition. We believe these services will prove of signal value in advancing chemistry. The steady growth in the circulation of INDUSTRIAL AND ENGINEERING CHEMISTRY, together with the extent to which articles are reprinted from its pages, speak eloquently of the appreciation with which the publication is generally received.

Duplication

AT THE second session of the Institute of Chemistry of the American Chemical Society held last year at Northwestern University, in a round-table discussion on research with special reference to government activities the subject of duplication in laboratories of various bureaus naturally arose. It is appreciated that often a certain duplication is desirable to insure adequate checking, accuracy, and security against the omission of important data by a single group of investigators. On the other hand there have been cases of appropriation of promising problems, particularly where success might lead to valuable publicity and increased funds. The questions turned to what is done elsewhere and Sir James Irvine, our guest from St. Andrews, told something of the British machinery for dealing with research conducted with public funds. What is done in Great Britain might not fully apply to American conditions, but the plan should be carefully studied by those in authority for constructive ideas.

To begin with, the Department of Scientific and Industrial Research, which began as an honorary council during the war, has been set up to encourage, organize, and assist in the direction of work in government departments, as well as in trade association laboratories established with government aid. The department is under the guidance of an advisory council, which has very wide powers and which is composed of men, distinguished in science or business, who are appointed by the Lord President of the Privy Council—at the moment Earl Balfour. The National Chemical Laboratory and the National Physical Laboratory are managed by the Council, as are the laboratories of twenty research associations. The Council is grouped into numerous committees and augmented with coöperative members to form boards, the work of which is familiar in reports on fuel, building, food research, etc.

As all committees and boards in research associations report through the Council, it is an easy matter to note the tendency toward duplication, and indeed all research programs being submitted in advance to Council for the sake of obtaining the necessary financing make it a simple matter to prevent duplication in cases where it is not considered best. It must be remembered that all this refers only to activities directly under government supervision, or carried on in coöperation with government officials. Private establishments conduct their programs of research in their own way, but even here many a piece of needless work may be saved by discussing projects with those in position to know what is in progress.

Various conditions require different treatment and the British plan could not be adopted in detail in America. Could not a group of disinterested scientists and business men be brought together to study plans for research as initiated by the various government bureaus, and advise upon coördination and the elimination of duplication before requests are made for appropriations? Civilian boards have been used to advantage by the War and Navy Departments, and many government bureaus have consultants who aid in various ways. Why not accomplish, through a civilian board, what has been so difficult under official auspices? The first step in a major piece of research involves breaking it into small parts which may be more successfully handled by specialists. All of these may not be in a single bureau or department. The allocation of problems to those laboratories where the most can be accomplished in view of personnel and facilities would benefit the public at large and directly the bureaus and scientists involved.

An Unwise Policy

THE War Department has decreed that after one term of service as chief of an army branch the incumbent shall not be eligible for reappointment, but shall be returned to the grade from which he was elevated to be chief, making way for another. This policy is contrary to the spirit and letter of the law as well as to precedent, and is particularly unwise when applied to the services of Ordnance Department, Quartermaster Corps, Medical Department, Chemical Warfare Service, and Finance Department.

The law states that chiefs shall be appointed for a period of four years and says nothing on the subject of reappointments, but Mr. Root, when Secretary, stated before the Senate Committee on Military Affairs, December 14, 1900, that by omitting reference to reappointments the chiefs of the various services would feel that reassignment to duty at the end of four years would depend upon their satisfactory performance and tend to make them more effective officers. The practice of reappointing efficient chiefs when eligible has been followed for twenty-six years, and Congress in the National Defense Act of June 4, 1920, recognized the value of permanency of rank in special services by providing that all officers in the various branches should be commissioned permanently in those branches. Congress still further indicated the importance of keeping special technical men in places for which they were particularly fitted by providing that the President might exempt officers in the Ordnance Department, Medical Department, and Chemical Warfare Service from duty with troops, as prescribed in the National Defense Act for all officers serving in grades below that of brigadier general.

It may not be generally understood that officers in the services of the military establishment are not eligible for promotion to brigadier generals or major generals of the arms. As officers in noncombatant branches, their chance for promotion is limited to that of assistant chief, or chief of their branches. If, by meritorious service, they win such distinction they have a right to expect, if efficient, to be continued in that assignment until retired for age or disability, as in the case of other general officers. Brigadier generals and major generals of the arms, that is, of the Infantry, Coast and Field Artillery, Cavalry, Air Corps, Corps of Engineers, and Signal Corps have permanent appointments. It is evident that to adopt a policy making impossible the reappointment in the services is such a discrimination as to discourage able young officers from entering them and tend towards transfers. The result will inevitably be to fill those branches with the less efficient men, and in the case of another emergency an inevitable breakdown would occur in the supply and production of ordnance, gas masks, air planes, tanks, and all manner of vital necessities.

When life was relatively more simple there may have been some justification for the belief that a graduate of West Point was fitted to undertake any task, no matter how technical. But these are days of specialties which even the War Department recognizes in the practice of sending officers for postgraduate work to highly specialized schools. West Point makes no effort to give technical training for specialties in the services, but leaves it to be acquired through years of special contact and work at other institutions. Surely in the Army, as in business, when a man has proved himself efficient and has mastered the details of his assignment, it is the height of unwisdom to make changes. What business would declare a policy of removing the heads of departments and the officers of the company at the end of every four years, retiring them on a greatly reduced salary to make way, by the clock, for younger men who may or may not know the business? We fancy it would be difficult to finance such an institution.

The Chemical Warfare Service is a conspicuous example of a highly technical branch of the service where, if the present policy of the War Department is applied, great damage may be done. It requires years to become familiar with the details of chemical warfare, without which knowledge no officer, however well trained in other branches, can expect to give a constructive administration as chief. It takes time for the chief of this service to perfect scientific and industrial contacts, without which he cannot succeed. The War Department policy proposes to demote the chief of a service to the grade from which he was appointed, usually that of a colonel. The men who become chiefs of branches reach this grade after many, many years of army service and in nearly every case they are eligible to retirement on the basis of the term of thirty years of service, if not upon age.

To force a chief to choose between retirement as a major general and continuation in the service as a colonel will, as it has where the policy has been applied, result in losing the services of the specialist at the very time the tax payer begins to get a return on the Government's investment in him. If there is anything in the contention that the new policy will be an incentive to younger men, then surely the certain loss to the service which must come from its logical pursuit might be compensated to a degree by retaining in some capacity, compatible with the rank they have held, the chiefs of branches following their single four-year term. To leave matters as they now stand forces the appointment of chiefs of these branches into politics of the worst order. Efficiency as chief will not count, and as reappointment will not depend upon satisfactory service there is no good reason why the friends of those making appointments should not be given preference.

The new procedure seems particularly unfortunate in the case of the Chemical Warfare Service, for it is the youngest as well as the smallest of the branches and there has not been time to train a sufficient number of officers to permit frequent changes in the chief of the branch without a considerable setback to the service. The number attached to the branch is so small that only one or two men are eligible by rank at present to be promoted to chief. This increases the danger to this service, for should the policy be maintained someone wholly unfamiliar with the work, traditions, and history, and with the science underlying the service may be brought in from some other branch to be made its chief.

The policy is evidently unwise as applied to the Army as a whole, and particularly unsound as applied to the Chemical Warfare Service. Unless changed it may lead to a loss of the interest which has been obtained widely in the chemical industry and among the chemical profession. Should this take place, the safety of the country will inevitably suffer.

Some Important Events of 1928

THE year that has just ended has seen accomplishments in the field of chemistry comparable in number and in importance to those that have been recorded year by year. If anything, there has been an increase in the volume of chemical research; new laboratories have been established in industry, old ones have been bettered, and fundamental research as a distinct department to be maintained almost regardless of business conditions has been added in at least one great industry. On the purely commercial side chemistry has given a good account of itself, as indicated by published statistics with respect to imports and exports, as well as the volume of manufactured materials, the employment situation in the industry, the capital turnover, and the dividends paid.

The AMERICAN CHEMICAL SOCIETY has enjoyed one of the best years of its history, with an increase in membership, a realization of its hope that *Chemical Abstracts* would be directly supported by the chemical industry, and the maintenance of its publication program on an established high plane.

Among the outstanding accomplishments of the year should be noted the synthesis of sucrose from fructose and glucose by Amé Pictet and Hans Vogel. It will be recalled that the tetraacetate of glucose was combined with the tetraacetate of gamma fructose. This work, which reveals the structure of sucrose, is without present commercial significance, but is recognized as an important step in organic research bringing us much nearer to the synthesis of carbohydrates.

In his investigation of abietic acid Ruzicka has pushed almost to completion details proving the composition and chemical structure of this compound. We now know within one position of the carboxyl group how the atoms are arranged in this complex molecule.

Although the work incident to commercial production had been in progress for some time, the first publication of details relative to the synthesis of phenol from benzene halides was made by Hale and Britton in INDUSTRIAL AND ENGINEERING CHEMISTRY, in February, 1928. This process is now being operated on a scale sufficient to produce several hundred thousand pounds of synthetic phenol each month.

In November, A. O. Jaeger announced new catalytic processes for the utilization of coal-tar crudes. This paper appears in our December, 1928, issue, and is considered to be a development in organic chemistry of more than usual importance, since it will directly affect the cost of anthraquinone, an important raw material in the production of vat dyes.

In the interesting and rapidly developing rayon industry one of the most important advances is covered by the Lilienfeld patents. Leon Lilienfeld has found that, by the action of chloracetic acid and aniline on viscose, anilides of cellulose are formed, yielding rayons in the molecules of which nitrogen has been introduced, thus constituting another important step toward protein-containing natural silk. His patents, Nos. 1,683,199 and 1,683,200, dated September 4, 1928, cover an important advance in the processing of viscose involving sulfuric acid to yield rayon possessing greatly increased strength under all conditions.

The year saw the commercial realization in Germany of the project of producing motor fuels by the direct hydrogenation of coal, using the Bergius process. Production at the Leuna works was at the rate of 70,000 metric tons per year during 1928, and this is to be trebled during 1929. Here again the research upon which this commercial development rests goes back at least to the beginning of the century. The motor fuel resembles gasoline from petroleum so closely as to be entirely acceptable for the purpose and is said to be produced at a modest profit while competing in the German market with imported motor fuel.

Another interesting development in motor fuels centered about the investigation of tetraethyl lead in Great Britain where, after a round of investigating committees, permission was given to market and use this antiknock compound.

From time to time the lay press has given much space to progress in the synthesis of rubber; but while that problem has been pushed somewhat nearer to completion, it is still far from a commercial success. To find plenty of raw materials sufficiently low in price to compete with the abundance of latex offers a real difficulty. The producers of natural rubber are alive to the situation and look to increasing production through bud grafting, the application of fertilizers, seed selection, and other scientific methods.

Amateur motion pictures in colors became a reality in July, 1928, when demonstrations were made by the Eastman Kodak Company before a group of notables in Rochester, N. Y. An important point in the success of this enterprise is the method of so developing the exposed film as to convert it into a positive for direct projection upon the screen.

Toward the close of 1928 the erection of a semi-commercial plant was begun at Anniston, Ala., where there will be worked out the next stage in the process for the manufacture of xylose from cottonseed bran and peanut shells. The laboratory work at the Bureau of Standards indicates the feasibility of producing this comparatively rare substance on a commercial basis. The market for all that can be produced has not been developed, but there is reason to believe that the availability of commercial quantities at attractive prices will secure a utilization which would not otherwise develop. Trihydroxyglutaric acid may be prepared by the oxidation of xylose and is expected to compete with lactic acid, particularly in the tanning of leather.

A year ago the manufacture of cellulose from cornstalks was still in the laboratory investigation stage. A small tonnage of this material is now being produced in the plant at Danville, Ill., and some book paper and newsprint have been made from it. Experiments have been begun looking to the production of corn to be grown primarily for its stover, and the by-product pentosans secured in the course of the process are under investigation to ascertain their utility as a sizing material for various papers. The machinery required for the collection of cornstalks from the field has been further developed with a corresponding reduction in costs. At Iowa State College Professor Davidson has succeeded in improving upon his earlier devices, so that now a unit in the field may be operated by two instead of by five men.

The interest in insulating boards and lumber substitutes has attracted a number of investigators to the several sources of cellulose materials. The market now affords such boards made on a commercial basis from cornstalks, straw, exhausted licorice root, exploded wood chips—to mention a few—in addition to the pioneer boards from wood fiber and from bagasse.

Borax in amounts and at prices to make it attractive as an alkali for the chemical industry may be said to have made its bow in 1928. It has been known as a commercial chemical for many years in such industries as the enamel industry, where it is a vital raw material and was used even at prices up to eight cents per pound. It also held an undisputed place in the manufacture of certain heat-resisting glasses, such as Pyrex. But during the past year data secured through scientific research applied to production have made it possible to bring the price level down to the point where other manufacturers can afford to use borax. In some industries the material is still under investigation, and 1929 may expect to see commercial developments of far-reaching importance in this field. Incidentally, Matheson and Henning, of Cornell University, discovered that a concentration of 1.5 parts of borax in 1000 parts of water is quickly fatal to the larvae of mosquitoes that breed in rain-water barrels, cisterns, and other exposed reservoirs. The presence of this borax protects against larvae for long periods. One experiment from July 25 to September 7 showed the solution as effective at the conclusion as at the beginning of the period.

The Dead Sea project, like the operation of Muscle Shoals, remains at the beginning of 1929 in very much the same status as at the beginning of 1928. Authorities in Great Britain regard the Dead Sea exploit as highly experimental and do not propose to risk taxpayers' money upon the experiment.

With respect to Muscle Shoals, the effort to put the Government in business to operate a chemical plant there failed with the pocket veto of President Coolidge. Senator Norris champions the opinion that the pocket veto is only effective at the close of a session, holding that the first session of the Seventieth Congress adjourned to reconvene in December and did not end its labors on May 29. This technical question is being examined and discussion was renewed with the opening of Congress in December.

Carboloy, an alloy of tungsten carbide with cobalt, had been used for two years in the General Electric Company, but was announced as a new tool material in the fall of 1928. It is a tough, strong metal, affording the hardest cutting material yet developed in a research laboratory. Natural sapphire, which stands second only to diamond in the scale of hardness, can be scratched with Carboloy, which will also cut an emery grinding wheel. It has been employed satisfactorily in cutting threads upon glass, in cutting concrete, porcelain, molded compounds, nickel steel, and numerous other materials. The tests indicate Carboloy to be another one of those contributions of the research laboratory which mark the perfection of a new structural material and a new tool from which great things may be expected.

While not a chemical device, the development of an electrical appliance to register minute cracks in railway rails promises to be of such importance that it is included here. It is well known that the most serious accidents of railroads are caused by broken rails. Elmer A. Sperry has perfected an invention making it possible to detect cracks in rails that are invisible even under the microscope. These cracks, known as transverse fissures, develop inside the rail and do not show until it breaks. The Sperry device, mounted in a covered small car, proceeds along the rails at the rate of seven miles an hour. When it reaches a rail in which a crack exists, the sensitive electrical appliance is affected and a stream of white paint is automatically released on the rail. As the car travels on the track an electrical current passes through the rails. The most minute crack interrupts this current and a vacuum device magnifies the interruption about six thousand times, producing enough energy to operate the mechanism for painting the rail, while at the same time a pen records its data on a chart. Rails thus marked are at once replaced. The vacuum tube thus finds new and important work to do.

Many regard the development of the Allied Chemical & Dye Corporation at Hopewell, Va., as one of the brightest spots in the nitrogen fixation program in the United States. During 1928 this plant has begun operation, our information being that with the close of the year one 30-ton unit was in production. The product, synthetic sodium nitrate, has been delivered at prices competing with Chilean nitrate, and its quality has earned much commendation for it. Heretofore fixed nitrogen has appeared upon the market in some form other than that required to compete directly with the natural material for some uses. Here, then, is a really notable achievement for 1928 and the initiation of another phase of the new competition which will be watched with great interest. When the details can be written of all that is involved in starting with salt at one point to produce sodium carbonate and with coal at another to produce nitric acid, that the two may be brought together at a price to compete with the naturally occurring product and yet earn a profit, we will have one of the great romances of chemistry.

An important forward step was taken in the tanning of leather during 1928, when the use of methylamine to produce mellow limes in the tannery became a commercial possibility. The research laboratory of the Tanners' Council proved that the reaction between lime and skin epidermis is purely chemical in nature and found that the efficiency of "mellow" lime is due to methylamine and traces of other mono- and diamines which are formed in the skin by the action of proteolytic bacteria upon the skin prior to its entry into the lime solution. It has been proved that the action of the amine is catalytic, and even so small a concentration as 0.0031 per cent methylamine added to fresh lime solutions has a marked mellowing effect. Heretofore a part of the valuable skin had to be destroyed in order to obtain the desired mellowness in unhairing solutions. Now better and more leather per hundred pounds of skins is a possibility.

Great progress has been made during the year in the broadcasting of photographs, in television, in loud speakers of unusual power for outdoor use, and in many details connected with radio. Many of these have depended upon materials supplied through the research laboratories where chemists work side by side with physicists and with engineers. We cannot call attention to these various accomplishments here, but we would remind you of the part chemistry is playing in these various marvels of communication.

Among the legislative actions of interest to chemistry may be noted amendments to existing laws intended to clarify any ambiguity in previous legislation which has led to an entirely new situation as regards patents that may be secured and retained by federal employees. It is now held that federal employees may own and profit from patents taken as a result of their research, the Government retaining only the right to use or have used for it, without royalty, the processes and products otherwise protected by the patents. Some criticism of this development has been noted, but it is too early to say just what effect upon relations between industry and federal bureaus will result.

Congress provided for the return of alien property still in the hands of the alien property custodian and the task of determining sums due former alien enemies was begun. Many applications may be expected in unraveling this more or less tangled situation, but with a desire that full justice be done, satisfactory results may ultimately be expected.

An international incident which attained great publicity was the arrest in Germany of Guido Meisel, an American chemist of Portsmouth, N. H., who was accused of commercial espionage in seeking to obtain German chemical and dye secrets. Meisel had spent eight months in prison before he was brought to trial and was sentenced on February 18 after hearings held in secret, the reason being given that important secrets of the German dye trust might be revealed. He was finally released from prison on May 22, after he had paid a fine of five thousand marks. Much publicity was given to the way in which the German authorities handled the case and the circumstances surrounding his arrest and incarceration.

Agreements and Mergers

A number of agreements were reached and several mergers and cartels formed during the past year. The most notable in America was the acquisition by the du Pont Company of the stock and properties of the Grasselli Chemical Company. Announcements made late in the year indicate that the chemical business of the two groups will be continued by the du Pont interests in the name of the Grasselli Chemical Company, while the explosive business of the latter company will be merged with that of the du Pont Company. Procter & Gamble purchased the Globe Soap Company during the year, and Colgate & Company and the Palmolive interests formed a new company to carry on the business of these two concerns.

In some respects the most interesting international business activity was the formation, by Imperial Chemical Industries, Ltd., and the Chase National Bank, of a new international finance corporation, known as The Finance Company of Great Britain and America, Ltd. This is unique in that it does not directly represent an agreement between two like industrial enterprises. Manufacturers reach international agreements, as do financial institutions, but it is rare that a manufacturing company joins with a banking house to set up a new financial enterprise. It is understood that the company will be active in exploiting new processes.

Of considerable domestic interest is the agreement between the Standard Oil Company of New Jersey and the Interessengemeinschaft, whereby the Standard Oil Company has acquired the American rights to the Bergius process and has reached an approved basis for an exchange of research information, patents, and the like. Research is in active progress looking to the application of the Bergius process to some products of the petroleum and natural gas industries.

Abroad there was great activity late in 1927 and in 1928 looking to the combination of great groups in various parts of Europe into international cartels of tremendous power. It appeared that international cartels were being formed abroad to take the field against the United States in world markets, and various plans were proposed for the protection of American industry against such tremendous odds. In connection with this Americans were urged to refrain from loaning substantial sums to foreign industries, and it was feared that a continuation of the practice of sending great sums abroad to strengthen industries there would not only work to the detriment of the domestic industry, but actually affect tariff policies and other fundamental economic structures. The full program as originally announced has not been carried out in all details, but the year has seen formed in Europe a considerable number of cartels in special fields, and apparently there is still need for the great alertness on the part of the American industry.

International Meetings

The year just past showed great activity in international meetings and conferences. Of particular interest to chemists were the International Union of Pure and Applied Chemistry, which met at The Hague; the Nitrogen Conference held on the *Lützow* during a cruise on that vessel in the Adriatic; the celebrations to commemorate the work of Wöhler and Liebig, the Power Conference in Great Britain, the annual meeting of the Society of Chemical Industry in New York, and the joint meeting of the Institution of Chemical Engineers of Great Britain with the American Institute of Chemical Engineers at Niagara Falls and with an industrial tour in Canada and the United States. The Second International Conference on Bituminous Coal was held successfully in Pittsburgh in November, and the second session of the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY was held at Northwestern University during the summer.

Important Patent Decisions

One of the most important decisions of the year is that of the Circuit Court of Appeals for the Third Circuit in the tungsten patent infringement case General Electric Company *v.* De Forest Radio Company and the Robelen Piano Company. The suit has to do with patent No. 1,082,933, issued to the General Electric Company as assignee of William D. Coolidge, in 1913, for improvements in tungsten and methods of making tungsten for use in filaments of incandescent electric lamps and other purposes. The De Forest Radio Company was charged with infringement of certain process claims and the De Forest Radio Company and the Robelen Piano Company with infringement of certain product claims, and this was denied by the District Court of Delaware in January, 1927, which declared the General Electric patents invalid. The Court of Appeals sustained the decision of the lower court concerning the product claims, but reversed the opinion in regard to the process claims. The Court declared that, inasmuch as the process for the production of tungsten required different procedure than the process for working other metals, the process claims of the General Electric Company were valid. The Court stated:

> Being convinced that tungsten differs from other metals in essential characteristics, that to produce ductile tungsten from impure tungsten, problems different from those incident to ductilizing other metals are present, and that to meet these problems different methods of ductilization were required and that those disclosed by Coolidge are different, new and useful in a degree amounting to invention, we are constrained to hold, against the decision of the learned trial court, that all process claims of the patent which are in issue are valid except claims 14 and 16, "the additional material" and "beneficial additions" claims. These we hold invalid for lack of invention in view of the prior art.

In Corona *v.* Dovan (276 U. S. 385),[1] the Supreme Court forcefully reiterated the law concerning the proper scope of chemical claims, and held the broad claims related to "a disubstituted guanidine" of the Weiss patent relating to rubber accelerators invalid.

In Holland Furniture *v.* Perkins Glue (277 U. S. 257) the Supreme Court had under consideration one of the Perkins patents relating to glue made from starch, which patents have been the subject of much litigation. The Court made a finding of non-infringement, saying:

> A claim so broad, if allowed, would operate to enable the inventor who has discovered that a defined type of starch answers the required purpose to exclude others from all other types of starch * * * the attempt to broaden product claims by describing the product exclusively in terms of its use or function is subject to the same vice as the attempt to describe a patentable device or machine in terms of its function.

In Tolfree *v.* Wetzler (22 Fed. (2nd) 214) the Circuit Court of Appeals for the Third Circuit sustained the "X-liquid" patent relating to a solution for stopping radiator leaks.

In Haynes Stellite *v.* Chesterfield (22 Fed. (2nd) 635) the Circuit Court of Appeals for the Sixth Circuit reversed the lower court in sustaining Haynes patent No. 1,057,423 for a tool alloy containing cobalt, chromium, and tungsten.

In Bellis Heat Treating *v.* Heatbath (23 Fed. (2nd) 239) the Circuit Court of Appeals for the First Circuit sustained

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[1] See Deller, IND. ENG. CHEM., 20, 1361 (1928).

the District Court in holding invalid a patent relating to a steel-tempering bath comprising a mixture of fusible salts.

The U. S. District Court for the District of Maine sustained a much litigated flotation patent (No. 835,120) in Minerals Separation *v.* Magona Copper (23 Fed. (2nd) 931).

In U. S. Industrial Alcohol *v.* Theroz (25 Fed. (2nd) 387) the Circuit Court of Appeals for the Fourth Circuit had under consideration certain patents relating to so-called "solid alcohol" useful for fuel. The Schaub patents, relating to compositions and processes in which the alcohol is combined with nitrocellulose to form a solid fuel, were held valid and infringed by the U. S. Industrial Alcohol Company.

The first patent litigation relating to the "dry ice" industry occurred during the year. In American Patents Developments *v.* Carbice (25 Fed. (2nd) 730) the District Court for the Eastern District of New York held patent claims for a combination of a container and "dry ice" as not infringed by a party supplying solid carbon dioxide for such container.

The Hoffman and Gottlob patent (No. 1,149,580) relating to rubber accelerators was considered by the Circuit Court of Appeals for the Second Circuit in Grasselli *v.* National Anilin (26 Fed. (2nd) 305). This patent contained claims which define the useful accelerators as "bases having a disassociation constant greater than 1×10^{-8}. The claims in suit were those relating to ammonium bases and the court found them invalid on the ground that the specifications were insufficient and the claims too broad.

The Carson patents for smelting furnaces were sustained by the Circuit Court of Appeals for the Ninth Circuit (26 Fed. (2nd) 650) in Carson *v.* Anaconda. This litigation has excited public curiosity and sympathy in view of the immense sums involved and because of the hardships the inventor has encountered in establishing his rights.

In an interesting flotation case, Metal Recovery *v.* Anaconda (26 Fed. (2nd) 730), the District Court for Montana held claims for non-oleaginous flotation agents having certain generally described characteristics as invalid for insufficiency and indefiniteness of description. Expert testimony showed that such compounds might be found anywhere in a group of three-hundred thousand compounds.

Further litigation of the patents relating to the removal of wild gases by weathering gasoline resulted in another finding of invalidity of the patents involved (28 Fed. (2nd) 217, D. C. Delaware).

Patents relating to the production of pectin were sustained by Circuit Court of Appeals for the Second Circuit in the case Douglas Pectin *v.* Armour (27 Fed. (2nd) 814).

In the Circuit Court of Appeals for the Second Circuit an infringement suit relating to ore sintering—Dwight & Lloyd *v.* Greenewalt (27 Fed. (2nd) 823)—failed on the ground of the invalidity of the patents and because an accounting was denied in view of laches, the evidence showing thirteen years delay in bringing suit.

Medal Awards

The special recognition given chemists by their fellows includes the award of medals and similar honors in various countries. Below is given a record of certain medal awards of 1928, but it should be noted that this is not a complete list. Details from some correspondents have not been received and many medals and prizes are awarded which call for no decision in 1928. Some important honors are given on a biennial or five-year basis.

United States—The principal medal awards in the United States were as follows:

Chandler Medal to John Arthur Wilson for his work on chemistry and leather.

Willard Gibbs Medal to W. D. Harkins for researches on isotopes and atomic structure.

Grasselli Medal to H. J. Rose for his paper on "Importance of Coal Preparation in the Manufacture of Gas and Coke."

Thomas Burr Osborne Medal to T. B. Osborne in recognition of his contributions to cereal chemistry.

Nichols Medal to Hugh Stott Taylor in recognition of his work on catalysis.

Perkin Medal to Irving Langmuir in recognition of his work on atomic hydrogen and its application to welding.

A new prize was established through the generosity of Edward Goodrich Acheson, who presented a fund of $25,000 to the American Electrochemical Society. This fund is to be used for a biennial award of a gold medal and a prize of $1000 to any man who has made a distinguished contribution to any of the branches of science fostered by the society.

Cash awards were made by the American Society of Agronomists from funds provided for the purpose by the Chilean Nitrate of Soda Educational Bureau and were won by J. G. Lipman, T. L. Lyon, E. B. Fred, and F. T. Shutt.

Austria—Fritz Hohlrausch received the Haitinger Prize for Physics, for excellent work in physical chemistry.

Germany—The Emil Fischer Medal was awarded by the Verein deutscher Chemiker to Werner Schulemann, Fritz Schönhofer, and August Wingler, for outstanding and successful coöperative work in chemotherapeutic fields, leading to production of the valuable malaria remedy, Plasmochin; the Liebig Medal to Friedrich Bergius, for pointing out methods for the conversion of coal oils and mastering the difficulties which rose in the way of its technical application.

Japan—The Sakurai Prize, awarded by the Chemical Society of Japan to Matsusuke Kobayashi for his work on the application of amalgam on volumetric analysis and other works on analytical chemistry.

The Society of Chemical Industry (Japan) awarded its prize for special merit in research work on chemical industry to Seiichi Ueno for his papers on the hardening of oils, published in the *Journal of the Society of Chemical Industry* (*Japan*).

The Prize for the Memory of the Wedding of the Crown Prince, donated by the Osaka Mainichi Shimbun and the Tokyo Nichi-Nichi Shimbun, was awarded by the Imperial Academy to Heizaburo Kondo, of the Tokyo Imperial University, for his "Study of Some Alkaloids Produced in This Country."

Great Britain—The Davy Medal of the Royal Society, awarded annually for the most important discovery in chemistry made anywhere in Europe or in Anglo-America, was given to F. G. Donnan for contributions to physical chemistry and particularly for his theory of membrane equilibrium.

The Messel Medal, founded to be given to the most distinguished man in science, literature, or the arts that the world may have at the time of its presentation, was given by the Society of Chemical Industry to R. A. Millikan in 1928.

The Frankland Medal and Prize is offered annually by the Institute of Chemistry for the best essay of three thousand words on a set subject of professional, as distinct from technical or purely chemical, importance. It was awarded in 1928 to Malcolm Gilles for an essay on "The Importance of Chemistry to the Welfare of the People."

The Meldola Medal is presented annually by the Society of Maccabaeans for the most meritorious chemical work of the year, with primary regard to work done in analytical chemistry, to some British subject not more than thirty years of age. The 1928 recipient was Juda Hirsch Quastel for his studies in reduction-oxidation systems.

The Perkin Medal of the Society of Dyers and Colourists is awarded at intervals of from two to five years to persons who have rendered conspicuous service to the tinctorial industries by their inventions. In 1928 it was awarded to Robert E.

Schmidt for "Epoch-Making Discoveries of Anthraquinone Derivatives and Dyestuffs Therefrom." The Gold Medal of Society of Dyers and Colourists is awarded occasionally in recognition of work of exceptional merit. The 1928 recipient was Ernest Hickson, "for exceptional services rendered to the Society."

SWEDEN—The Nobel Prize for 1927 has just been given to Heinrich Wieland, of Munich, for his investigations of the structure of cholic acid and allied substances. The prize for 1928 has been awarded to Adolph Windaus, of Göttingen, for his research on the constitution of the stearins and their relation to the vitamin group.

The Great Gold Medal of the Academy of Technology has been awarded to Peter Klason for research in cellulose chemistry.

The Norblad-Ekstrand Medal of the Swedish Chemical Society is given every second year for the best original dissertation published during the past two years in the *Svensk Kemisk Tidskrift.* Work in the chemistry of foods is preferred. In 1928 the prize has been given to Peter Klason.

Progress in the Synthetic Organic Chemical Industry in 1928[1]

Frank Talbot and W. N. Watson

WASHINGTON, D. C.

PROGRESS in recent years in the synthetic organic chemical industry is an outstanding development in American industrial enterprise. The public has become generally familiar with those organic chemicals which enter into common usage. Rapid expansion in the automotive, rayon, pharmaceutical, and other fields of industry has created a large demand for synthetic organic chemicals. The general prosperity of the country has contributed to the growth of this branch of the chemical industry, which supplies raw materials, not only for a number of the essentials, but for many of the luxuries of life which are today enjoyed by the majority of Americans.

The introduction of new organic chemicals to meet the ever changing requirements of industry and the use of cheaper and improved processes in their manufacture are marks of distinct progress. Large quantities of these chemicals serve as raw materials for the following:

(1) Pyroxylin lacquers, used as a finish for practically all automobiles.
(2) Derivatives of cellulose, used in the pyroxylin plastics and rayon industries.
(3) Synthetic resins, with their manifold uses in varnishes, plastics, insulating materials, and articles of personal adornment.
(4) Flotation agents, used in treating ores.
(5) New pharmaceuticals which are of value in preventing the spread of disease.

Synthetic organic chemicals may be subdivided generally into (1) aromatic or coal-tar derivatives and (2) aliphatic, or noncoal-tar derivatives. Certain organic compounds are not included in the synthetic classification. Originally, they were eliminated in the administration of the Import Control Act by the War Trade Board. This classification was commonly accepted in the United States after the termination of the World War. Products excluded from the synthetic organic group are: organic chemical compounds, or their salts, derived from natural sources by isolation, distillation, extraction, hydrolysis, or purification—examples include the alkaloids, constitutents of essential oils, sugars, and such acids as tartaric and stearic—and the cyanides, cyanamides, and carbides of metals.

Finished coal-tar products, such as dyes, medicinals, and resins, are derived from intermediates which, in turn, are made from coal-tar crudes by complex chemical processes. Noncoal-tar chemicals are manufactured from many kinds of raw materials, including petroleum, natural gas, turpentine, corn, wood pulp, carbide, chlorine, and glycerol. The production of coal-tar chemicals showed a rapid expansion during the war, and notable progress has been recorded since that time. The most striking developments in the production of synthetic organic chemicals have been in the output of the noncoal-tar chemicals within the last decade. Many of these chemicals are of world-wide interest.

Coal-Tar Derivatives

Domestic coal tar used in producing aromatic chemicals is obtained largely in the manufacture of by-product coke. The by-product coke oven is the source of more than 95 per cent of all coal tar produced in the United States, of which over half is used as fuel—largely in metallurgical plants. In addition to coke, the main product, gas, light oil, and ammonia, are also evolved in by-product coke-oven operations. Continued improvement in coking processes and in design of the ovens has resulted in an increased yield of coke and of by-products, has decreased the time of carbonization, and permitted the use of coal of higher oxygen content. Work still under way is directed toward stripping the coal tar of phenol and cresylic acid and using the tar as fuel. This process offers a large potential supply of both phenol and cresylic acid in addition to that obtained by coal-tar extraction, and of phenol by synthetic methods.

According to current reports, phenol is being recovered in four domestic plants in small available quantities from the crude ammonia liquors obtained in by-product coke-oven operations. Recovery is made by extraction with benzene and subsequent treatment with caustic soda. In the purification of coke-oven gas there is obtained by a new process many tons of finely divided, almost colloidal, sulfur, which is valuable as an insecticide. Sodium thiocyanate is also recovered which may be of value as an agricultural chemical because of its favorable effect on the germination of potatoes.

The low-temperature carbonization of coal is receiving considerable attention in this country, but as yet production has not reached commercial importance. The profitable operation of the low-temperature processes, which give higher yields of tar, light oil, and coke, depends in no small degree upon a large-scale market demand for the tar produced, which differs considerably from coke-oven tar.

Heretofore, imports of creosote oil were uniformly greater than domestic production, but indications point to a production that will exceed imports in 1928. Several new plants operating on a large scale for the recovery of creosote oil from coal tar are reported for 1928, and it is to be expected that the quantity of tar distilled will be increased.

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[1] Received November 20, 1928.

Because of developments in 1928 anthracene, a coal-tar crude, also promises to be of increasing importance. Up to the present time its recovery with a purity sufficient for use in producing anthraquinone has been a difficult and expensive operation; therefore, a supply of cheap high-grade anthracene would be decidedly advantageous to the industry. In the early years of vat-dye production in the United States producers of anthraquinone used anthracene as the raw material, but recently the entire domestic supply of anthraquinone is the synthetic product made by the condensation of phthalic anhydride with benzene by means of aluminum chloride. This gives a product of high purity which yields dyes clearer in shade than those obtained from anthraquinone from anthracene. Disadvantages in the use of the synthetic process are: (1) the high cost of aluminum chloride and the difficulty in storing and handling; (2) the simultaneous production of corrosive hydrochloric acid; (3) the use of larger quantities of benzene than are theoretically necessary.

Anthracene is used in Great Britain and Germany as a raw material for anthraquinone, and in Great Britain its synthetic production is also noted.

Anthracene is obtained from anthracene oil (green oil). From this fraction, by filtration, centrifuging, and hot- and cold-pressing, 6 to 10 per cent is recovered as crude anthracene with a content of 15 to 30 per cent. By washing with solvent naphtha or creosote oil, a product is obtained which contains 30 to 50 per cent of anthracene and impurities of carbazole and phenanthrene—a grade of anthracene difficult to purify.

Following Doctor Jaeger's discovery[2] that furfural dissolves anthracene, and that 94 to 98 per cent of the anthracene content of the crude product may be recovered as purified anthracene, the content has been raised from 31 to 86 per cent by one crystallization, and conversion to anthraquinone is effected by catalytic oxidation.

Furthermore, a process is under development for the purification of low-grade anthracene by means of a catalytic oxidation. By this process crude anthracene is vaporized, mixed with air, and passed over a catalyst which favors total combustion of heterocyclic impurities and aliphatic compounds. It is understood that anthracene is not attacked, but that carbazole and the other nitrogen compounds are burned. No considerable oxidation of the aromatic compounds present occurs, and a high grade of anthracene is obtained which contains varying amounts of phenanthrene. The latter cannot be burned completely without the loss of anthracene. Commercial development of these processes on a large scale will probably result in cheaper anthraquinone, which will be further reflected in cheaper vat and other anthraquinone dyes.

INTERMEDIATES—Over three hundred intermediates are produced in the United States and represent an annual output of approximately 250 million pounds. They are used extensively in the production of finished coal-tar products, such as dyes, and there is a large consumption for rubber accelerators, as camphor substitutes, insecticides, flotation agents, and other products.

The history of phenol, one of the most important intermediates, affords an interesting example of conditions always to be anticipated by manufacturers, consumers, and even by bankers, to the end that they may safeguard investments by keeping abreast of any change which tends to have a vital influence on business. After the war the Government's stock of phenol, approximating 35 million pounds, represented a carryover from the more than 106 million pounds produced in 1918. It was expected at the close of the war that stocks on hand would be sufficient to supply domestic consumption for several years. But a scarcity developed in the latter part of 1922. Synthetic phenol plants erected during the war had been dismantled and tar distillers in the United States were not prepared to meet the demand. Several firms in 1923 began the production of synthetic phenol from benzene with a large capital investment in plant and equipment. Recently the situation confronting these manufacturers has changed, owing to competition from a new process using monochlorobenzene and caustic soda. In addition, another firm is developing a new synthetic process using benzene as a raw material. Improvements in method and yields are reflected in the steady reduction in price from 30 cents per pound in 1924 to about 13 cents in 1928.

The production of intermediates as rubber accelerators is in itself a large industry in the United States, where tire and rubber goods manufacture is so extensive. Accelerators decrease by about three-fourths the time of vulcanization and increase the life of tires about one year. Each year brings new accelerators with advantageous properties which result in a replacement of certain of the older products. The di- and tri-substituted guanidines and the aldehyde condensation products have recorded advances in production. The economic relationship of a group of products may change almost overnight. This was exemplified in a decision of the United States Supreme Court, April 8, 1928, which declared invalid U. S. Patent 1,411,231, covering the use of diphenylguanidine as a rubber accelerator. Before this, diphenylguanidine was quoted in trade journals at 64 to 71 cents per pound, but following the decision, in April, 1928, it was quoted at 40 cents and the related product, di-*o*-tolylguanidine, at 49 cents per pound. On April 2, 1928, the Circuit Court of Appeals of the District of Columbia handed down a decision establishing the patent rights of both di- and tri-*o*-guanidine. On a price basis these two products are competitive with diphenylguanidine, which will undoubtedly show an increased production in 1928.

A development of interest in 1928 is the commercial output of diphenyl. Formerly produced on a laboratory scale only, it is now available at a relatively low cost to consumers. Its stability and other desirable properties render it an important agent in heat transfer.

DYES—The production of dyes in the United States supplies about 95 per cent of domestic consumption and provides a large exportable surplus, principally of the low-cost bulk colors. Excessive competition in the dye industry in recent years has effected a reduction in the number of producers. In 1927 fifty-two firms were engaged in the production of dyes. Elimination or amalgamation of plants is the natural result of severe competition, and this will probably continue until the domestic capacity to produce more nearly conforms to the demands of our home and export markets. An increase is noted in the number and quantity of fast dyes made in the United States in 1928. The many new dyes placed on the market and the appreciable reduction in the selling price of products previously manufactured are the best evidence of progress in the industry. Research has been directed toward a reduction in manufacturing costs, improvements in quality, an increased yield in dyes and intermediates, and more especially toward the development of additional products not heretofore produced in commercial quantities. New dyes in the following groups were made in 1928: (1) vat dyes, including anthraquinone and the thioindigoid derivatives; (2) fast types of direct azo dyes; and (3) derivatives of alizarin and the acid mordant dyes.

In 1927 the production of vat dyes other than indigo by eight firms was approximately 6 million pounds, an increase over 1926 of 2 million pounds. Further reductions in price are due to increased production, improved methods of manufacture, and to better sales and distribution. The increased

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[2] IND. ENG. CHEM., 20, 1330 (1928).

production has affected imports of vat colors, which show a decrease during 1925–1927 and a small increase in 1928. The total consumption (sales plus imports) has increased steadily each year, and about three-fourths of our consumption is produced in the United States.

MEDICINALS—In the past many of the drugs used in the treatment of disease were plant products of varying strength and therapeutic value. Today we have, in addition to the products derived from natural sources, extracts from various glands of the animal body and many valuable synthetic medicinals prepared by chemical processes. In the last decade America has given to the world many synthetic medicinals, including anesthetics, such as ethylene, butyn, and tutocaine; antiseptics, such as dibromine and hexyl resorcinol; mercury compounds, such as mercurochrome and metaphen; dyes, such as tetraiodophenolphthalein and acriflavine.

Lately, the use of ethylene as an anesthetic has been demonstrated. It acts directly on the nervous system and when administered with oxygen produces a deep surgical anesthesia. Cocaine was for years the leading local anesthetic, but its undesirable properties led to a search for new and better substitutes. As a result many local anesthetics have been introduced which are valuable and effective in the treatment of the eyes, nose, and throat, and for surface and subcutaneous injections.

Research work on biological stains has continued through the year, and nearly all important stains are now made in the United States. They are valuable aids in the diagnosis of cancer in its early stages and in suspected cases of diphtheria and tuberculosis. Extensive research under way is finding the use of stains essential.

In the use of dyes as medicinals advance is slow, but a great deal of work is being done in the field of chemistry.

OTHER COAL-TAR CHEMICALS—In addition to their use in the production of dyes and medicinals, intermediates are the raw materials used in such other groups of finished products as color lakes, perfumes, flavors, synthetic resins, photographic chemicals, and synthetic tanning materials. Space does not permit a discussion of the progress in each group, but a few examples may be cited to illustrate the important advances. Production of the three synthetic musks is now a commercial accomplishment in the United States. The domestic production of musk ambrette, musk ketone, and musk xylene, used in large quantities in the manufacture of perfumes, is an important contribution in rounding out a division of the organic chemical industry in this country capable of supplying a full line of basic synthetic chemicals to American perfumers.

Synthetic resins are finding a wider range of application in industry, and are made by many firms in increasing quantities each year. The largest use is as a binder in molded plastics, including laminated sheets and panels for automobiles and radio parts. These resins are also used in the manufacture of varnishes and lacquers for insulation. Several new types have been developed, those of the glyptal type, made from phthalic anhydride and glycerol, being used to produce insulating materials, mica sheets, and as a synthetic resin in lacquers. It is quite likely that other new resins will be developed from hitherto unused raw materials. Acetaldehyde, obtainable in large quantities from acetylene, is a possible source which may be responsible for the production of phenol-aldehyde resins. A synthetic glass made from urea and formaldehyde is also attracting attention.

A general increase in the production of synthetic resin is anticipated, since indications point to a reduction in manufacturing costs and in the selling price of many of the raw materials necessary for their production. Among these, phenol and cresylic acid may be mentioned as potential products for mass production at lower cost to the consumer. Formaldehyde is produced from methanol which is made, synthetically, by two methods in this country at relatively low cost. In the one, in manufacturing synthetic ammonia, the raw material, producer or water gas is freed from carbon monoxide by combination with sufficient hydrogen to yield methanol; in the other, waste gases, from butyl alcohol fermentation, containing hydrogen and carbon dioxide are used to produce methanol. The production of methanol from natural gas is also reported. Glycerol, another raw material used in the production of synthetic resins, is now obtained as a by-product in the manufacture of alcohol by molasses fermentation.

Noncoal-Tar Organic Chemicals

The United States is one of the few countries endowed with natural and developed resources for the production of coal-tar and noncoal-tar organic chemicals. In the production of the coal-tar chemicals, Germany for many years led all other countries. Recently the United States and other nations have made rapid progress in this field, and in the production of noncoal-tar products the United states has attained the position of leadership. It is freely predicted that this group of chemicals may soon rival in importance those of coal-tar origin.

In the last seven years the production of aliphatic chemicals has increased about thirteen times in quantity, from 21,500,000 pounds in 1921, to 281,000,000 in 1927. They have a wide range of application, including their use as lacquer solvents, medicinals, perfumes, flavors, rubber accelerators, flotation agents, photographic developers, and explosives.

SOLVENTS AND LACQUERS—In 1927 the production of nitrocellulose lacquers, or varnishes, was 29 million gallons, and in 1928 it will probably exceed that quantity. The successful large-scale domestic production of these lacquers is in no small measure due to a corresponding success in the manufacture of low-priced solvents, such as butyl acetate. The Weizmann process of fermenting corn for butyl alcohol has been one of the most important factors favorable to the large-scale production of lacquers.

Two types of solvents are generally used for lacquers: the esters, such as butyl acetate; and the alcohol ethers, such as ethylene glycol monoethyl ether; in addition, practically all lacquers contain benzene and toluene. The alcohol ethers, some of which are odorless, have a higher dilution ratio and are more expensive than the esters. Ethyl lactate and ethyl oxybutyrate are two lacquer solvents developed for use with cellulose acetate instead of nitrocellulose. Practically no acetone is used in lacquers for solvent purposes, but large quantities are used for celanese, a cellulose acetate silk.

Lacquers are composed of solvents, nitrocellulose, or cellulose acetate, gum, and a plasticizer. The nitrocellulose so used contains from 10.8 to 11.2 per cent of nitrogen by weight, and its physical properties differ from that used for pyroxylin plastics in that its solubility is increased by treatment with alcohol in an autoclave. Lacquers contain from 3 to 5 per cent of plasticizers, which impart elasticity to the film. These include dibutyl phthalate, tricresyl phosphate, blown castor oil, and many other high-boiling liquids. Plasticizers and solvents are today the subject of extensive research and improvements and changes in these organic products are reported continually. Gums used for lacquers include, among others, dammar, a natural gum which is treated to remove the wax; ester gum, made from glycerol and rosin; and synthetic resins of the glyptal type. The use of gums decreases the cost of the finished lacquer and increases the durability of its film and the amount of surface covered.

ACETALDEHYDE AND DERIVATIVES—Large increases in production are shown for acetaldehyde and paraldehyde. Quantities of acetaldehyde and derivatives are consumed annually in the manufacture of rubber accelerators. Acetylene, the raw material for acetaldehyde, is also a raw material for glacial acetic acid, the demand for which is increasing to meet the requirements of the rayon and lacquer industries. Operations were started in 1928 at a plant in Niagara Falls for the production of acetic acid and other derivatives of acetylene. Up to the present time the wood chemical industry has supplied the bulk of the domestic requirements, but that industry has encountered competition from the synthetic acid as well as from the synthetic methanol. The wood chemical industry must dispose of wood charcoal at favorable prices to the iron and steel industry, which is using it in constantly decreasing quantities. The electric steel process using relatively impure raw materials has largely replaced the need for pure iron made with wood charcoal.

Improvements have been made in the conversion of acetate of lime to acetic acid. The Brewster process, by which acetic acid is made directly from pyroligneous acid by ether extraction, has been operated for more than a year on a commercial scale. Other processes include the Suida, the American rights to which were purchased by a group of domestic manufacturers.

Derivatives of acetylene include crotonaldehyde, a by-product in the catalytic conversion of acetylene to acetaldehyde. Crotonaldehyde, an alcohol denaturant, is used as a solvent for cellulose acetate and is a source of butadiene.

Butyraldehyde is made by the oxidation of butyl alcohol and by the synthesis of crotonaldehyde. It is used in the production of butyric acid, which, in turn, is used in making fruit esters.

ETHYLENE GLYCOL AND DERIVATIVES—Because of favorable physical and chemical properties, ethylene glycol and its derivatives offer many industrial possibilities. It is only within the last few years that large-scale production from natural gas has become economically feasible. The main steps in the production of ethylene glycol are: the natural gas is cracked and the ethylene isolated and chlorinated to produce chlorohydrin, which is converted into ethylene glycol by hydrolysis.

On account of its effective use in dynamites, in solvents, and as an "antifreeze," ethylene glycol is rated as one of the important industrial chemicals. It competes with glycerol in the production of dynamite and as an antifreeze in automobile radiators. As a result of developments in the chlorination of natural gases, its production at a cost comparable with that of glycerol is established. Ethylene glycol is a synthetic chemical and not a by-product. It is therefore not dependent upon conditions in another industry, as is glycerol on the soap and fats industry.

Millions of pounds of glycol dinitrate, a derivative of ethylene glycol, are used in the production of dynamite. For use in coal mines the Bureau of Mines has approved more than twenty-five explosives which contain glycol dinitrate. Its most important advantage is that it freezes at $-22.75°$ C., as against 13° C. for nitroglycerin. Explosives containing the two products have a lower freezing point than those made with nitroglycerin alone or with a mixture of nitroglycerin and nitropolyglycerin.

TRIETHANOLAMINE—This product, as made commercially, contains about 75 per cent triethanolamine, 20 per cent diethanolamine, and 5 per cent monoethanolamine. It increases markedly the penetrative power of various oily materials. For example, 0.5 per cent of triethanolamine added to creosote will reduce considerably the time required to penetrate wood. Triethanolamine also combines with fatty acids to form soaps which are soluble in water, gasoline, kerosene, and oils. These soaps have promise of commercial use.

CITRIC ACID AND OTHER FERMENTATION PRODUCTS—Citric acid is manufactured extensively in the United States by a fermentation process, using the mold known as *Aspergillus niger* with sterile sucrose solution containing certain nutrient salts.

Fermentation is a chemical decomposition or rearrangement of an organic compound induced by living organisms or by enzymes produced by these organisms. In growing molds for chemical operation, the greatest care against contamination must be observed. The following acids have been found in the action of molds on solutions of sucrose: acetic, succinic, malic, fumaric, lactic, oxalic, citric, and gluconic. Practically all work done on sugars has been with sucrose, but recently glucose of high purity has been available in large quantities and could probably be used in all these reactions. Molds may be of value in the production of tartaric acid. Some molds produce esters of various kinds, others alcohols, and in some the carbohydrate is oxidized to carbon dioxide and water.

AMYL ALCOHOL—The synthesis of a blend of pure amyl alcohol from pentane, a constituent of natural gas, is a recent commercial development. Formerly, the only commercial source of amyl alcohol was fusel oil. The use of the synthetic amyl alcohols as a starting point for amyl acetate and other synthetics present many interesting possibilities.

FURFURAL AND DERIVATIVES—Furfural is an aldehyde, first used in commercial quantities for the manufacture of resins of the phenol-aldehyde type. Because of its solvent action, low toxicity, and high power of penetration, it is used to replace aniline and nitrobenzene in shoe dyes and in leather dressings. It is an excellent solvent for nitrocellulose, and its use in the lacquer industry is limited only because of a tendency to darken on exposure to light and air. Furfural is also used to some extent as a tobacco flavor.

It is only within the last few years that furfural has been manufactured in commercial quantities. A large-scale production is from oat hulls, a by-product of rolled oats. The increasing use of furfural may result from the increased demand for resins and plastics.

OTHER PRODUCTS—The use of flotation agents in mining has been one of the more important developments in that field. Of the many products used, potassium xanthate is of interest to the organic chemist. In 1926 approximately 51 million tons of ore were treated by various flotation agents, among which were nearly 4 million pounds of potassium and other xanthates. The principal use of the xanthates is for the treatment of copper ores. Its use has resulted in a marked decrease in the quantity of flotation agents per ton of ore treated.

Included in the aliphatic group of chemicals are the perfume and flavoring products, such as ionone, and important base for violet odors, heliotropin, citronellol, rhodinol, and terpineol.

An unusual application of a synthetic organic chemical is demonstrated in the recent use of calcium gluconate. As one of the most efficient lime salts it is used in poultry feed to harden the shells of eggs. For this purpose it is especially fed to poultry raised for the high-priced hatchery eggs.

Textile Section to Include Chemical Work

The Textile Section, Bureau of Standards, is to be reorganized to include the work in dyestuffs and other allied branches now under the Chemical Division. W. D. Appel, a Bureau of Standards dye expert, is to head the combined unit. The former chief, C. W. Schoffstall, is going into private work as director of the Chicago laboratory of Marshall Field & Company. Mr. Appel for several years has been in a field closely related to that of the Textile Section. He has a wide acquaintance with textile men and with the problems of that and allied industries.

The Drying of Solids—I[1,2]

T. K. Sherwood[3]

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

The possible ways in which the drying of a solid takes place are classified under four cases; evaporation of water may take place at the solid surface or at points within the solid structure, and under each heading the possibilities occur of the resistance to internal liquid diffusion being great or small as compared with the total resistance to removal of vapor. The drying of a particular material is not necessarily restricted to one case, as the mechanism may change from one case to another as the drying proceeds.

The case of drying by internal diffusion of liquid to the surface, with negligible resistance to the removal of vapor, is discussed in detail. The Fourier equations of heat conduction in solids are shown to apply to the drying of solid slabs by this mechanism, and a method is described by which the equations may be used in the analysis of drying data without tedious calculation or an intimate knowledge of the mathematics involved.

The theoretical drying equation is shown to fit the data well for cases of the drying of wood and of clay, and to approximate the results obtained in the drying of soap. The diffusion constant of water in soap changes with moisture content in the soap, explaining the deviation of the actual from the theoretical curve. Data obtained on moisture gradients in soap during drying illustrate the same point.

THE air-drying of a solid involves the vaporization of the liquid contained by the solid, followed by the removal of the vapor in a stream of air. Wet- and dry-bulb thermometry, air-conditioning, and the theoretical moisture-carrying capacity of air under different conditions are fairly well understood, but relatively little has been published regarding the important processes of liquid and vapor diffusion by which the liquid is conveyed from solid to air.

In the drying of solids of appreciable thickness, it is obvious that the water of the solid must by some mechanism or other travel from the interior out to the surface before it can escape into the surrounding air. In the past it has been assumed[4] that the water travels through the solid by diffusion as liquid, although the possibility of it diffusing as water vapor has been pointed out.[5] The outstanding problems in the drying of solid materials are the questions as to exactly how the water travels through the solid up to the surface, how and where evaporation actually takes place, and how these factors influence the moisture distribution through the solid; the temperature of the material; and the rate of evaporation under different conditions of the drying air as to temperature, humidity, and velocity.

The drying conditions may be defined as the temperature, humidity, velocity, and direction of the air. In the drying processes discussed below it is assumed that these conditions are maintained constant, and further, that the latent heat of vaporization of the water is received by the solid directly from the air by convection, and that the heat received by the solid by radiation from the surroundings is negligible.

Classification of Drying Mechanisms

If one assumes that the mechanism by which the water travels from the interior to the surface is that of diffusion, either of liquid water or of water vapor, one can visualize two distinctly different ways in which the drying process as a whole can proceed. These are (*a*) the diffusion of liquid from the interior to the solid surface, followed by vaporization of the liquid at the surface and diffusion of the vapor into the surrounding air; or (*b*) vaporization of the liquid at a point beneath the surface of the solid structure, followed by diffusion of water vapor from that point through the porous solid to the surface and thence out into the air. Both procedures may be divided into those cases where the resistance to internal diffusion is small or great as compared to the resistance to the removal of the vapor. Four general cases result:

I—Evaporation at the solid surface; resistance to internal diffusion of liquid small as compared with the resistance to removal of vapor from the surface.

II—Evaporation at the solid surface; resistance to internal diffusion of liquid great as compared with the resistance to removal of vapor from the surface.

III—Evaporation in the interior of the solid; resistance to internal diffusion of liquid small as compared with the total resistance to the removal of vapor.

IV—Evaporation in the interior of the solid; resistance to internal diffusion of the liquid great as compared with the total resistance to the removal of vapor.

It should be made clear that the drying of a particular material need not be restricted to one of the above cases. Thus, the drying of very wet solids is similar to the evaporation of a liquid from a liquid surface, and is an example of case I, in which the rate of drying usually remains constant. However, as the liquid content decreases the mechanism usually changes to one of the other three cases, and the rate of evaporation falls as the evaporation proceeds. Furthermore, under different air conditions the same solid at the same liquid content may dry by different mechanisms, a phenomenon which will be illustrated below by experimental data. When the solid is wet enough to dry initially at a constant rate, the drying process may be divided into the constant-rate and falling-rate periods. The former is an example of case I, the latter may be any one of the four cases described. It is with the falling-rate period (often constituting the whole of the drying process), and with case II in particular, that this paper will deal.

Discussion of Case II

Case II is that of the diffusion of liquid through the solid to the solid surface, where evaporation takes place, followed by diffusion of the vapor into the main body of the air. A more or less stagnant air film on the solid surface presents a

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[1] Received August 15, 1928. Presented before the Division of Industrial and Engineering Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Abstracted from a thesis entitled "The Mechanism of the Drying of Solids," submitted in partial fulfilment of the requirements for the degree of doctor of science in chemical engineering at the Massachusetts Institute of Technology, 1928.

[3] Present address, Worcester Polytechnic Institute, Worcester, Mass.

[4] Lewis, J. Ind. Eng. Chem., **13**, 427 (1921); see also Walker, Lewis, and McAdams, "Principles of Chemical Engineering," McGraw-Hill Book Co., New York, 1927.

[5] Lewis, McAdams, and Adams, *Pulp Paper Mag. Can.*, **25**, 122 (1927).

resistance to the passage of vapor from the surface into the air. The sum of this surface resistance to vapor diffusion and the internal resistance to liquid diffusion through the solid together constitutes the total or "over-all" resistance to transfer of liquid from the interior of the solid to the main body of the air. Thus, in a case where the surface resistance is negligible compared with the interior resistance to liquid diffusion, variables affecting the latter will affect the over-all drying rate to the same degree, and laws governing the internal diffusion of liquid will apply equally well to the drying process as a whole.

The assumption of a negligible surface resistance to vapor diffusion corresponds to the assumption of a negligible free-water concentration at the solid surface, since no moisture gradient is necessary to cause the water to diffuse through the surface air film. The moisture concentrations across the slab thickness may be shown graphically as in Figure 1, which represents the cross section of a slab, drying taking place from faces *AC* and *BD*. *AB* represents the initial concentration gradient, and *CD* the ultimate gradient which corresponds to the equilibrium water content. Realizing its limitations, Lewis[4] made the assumption that the moisture gradients during the drying were linear from surface to center line, as *EC*, *ED*. This assumption was found serviceable in the derivation of approximate equations. Since the slope of the gradient curve is proportional to the rate of diffusion of water at any point, this slope must fall off from surface to center line, and approach zero at the center. The actual gradient curves are, therefore, of the nature of *CFD*.

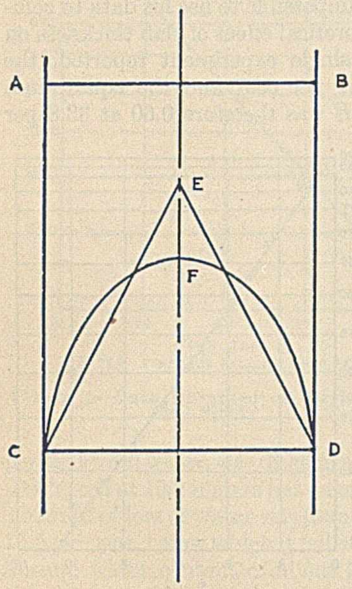

Figure 1—Graphical Representation of Moisture Concentrations across Slab Thickness

In terms of the calculus, Newton's law of diffusion in an infinite sheet may be written

$$\frac{\delta v}{\delta \Theta} = K\frac{\delta^2 v}{\delta x^2} \qquad (1)$$

where *v* is the moisture concentration (per unit volume) at any point in the sheet, Θ represents time, *x* the distance of the point from the sheet surface, and *K* is a constant. A solution of this equation, which is identical with that for the diffusion of heat in a similar solid, may be written.

$$\Delta = \frac{4}{\pi}\left[e^{-\left(\frac{\pi}{2}\right)^2\tau} \sin\frac{x\pi}{2R} + \frac{1}{3}e^{-9\left(\frac{\pi}{2}\right)^2\tau} \sin\frac{3x\pi}{2R} + \frac{1}{5}e^{-25\left(\frac{\pi}{2}\right)^2\tau} \sin\frac{5x\pi}{2R} + .. \right] \qquad (2)$$

where

$\Delta = \dfrac{\text{free liquid concentration per unit volume}}{\text{initial free liquid concentration per unit volume}}$

x = distance from surface

R = half slab thickness

τ = $K\Theta/R^2$

Θ = time

K = diffusion constant, where driving force is expressed as a concentration gradient with concentration as weight of liquid per unit volume

The "free" liquid concentration is that over and above the liquid concentration in equilibrium with the surrounding air. The assumptions involved in the derivation of this equation are: (*a*) the validity of Newton's law of diffusion; (*b*) the constancy of the diffusion constant; (*c*) a uniform liquid concentration throughout the solid at the start; (*d*) that the diffusion is wholly normal to the surface plane; (*e*) that the evaporation takes place at the surface and that the surface resistance to vapor diffusion may be considered negligible, i. e., that the liquid concentration on the surface falls to zero immediately after the start of the drying.

Equations (1) and (2) are familiar in connection with the mathematics of heat conduction in solids. In 1923 Gurney and Lurie[6] published a series of curves which represents the solution (2) of the differential equation (1) in a general form of a character such that by means of these curves one can readily evaluate the series (2) for any values of the variables τ and x. This makes it possible to employ the exact equation without the tedious algebraic computations that formerly made its use impracticable.

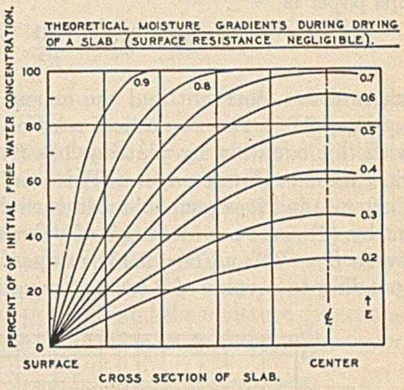

Figure 2

A similar procedure may be followed in the use of equation (2) in connection with the drying of solids, as shown in Figure 2. The percentage of the initial free liquid concentration, which is 100 times the variable Δ, is shown plotted against the location in the slab of the point considered. The various curves represent the relations at different stages in the drying process, as indicated by the values of *E* noted on the plot. *E* represents the ratio of the total free-liquid content to the initial total free-liquid content, and is therefore equal to the area under the liquid gradient curve at any time divided by the area under the liquid-distribution curve at the start of the drying. Since the first term of the series in equation (2) becomes large compared with the later terms when *E* is less than 0.7, the liquid gradients may be seen to be represented by sine curves on Figure 2 for such values of *E*.

Equation (2) gives the theoretical liquid distribution at any time in a slab where internal liquid diffusion controls the drying. Knowledge of the total free water left, or of the variable *E*, is, however, of greater practical interest. *E* might be determined by graphical integration of the area under the liquid distribution curve at any time, or, since

$$E = \frac{1}{1xR}\int_0^R \Delta dx$$

$$\therefore E = \frac{4}{\pi R}\int_0^R\left[e^{-\left(\frac{\pi}{2}\right)^2\tau} \sin\frac{\pi x}{2R} + \frac{1}{3}e^{-9\left(\frac{\pi}{2}\right)^2\tau} \sin\frac{3\pi x}{2R} + \ldots \right]dx$$

$$= \frac{8}{\pi^2}\left[e^{-\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{9}e^{-9\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{25}e^{-25\left(\frac{\pi}{2}\right)^2\tau} + \ldots \right] \qquad (3)$$

which is the theoretical drying equation when internal diffusion is controlling. From its derivation it is seen to be subject to the same limitations as equation (2).

Figure 3 shows equation (3) plotted on semilog paper, as *E* vs. τ. Since $\tau = K\Theta/R^2$, equation (3) or Figure 3 obviously represents the relation between *E* and Θ for any given slab. If the assumptions are valid, experimental data obtained under conditions where the surface resistance was negligible would indicate a similar relation between *E* and Θ.

[6] IND. ENG. CHEM., **15**, 1170 (1923).

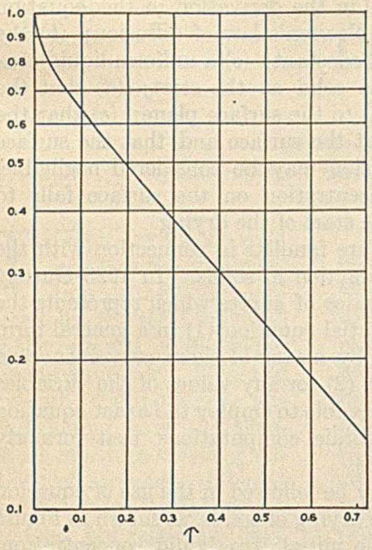

Figure 3—Plot of Equation (3)

In order to compare experimental data with the theoretical curve, a special plotting paper was constructed, using a uniform abscissa scale but so changing the ordinate scale as to force the theoretical relation (3) to be a straight line. With this special paper, since the abscissa scale is uniform, data following the theoretical relation (3) will fall on a straight line when plotted as E vs. τ, as E vs. Θ/R^2, or as E vs. Θ. By comparison of the location of such a straight line with that of the theoretical line, the value of K may be calculated directly. The data of several runs on slabs of the same material but of different thicknesses, when plotted as E vs. Θ should fall on straight lines, the slopes of which vary inversely as the square of the slab thickness.

Lewis[4] has derived an equation for the drying of such materials as soap where the internal liquid diffusion is very slow, which when rewritten in terms of the symbols used in this paper is

$$(1 - E)^n = \frac{C\Theta}{R^2} \tag{4}$$

where C is a constant and the exponent n is approximately equal to 2.0. The theoretical relation (3) may be compared with this equation by plotting $1 - E$ as calculated from (3) vs. τ on logarithmic paper. This has been done as shown in Figure 4, and it is seen that a linear relation results, as called for by (4), over a wide range of values of E. Moreover, between $E = 0.9$ and $E = 0.4$ the slope is very nearly 0.5, corresponding to a value of 2 for n in equation (4). Lewis' equation (4) is therefore seen to compare closely with equation (3) for the drying of a slab under conditions of negligible surface resistance, during the period in which the first 60 per cent of the free water is being removed. Since E approaches zero as the drying proceeds, the curve on Figure 4 must approach $1 - E = 1$ as an asymptote at large values of τ. Equation (4) is similarly limited to values of $1 - E$ less than unity.

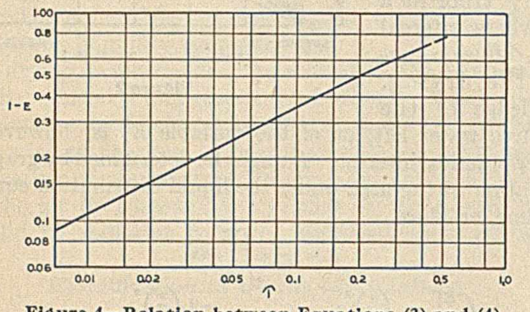

Figure 4—Relation between Equations (3) and (4)

Application of Fourier Heat-Conduction Equations to Drying of Wood

The use of the Fourier heat-conduction equations in the analysis of wood-drying data was suggested in 1925 by Tuttle and Loughborough.[7] Moisture-gradient data on 5.08-cm. slabs of Sitka spruce were compared with the theoretical equation and a value of K so found. This value of K was then used with the theoretical drying equation to predict the drying curve for a similar 5.08-cm. spruce slab. The predicted curve was found to compare well with experimental data obtained in drying such a slab. It is believed that the special plot method described above is a considerable improvement over their method of finding K from experimental data, since not only are the required calculations much less, but little knowledge of the mathematics involved is necessary. The data of only one experiment are shown by Tuttle, and that in the form of a plot, so it is impossible to use his data to compare the actual with the theoretical effect of slab thickness on the drying time. In this single experiment reported, the initial water content was 51 per cent and the equilibrium water content 8 per cent. E was therefore 0.60 at 33.8 per cent water, which from the plot corresponded to about 28 hours. From Figure 3, E = 0.60 when τ = 0.126.

$$\tau = 0.126 = \frac{K\Theta}{R^2} = \frac{28}{(2.54)^2} \times 3600 \times K$$

whence $K = 8.05 \times 10^{-6}$ in c. g. s. units. This is an approximate value of K for Sitka spruce used, diffusion across the grain, the calculation assuming that the data follow the experimental relation as indicated by the plot shown by Tuttle, and that E = 0.60 at 28 hours is a representative point.

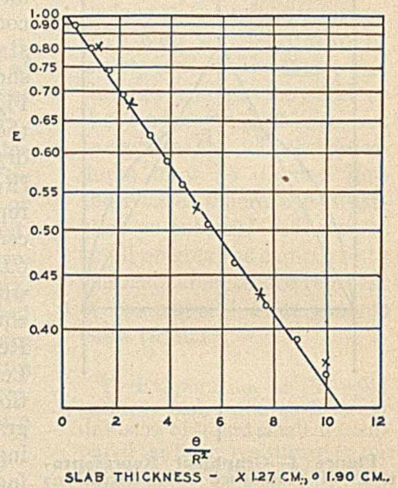

Figure 5—Data Obtained on Drying Poplar Slabs

Data were obtained by the author on the drying of poplar slabs of several thicknesses, in a tunnel drier using a forced air circulation of approximately 1.0 meter per second at 31–35° C. Figure 5 shows E vs. Θ/R^2, using the special plotting paper, as calculated from data obtained in the drying of two slabs 1.27 and 1.90 cm. thick. The dimensions were 15.5 × 20.3 cm. and 15.2 × 15.2 cm., respectively, the edges being covered with a waterproofing cement. The samples were soaked under water for 3 to 10 days, the initial water contents being 49.4 and 39.7 per cent on the dry basis, respectively. As may be seen from the plot, the curves are practically linear down to values of E of less than 0.40. Furthermore, the points representing the two slabs fall on a single line, although there is more than a twofold variation in the term R^2. The value of K may be calculated similarly to the above method using Tuttle's data. Again arbitrarily taking the point at E = 0.60 as a representative point, we have

$$\tau = 0.126 = \frac{K\Theta}{R^2} = 3.72 \times 3600 \times K$$

whence $K = 9.4 \times 10^{-6}$, which compares well with the value of 8.05×10^{-6} obtained from Tuttle's data on spruce.

Application of Drying Equation to Drying of Clay

As pointed out above, various factors may determine in which of the possible classifications of drying mechanisms a given example will fall. Practically any material, if wet

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[7] Fordyce Tuttle, *J. Franklin Inst.*, **200**, 609 (1925).

enough, will dry at a constant rate and the drying will be classed under case I. The thickness of the material will also affect the drying mechanism, as will be seen when it is considered that the drying of an infinitely thin sheet must be an example of case I, no matter what the material or how wet it may be. A thin poplar slab, 4.1 mm. thick, when dried similarly to those samples described above, gave indications that the drying should be classed under case I over nearly the whole drying range. The drying conditions, such as the air velocity used, may also affect the drying mechanism, as suggested above.

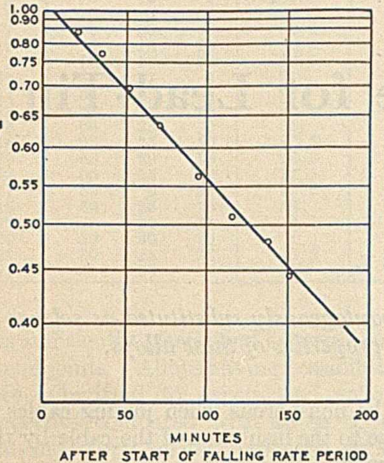

Figure 6—Data Obtained on Drying of Clay Blocks

As an example, the data obtained on the drying of identical blocks of brick clay 7.0 × 7.0 × 2.54 cm. thick may be noted. No wood frames were used, but drying from the edges of the blocks was prevented by covering these surfaces with tin foil. The first block, containing initially 27.3 per cent total water, was dried in a small flue through which air was forced at 15.2 meters per second and at room temperature. The rate of loss of water was found to remain constant down to 16.5 per cent, below which it fell off rapidly to zero at the equilibrium water content of about 3 per cent. Figure 6 shows the data of this experiment, taken during the falling-rate period, plotted as E' vs. time on the special plotting paper previously described. E' is defined as the free water content divided by the free water content at the start of the falling-rate period. The points are seen to fit a straight line fairly well, and the theoretical relation (3) is therefore approximated. Thus the drying of this clay under these conditions is an example of case I between 27.3 and 16.5 per cent total water, and of case II below 16.5 per cent total water. The other clay slab of the same dimensions was dried without forced air convection, and the drying rate remained constant down to about 8 per cent total water. During this constant-rate period the mechanism was that of case I, so that between 16.5 and 8.0 per cent total water the two slabs of the same material and of the same dimensions dried by different mechanisms. The rate of loss of water during the constant-rate period in the second case was only about one-sixteenth of the corresponding rate in the first case. With natural convection the surface resistance to vapor diffusion was therefore approximately sixteen times as great as with the forced convection used in the first experiment. The ratio of surface to internal-diffusion resistance was therefore changed approximately sixteen-fold, which was enough to change the drying mechanism from case II to case I over this range of moisture concentration.

Drying of Soap Slabs

In order to obtain additional data for comparison with the equations derived, several soap slabs were dried in a current of slightly warmed air. Borax laundry soap was cut up and well kneaded with water, and formed into five wood frames, each 14.2 × 14.2 cm. The wood frames were shellacked to prevent absorption of water from the moist soap. Five thicknesses were used—0.63, 1.27, 1.90, 2.54, and 3.17 cm., respectively—although the 2.54-cm. slab was used to obtain moisture-gradient data. The drying was carried out over a period of several months in a small tunnel drier at 23-30° C., with frequent weighings of each sample. The initial moisture content was 20.2 per cent on the dry basis, as determined by analysis of a sample of the batch of well-mixed wet soap. Although the purpose of the wood frame was to prevent loss of water from the slab edges, a certain amount of shrinkage took place, with consequent retreat of the slab edges from the wood frame. Since the length of this exposed edge surface was similar in each sample, the areas of these surfaces were roughly proportional to the slab thickness. It amounted to about 22 per cent of the face area in the case of the thickest slab, and to about 4 per cent of the face area in the case of the thinnest slab.

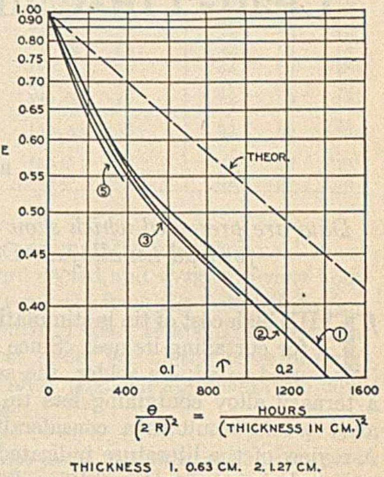

Figure 7—Data Obtained on Drying of Soap Slabs

Figure 7 shows the data obtained plotted as E vs. $\Theta/(2R)^2$, time divided by the square of the thickness, using the special plotting paper described above. The actual points, having an average deviation from the line of less than 2 per cent, are not shown, as there were so many as to make the plot confusing. Two abscissa scales are used, and the theoretical curve shown plotted as E vs. τ. The lines for the various slab thicknesses are seen to coincide fairly well, although there is a twenty-five-fold variation in the term R^2. Although the theoretical relation is represented by a straight line on this plot, the lines representing the data on soap are seen to curve in each case at values of E of 0.50-0.55. This curvature may be explained as being due to the decrease in the diffusion constant K as the drying proceeds and the moisture concentration falls off. The decrease in K is undoubtedly connected with the shrinkage of the soap. It shows up in the plot of the data as a decrease in the slope of the drying curve and a consequent curvature.

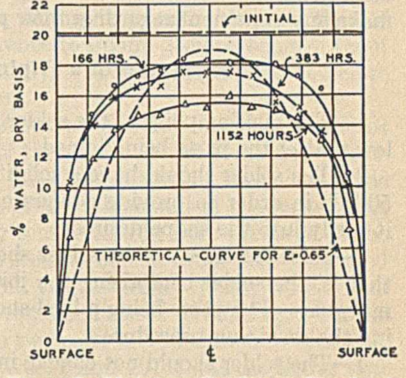

Figure 8—Moisture Gradients Obtained on Drying of Soap

The decrease in the diffusion constant K with moisture concentration is also indicated by the moisture concentration data, obtained on the 2.54-cm. slab. These were obtained by analyzing thin slices cut parallel to the drying face from a square chunk cut from the soap slab. After the chunk had been removed for slicing, the edges of the hole formed in the slab were lined with tin foil to prevent drying from these surfaces. Figure 8 shows the moisture gradients, or free moisture distribution, plotted as per cent free water on the dry basis *vs.* the location in the slab. The points are placed at abscissas representing the center lines of the slices analyzed. The initial moisture gradient is represented by a horizontal line at 20.2 per cent free water. Data were obtained on the moisture gradients in the same slab after 166, 383, and 1152 hours, and are represented by the three solid curves on Figure 8. By graphical integration of the area under the third curve the average free-moisture concentration at that time was 13.1 per cent; E is therefore 13.1/20.2 or 0.65. The theoretical moisture-gradient curve (from Figure 2) corresponding to a value of E of 0.65 is shown by the dashed line on Figure 8. The actual gradient curve is therefore seen to be much flatter than the theoretical curve for the same conditions. This may be explained as being due to the lower values of the diffusion constant K at the lower moisture concentrations—i. e., near the faces. Where K is low a steeper gradient curve is necessary to cause the water to diffuse than in the center where the moisture concentration and consequently K are greater.

Lead-Tin-Cadmium as a Substitute for Lead-Tin Wiping Solder[1]

Earle E. Schumacher and Edward J. Basch

Bell Telephone Laboratories, 463 West St., New York, N. Y.

Data are presented which show that certain lead-tin-cadmium alloys may be advantageously substituted as solders for lead-tin alloys. Data are given showing the physical and chemical properties of these alloys.

The high cost of tin is stimulating investigation of means for curtailing its use. Since large quantities of tin are used in wiping solder, the satisfactory substitution of a ternary alloy containing less tin for the present lead-tin alloy would result in a considerable saving of this metal. A review of the literature indicated that alloys of lead, tin, and cadmium offered good possibilities as substitutes. A phase diagram for these alloys has been prepared by Stoffel.[2] Burgess and Woodward[3] state that cadmium appears as a promising substitute for part of the tin in solders. This is not because cadmium is cheaper than tin, but because it allows the use of a higher percentage of lead. Physical properties of several lead-tin-cadmium solders are given by Schwartz.[4] Since the previous work did not include any examination of the behavior of these alloys as wiping solders, it seemed desirable to continue the work and examine their properties in this respect.

The results discussed in this paper were collected from laboratory tests. Field tests have not yet been made with these solders, and until their behavior under actual operating conditions has been ascertained it is, of course, unwise to make any statement regarding their practical value.

Properties of a Wiping Solder

1—The melting point of the solder should be somewhat below that of the parts being joined.

2—The solder should have a solidification range of at least 50° C. in order to provide adequate time in which to mold it easily into the shape desired.

3—Joints made with the solder should be readily unwiped; that is, the solder comprising the joint should be readily removable. The parts being joined should not be harmed during the unwiping procedure.

4—The solder should not change in composition when subjected to prolonged heating in the melting pot at temperatures ranging from 300° to 400° C.

5—Joints made with the solder should have tensile and shear strengths greater than the parts being joined.

6—The solder should have no injurious effects on the parts being joined and should readily tin them.

7—The joints must be non-porous when joining cables in order to prevent damage to the insulation of the cable by the introduction of moisture.

8—The joint should not deteriorate with age.

Procedure

Selection of Alloys to Be Tested—The main objective of this investigation was to find a wiping solder that would be at least as satisfactory as and cheaper than the 62 per cent lead–38 per cent tin alloy which today is generally used for wiping purposes. (This alloy is referred to hereafter as standard solder.) Since lead is by far the cheapest of the constituents of lead-tin-cadmium solders, and cadmium and tin are about the same price,[5] any cheaper solder in this system must contain a higher percentage of lead. (Figure 2)

Preparation of Alloys—High-purity constituents were used in preparing the test alloys. Bunker Hill and Doe Run leads, containing less than 0.01 per cent impurities, were used. The cadmium was 99.5 to 99.9 per cent pure; the tin, 99.9 per cent.

The constituents of the alloys were carefully weighed with a maximum possible error of ±0.1 per cent. The lead was melted in a graphite crucible under a covering of palm oil to prevent oxidation. As soon as the lead was molten, the tin and cadmium were added. Most of the melts were cooled in the crucible but those from which tensile specimens were to be cast were heated to about 50° C. above the liquidus and poured into molds only slightly cooler.

Experimental

Phase Diagram—Cooling curves of lead-tin-cadmium alloys containing a high percentage of lead showed arrests which agreed closely with those previously found by Stoffel[2] and Schwartz.[4] From Stoffel's diagram (Figure 1) the cooling ranges and the percentages of primary, binary, and ternary solidifications of the alloys given in Table I were calculated. In the range of compositions satisfactory as wiping solders the lead-tin-cadmium alloys have a longer cooling range than the lead-tin.

Workability Characteristics—Standard solder was arbitrarily chosen as having satisfactory workability; that is,

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[1] Received August 18, 1928.

[2] *Z. anorg. Chem.*, **53**, 137 (1907).

[3] Bur. Standards, *Tech. Paper* **109**, 8 (March, 1919).

[4] *Am. Inst. Min. Met. Eng. Tech. Pub.* **85** (1928).

[5] At the time of writing cadmium and tin are both selling for approximately 60 cents a pound.

Table I—Solidification Ranges and Phase Compositions of Some Lead-Tin-Cadmium Alloys

Alloy	Composition			Total Solidification Range	Primary Solidification		Binary Solidification					Ternary Solidification				
	Pb	Sn	Cd		Temp. of beginning	Primary crystals	Temp. of beginning	Binary eutectic	Composition Pb	Sn	Cd	Temp. of beginning	Ternary eutectic	Composition Pb	Sn	Cd
	%	%	%	° C.	° C.	%	° C.	%	%	%	%	° C.	%	%	%	%
1	90	5	5	129.5	275	80	194	10	68	..	32	145.5	10	32	50	18
2	85	5	10	107	252	60	216	30	71	..	29	145.5	10	32	50	18
3	80	10	10	103	248	63	193	16	68	..	32	145.5	20	32	50	18
4	78	16	6	110	255	68	...	..	..	..	..	145.5	32	32	50	18
5	75	18	7	103.5	249	64	...	..	..	..	..	145.5	36	32	50	18
6	75	3	22	91.5	237	7.8	233	86.2	75.7	..	24.3	145.5	6	32	50	18
7	70	22	8	94.5	240	56	...	..	..	..	..	145.5	44	32	50	18
8	70	15	15	87.5	233	40	194	30	68	..	32	145.5	30	32	50	18
9	70	10	20	85.5	231	23.7	216	56.3	71	..	29	145.5	20	32	50	18
10	68	27	5	97	242	54.5	160	17.7	34	66	..	145.5	27.8	32	50	18
11	68	23	9	90	235	52	...	..	..	..	..	145.5	48	32	50	18
12	68	17	15	85	230	37	190	29	68	..	32	145.5	34	32	50	18
13	66	25	9	87	232	50	...	..	..	..	..	145.5	50	32	50	18
14	65	25	10	82.5	228	47.2	150	2.8	65	..	35	145.5	50	32	50	18
15	65	20	15	78.5	224	36.6	182	23.4	67	..	33	145.5	40	32	50	18
16	65	15	20	77.5	223	23	202	47	69	..	31	145.5	30	32	50	18
17	65	9	26	79.5	...	..	225	82	72.5	..	27.5	145.5	18	32	50	18
18	62	38	0	58	239	40.7	181	59.3	36	64	..	...	..	..	..	..
19	60	29	11	72.5	218	42	...	..	..	..	..	145.5	58	32	50	18
20	50	50	0	27	208	21.9	181	78.1	36	64	..	...	..	..	..	..
21	50	25	25	48.5	...	..	194	50	68	..	32	145.5	50	32	50	18
22	32	50	18	0	...	..	...	..	..	..	..	145.5	100	32	50	18

it is sufficiently plastic and coherent to allow the easy formation of joints. Alloys having possibilities as substitute solders were submitted to experienced splicers and their wiping properties compared with those of the standard. Alloys that, in the opinion of the splicers, worked as well as, or better than, standard solder were considered to be satisfactory from the workability standpoint. When wiping characteristics of lead-tin solder were classified as good by the splicer, it was noticed also that the joints were generally non-porous. The data obtained are given in Table IV and show that certain lead-tin-cadmium alloys within a rather well defined area of the phase diagram (Figure 1) are satisfactory from the workability standpoint. This point will be discussed later.

UNWIPING A JOINT MADE WITH LEAD-TIN-CADMIUM SOLDER—Joints made from lead-tin-cadmium solders are unwiped by the same method as joints made from lead-tin solders. Molten solder is poured over the joint until its temperature is raised above 145° C., the eutectic temperature. The solder comprising the joint then becomes soft and may be wiped away with a wiping cloth. 145° C. is the lowest temperature at which joints composed of alloys of lead-tin-cadmium can be unwiped, and is 36° C. lower than the corresponding temperature for alloys of the lead-tin system.

Table II—Composition Changes of Alloys 11 and 18 when Heated for Different Time Intervals at Temperatures above Their Melting Points

Solder	Initial Composition			After Heating 2 Hours at 350° C.			After Heating a Third Hour at 400° C.		
	Pb	Sn	Cd	Pb	Sn	Cd	Pb	Sn	Cd
	%	%	%	%	%	%	%	%	%
11	68	23	9	67.8	23.15	8.83	67.6	23.45	8.92
18	62	38	0	61.8	38.16	0	62	38	0

OXIDATION LOSSES OCCURRING IN SOLDERS DURING PROLONGED HEATING—Since a satisfactory solder should not change in composition when subjected to prolonged heating at temperatures between 300° and 400° C., the lead-tin-cadmium solder, which compared most favorably in other ways with standard solder, was tested for resistance to heating losses. Two circular pots $4^1/_2$ inches (11.4 cm.) in diameter, one containing 6 pounds (2.7 kg.) of standard solder and the other containing the same amount of 68 per cent lead–23 per cent tin–9 per cent cadmium solder, were heated to 350° C. for 2 hours, and to 400° C. for an additional hour. (These temperatures are about 25° and 75° C. higher, respectively, than the temperature at which solder pots should be maintained.) The oxide that accumulated was removed every half hour; the samples were cooled and weighed every hour. Samples for analysis were removed from the pots before each weighing. The data, given in Tables II and III, show that oxidation losses for the test solder are of the same order as standard solder. Neither alloy changed appreciably in composition during the heating.

Table III—Rate of Oxidation of Some Molten Lead-Tin and Lead-Tin-Cadmium Solders[a]

Solder	First Hour		Second Hour		Third Hour		Total Loss in Weight
	Loss in wt.	Temp.	Loss in wt.	Temp.	Loss in wt.	Temp.	
	%	° C.	%	° C.	%	° C.	%
11	1.15	347	0.97	355	1.36	398	3.45
11	1.12	350	0.95	350	1.97	400	3.99
18	1.58	350	0.86	348	1.12	400	3.77
18	1.14	355	0.93	351	1.01	395	3.05

[a] The solder pot used had an inside diameter of $4^1/_2$ inches.

TENSILE STRENGTH—Tensile-strength measurements were made on some lead-tin-cadmium alloys. The alloys were tested as cast in a 600-pound (272-kg.) Amsler testing machine, whose speed was 0.4 inch per minute per foot (0.3 meter) of free length. The data given in Table V show that most of these alloys have tensile strengths comparable with that of standard solder and reference to Figure 2 shows some of them to be economically attractive. These alloys were therefore selected for further testing.

TENSILE STRENGTH OF WIPED JOINTS—It is not sufficient that the tensile strength of the solder compares favorably with that of standard solder, but the strength of the joints made from this solder must be greater than that of the parts being joined. The samples for tensile testing were prepared in the following manner: Two sections of lead cable were connected by a lead-tin sleeve. The two necessary joints were wiped with those alloys that appeared most promising. Tensile loads were applied to the two ends of the sample. Since, in every test (Table I, alloys 11 and 19) it was the sleeve that ruptured it follows that the cadmium solder tins satisfactorily and probably has no injurious effects.

"TINNING" OF SOLDERS—Since there is no established method of measuring "tinning," the lead-tin-cadmium alloys that were being considered for wiping solders were in all cases evaluated for this property by comparison with standard solder. All the alloys tested seemed to tin an alloy composed of 99 per cent lead–1 per cent antimony as satisfactorily as standard solder and at a lower temperature.

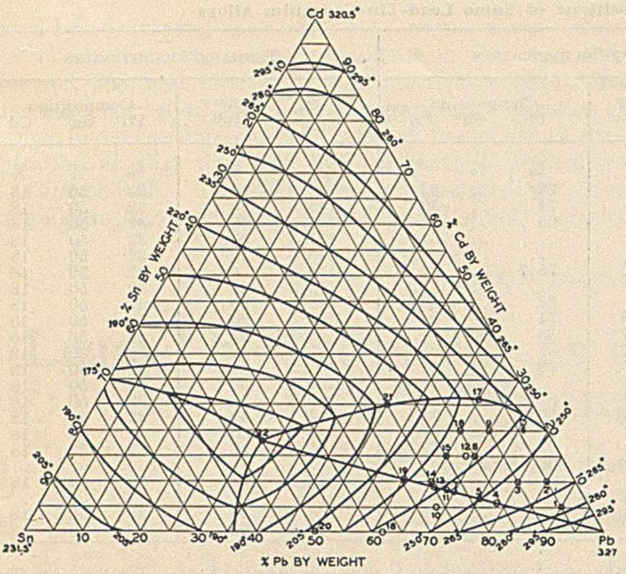

Figure 1—Lead-Tin-Cadmium Phase Diagram

Corrosion of Solders—The resistance of standard solder and the 68 per cent lead–23 per cent tin–9 per cent cadmium alloy to corrosion by saturated lime-water, distilled water, and 0.001 *N* acetic acid was measured by the following method: Samples of the two alloys, each with a total area of 1 sq. dc., were immersed in the corrosive liquids and maintained at 25° C. At various intervals the samples were cleaned with 1:5 acetic acid, dried with alcohol, and weighed. The results indicated that the corrosion of the lead-tin-cadmium alloy was of the same order as that of the standard solder.

Table IV—Porosity and Wiping Characteristics of Various Solders

Alloy	Composition Pb	Sn	Cd	Impurities	Splicers' Comments as to Wiping Characteristics	No. Joints Wiped	No. Joints Porous
	%	%	%				
5	75	18	7	0	Coarse	8	8
6	75	3	22	0	Not workable	..	.
7	70	22	8	0	Fair	8	3
10	68	27	5	0	Good	2	1
11	68	23	9	0	Good	58	0
11–1	67.9	23	9	0.1% Cu	Good	15	1
11–2	67.8	23	9	0.2% Cu	Good	2	1
11–3	67.5	23	9	0.5% Cu	Good	2	1
11–4	67.75	23	9	0.25% Sb	Fair	2	0
11–5	67.6	23	9	0.4% Sb	Coarse	2	0
11–6	67.9	23	9	0.1% Zn	Fair	2	1
11–7	68	23	9	High-Bi Pb[a]	Coarse	10	0
11–8	68	23	9	S. E. Missouri Pb[b]	Good	10	0
12	68	17	15	0	Coarse	2	2
13	66	25	9	0	Good	3	0
14	65	25	10	0	Good	8	0
17	65	9	26	0	Not workable	..	.
18	62	38	0	0	Good	4	0
23	62.6	37.4	0	0	Fair	6	3
24	63	37	0	0	Fair	6	3
25	64	36	0	0	Fair	10	8
26	65	35	0	0	Coarse	4	4

[a] Bismuth content of high-bismuth lead averages 0.155 per cent.
[b] Average copper content of southeastern Missouri lead is 0.07 per cent.

Porosity Measurements—In this work a soldered joint was considered to be non-porous if it could withstand an internal air pressure of 30 pounds per square inch (2100 grams per square centimeter) without leaking. The data obtained on porosity are given in Table IV and show, among other things, that an alloy composed of 68 per cent lead–23 per cent tin–9 per cent cadmium is satisfactory from the porosity standpoint.

Effect of Impure Leads—Two commercial leads, a high-bismuth lead containing 0.155 per cent bismuth and a southeastern Missouri lead containing 0.07 per cent copper, have been used in preparing the 68 per cent lead–23 per cent tin–9 per cent cadmium alloy. The high-bismuth lead decreases somewhat the ease of working the alloy; the southeastern Missouri lead seems to act about the same as high-purity lead, although it may make the solder slightly more workable. Joints made with solders containing the commercial leads were satisfactory from the porosity standpoint. When the copper content of the solder is increased to above 0.1 per cent, joints made with the solder show a tendency to be porous.

Table V—Tensile Data on Some Lead-Tin-Cadmium Alloys[a]

Alloy	Composition Pb	Sn	Cd	Ultimate Strength Average		Maximum		Minimum	
	%	%	%	*Lbs./in.²*	*Kg./mm.²*	*Lbs./in.²*	*Kg./mm.²*	*Lbs./in.²*	*Kg./mm.²*
1	90	5	5	4370	3.1	4400	3.1	4350	3.1
5	75	18	7	5450	3.9	5540	3.9	5280	3.7
6	75	3	22	6790	4.8	6930	4.9	6400	4.5
7	70	22	8	5950	4.2	6670	4.7	5400	3.8
8	70	15	15	4580	3.2	4665	3.3	4495	3.2
9	70	10	20	4910	3.5	5561	3.9	4500	3.2
11	68	23	9	6200	4.4	6500	4.6	5200	3.7
14	65	25	10	6510	4.6	6610	4.7	6460	4.5
15	65	20	15	5390	3.8	6042	4.3	4730	3.3
16	65	15	20	5520	3.9	7100	5.0	4710	3.3
17	65	9	26	5805	4.1	5980	4.2	5660	4.0
18	62	38	0	5385	3.8	5800	4.1	5170	3.6
19	60	29	11	7270	5.1	7310	5.1	6890	4.8
20	50	50	0	6300	4.4	6510	4.6	6180	4.4
21	50	25	25	6620	4.7	7190	5.1	5550	3.9

[a] Four samples of each alloy were tested.

Effect of Small Changes in Composition of the 68 Per Cent Lead–23 Per Cent Tin–9 Per Cent Cadmium Solder—If lead is added to the 68 per cent lead–23 per cent tin–9 per cent cadmium solder, the resulting alloy is more difficult to wipe, and is less reliable. Some of the joints wiped with a solder containing 69 per cent lead were porous. Additional tin makes the solder less coarse, as in the case of standard solder, and joints wiped with it are not porous. Solder containing even 1 per cent additional cadmium appears to oxidize appreciably more at high temperatures and is more difficult to work.

Discussion

Several lead-tin-cadmium alloys have physical and chemical properties comparable with those of standard solder. The

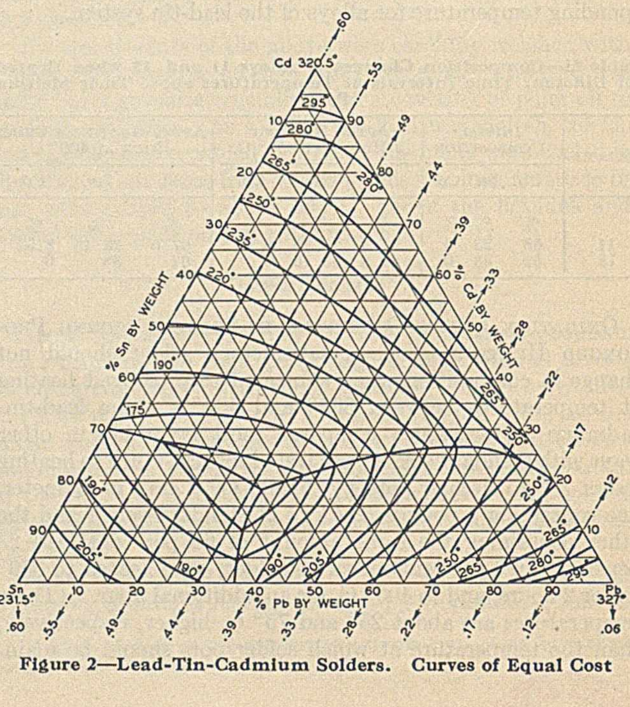

Figure 2—Lead-Tin-Cadmium Solders. Curves of Equal Cost

compositions of the alloys tested are marked in Figure 1. Those best suited for wiping purposes were found to fall on the line drawn from the lead vertex of the equilibrium diagram to the ternary eutectic point. These alloys, during equilibrium cooling, form no binary eutectic. The cooling is therefore very similar to that of a lead-tin solder. Several of these lead-tin-cadmium solders have longer cooling ranges than standard solder. This gives the splicer more time to wipe the joint.

Of the satisfactory lead-tin-cadmium alloys that composed of 68 per cent lead–23 per cent tin–9 per cent cadmium is the cheapest. The substitution of this solder for the standard 62 per cent lead–38 per cent tin may effect a saving of several cents a pound.

Conclusions

1—The addition of cadmium makes possible the use of higher percentages of lead in satisfactory solders.

2—These lead-tin-cadmium wiping solders are generally cheaper than corresponding lead-tin solders.

3—A solder containing 68 per cent lead–23 per cent tin, and 9 per cent cadmium is satisfactory as a substitute for standard 62 per cent lead–38 per cent tin solder.

Protection of Underground Pipe from Corrosion[1]

A Method Used in Southern California

E. O. Slater

Smith-Emery Company, 920 Santee St., Los Angeles, Calif.

The distributing systems of gas and water companies represent 65 to 75 per cent of their invested capital and a large proportion of oil companies' capital investment. The proper protection of this tremendous mileage of underground pipe—over 150,000 miles with its capital value of $1,500,000,000—is of vital and growing importance. The enormous annual repair bill represented by pipe-line corrosion will probably increase rather than decrease, as a large amount of this pipe has been in the ground long enough for accumulated deterioration to demand attention.

The average expenditure for protection is 1.6 cents per foot of pipe for each inch in diameter. This is a very small amount when compared with the cost of reconditioning or replacement while endeavoring to maintain efficient and dependable service.

The methods suggested for protecting against corrosion are:

(1) Manufacture of corrosion-resistant pipe. Progress is being made in this direction by the use of an all-alloy pipe or an ordinary pipe with a resistant shell, although costs, so far, are prohibitive.

(2) Modification of the condition of soil, as placing the pipe in Portland cement or lime.

(3) Use of protective coatings. This is the method most in use.

The rate of corrosion is determined in a broad way by the character of the soil and the soil water. Therefore, any coating, to be effective, must keep the soil and water from contact with the pipe. As one eminent chemist puts it, "Pipe will not corrode if you keep the moisture from it." As soil corrosion falls within the scope of electrochemical theory, it follows that, if the pipe in only known bad soils is protected, then the rest of the line, even in good soil, will be more or less affected. Therefore, the whole line should be protected. Old lines or products of corrosion should not be placed in proximity to the new lines, as electrochemical action is stimulated.

There are several methods of determining the corrosive power of soil. Among these are chemical analysis; ability to conduct electric current; rate of giving off gas when mixed with iron; and loss of weight of iron placed in the soil. These tests are of value when checks are run at the same time on soils of known corrosive power.

Method of Application of Coating

If the protective coating is expected to preserve the pipe, it must be applied to a clean, hard surface with which it can form a permanent bond and to which it will adhere tenaciously. The surface of the metal must be cleaned of all mill scale, rust, dust, and all traces of oil, grease, and moisture. Mill scale is electronegative to iron and steel and this tends inevitably to stimulate pitting. Even on new pipe mill scale is only a thin, brittle, loose covering, and if painted over will crack off because of the different coefficient of expansion between it and the pipe. Pipe may be cleaned by wire brushing, scratching, filing, hammering, pickling, and sand-blasting. Sand-blasting is the only method that gives a really clean surface with the least damage to the pipe. The cost of sand-blasting, as shown in a paper[2] by Fred Benson, of Los Angeles Gas & Electric Company, runs less than 2 cents per lineal foot of pipe 4 inches in diameter. The unit cost reduces as the diameter increases.

Note—Since this article was written one of the large companies has installed a plant especially equipped for sand-blasting pipe commercially, which charges one cent per square foot of surface.

The application of the protective coating is usually the last thing done to the pipe before lowering into the ditch and backfilling. For this reason the job is hurried by the men and slighted by the contractor and the result is generally little protection. Quoting D. R. Hiskey, of the Engineering Department of the Southern California Gas Company, "If we cannot afford to apply properly, why try to protect at all?" Pipe-cleaning and -coating crews should be hand-picked men who could be trained and relied upon to keep up the standard of the work. This part of the work should be dignified as an art for skilled labor as much as welding and should take its place as one of the important parts of pipe-lining. Inspection should be rigid and made by men familiar with the product being used.

Types of Coatings

Protective coatings available for underground pipe lines are:

(1) Bituminous, as native and residuum asphalts, coal-tar pitches, and gilsonite. These are applied cold as paint or hot by dipping or pouring.

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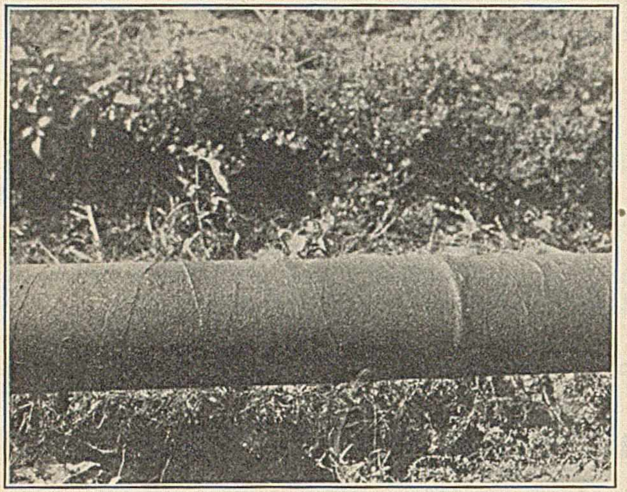
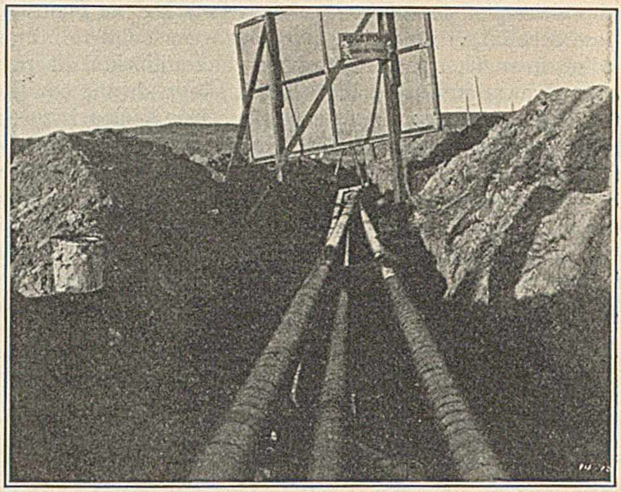
[1] Received August 21, 1928.

[2] *Western Gas*, 4 (May, 1928).



Wrap Applied to Joint in the Field

Note perfect bond at weld and overlapping section; also criss-cross method of wrapping.



Pan-American Line, through Salt Slough, near San Pedro, Calif.

This line was given a "McEverlast" wrap to protect from salt slush, as seen in bottom of trench.

(2) Reënforcing wrappers of felt, cotton, or mineral fiber usually impregnated with bitumen.

(3) Metal coatings.

K. H. Logan,[3] U. S. Bureau of Standards, says:

> The test has already shown definitely that rapid corrosion may occur without the presence of stray currents and that electrolytic corrosion cannot be distinguished from soil action by the character or distribution of corroded areas. As regards metallic coating; while specimens of sheet lead showed little corrosion in all but a few locations, so much cannot be said for specimens of lead coated pipe, this corrosion is attributed to the galvanic action where the lead coating was imperfect.
>
> The thicker coating obtained by the use of fabric impregnated with asphalt or coal-tar pitch appeared better but in several instances there was evidence of deterioration of the asphalts. All of the asphalts tested are of the air-blown variety. Whether a natural asphalt would give different results is not shown by these tests.

The asphalts are less brittle than the coal-tar pitches. Paints require time to dry but tend to adhere better than hot applications. Of the fabric reënforcing wrappers, cotton is the best as it will impregnate, while jute and sisal will only coat over the surface and this allows the fiber to deteriorate from within. Impregnated cotton fabric easily wraps the pipe and does not tend to unwind; it also allows change from square to spiral wrap and vice versa. A good coating should adhere tenaciously; be and remain water-tight; be inert to soil and soil water; have a firm tight bond; stand handling and not cut through on the skids; be dry and not sticky; not be brittle nor easily bruise or scar; be uniform without bubbles or pockets; be thick enough for durability; be free from dirt, dust, and moisture.

After a survey has been made of the soil in which the pipe is to be buried, it is possible to recommend the coatings best suited to meet the existing conditions, thicker coatings being used where natural soil conditions are most severe.

Method Used in Southern California

A coating successfully used by a number of gas and oil companies in southern California, where soil conditions vary, consists of a paint; or a combination of a paint and a reënforcing impregnated cotton wrapper; or a paint, a wrapper, and a hot bitumen. One product successfully used, which is of local manufacture, consists of specially processed native bitumens from Trinidad, Bermudez, and Utah. The priming coat, called "Penetration," made by the proper blending of the bitumens and dissolved in a suitable volatile thinner, is first applied, by hand-brushing or ragging on with a canvas sling. In either case it is rubbed well into the pipe and is put on immediately after sand-blasting, whether in the field or in the yard, 1 gallon covering about 300 square feet. This coat, which dries in 2 hours, forms a perfect bond with the pipe, is followed by a heavy coat called "Electrolysis Proof," made of the same base materials but blended to a consistency of molasses. This coat is flowed on and spread with a hand brush or canvas sling. After a day's drying a second coat of "Electrolysis Proof" is applied. One gallon of this coating covers about 160 square feet. This forms a tough, tight coat and is sufficient protection in good soils. Where greater thickness of the protection coating is desired, the above treatment is followed by a spiral wrap of impregnated reënforcing cotton. This wrapper is of special loose weave, being 20–20 count Osnaburg, and is wrapped with about 1 inch lap. It is then followed by one or two coats of heavy "Electrolysis Proof" coating. The loose weave allows the coating to penetrate and bond the undercoat, allows all air to escape, and eliminates air pockets due to welds or uneven pipe. It is strong, can be pulled very tight, and has a tendency to shrink still tighter when coated. This builds up a thick, tough coat, that will stand handling and abrasive action. When more protection is needed a second wrapper and extra coats are applied. If the ditch must be opened, the wrapped pipe lowered, and the ditch filled in a very short time, the coating on the welded joints would not dry properly. In this case the usual method is to use "Penetration," a wrapper, heavy "Electrolysis Proof," followed by a hot coat of properly blended bitumen. Very rigid inspection is maintained at all times, a mirror on the end of a stick being used for checking the under side of the pipe. Inspectors, trained first in the factory and then in the field, are made available by the company furnishing the material.

Electrolysis Resistance Test

Recently one of the oil companies, while reconditioning four lines at Los Angeles Harbor, encountered a very severe condition of pitting and corrosion. These pipes were in the same ditch buried about 6 feet underground. This ditch was so near the water that a pump was necessary to keep the water level below the pipe at high tide. Complete analyses of the soil and its water-soluble salts are given on page 21.

It was decided to have an electrolysis resistance test run on the coating material ("McEverlast" Electrolysis Paint),

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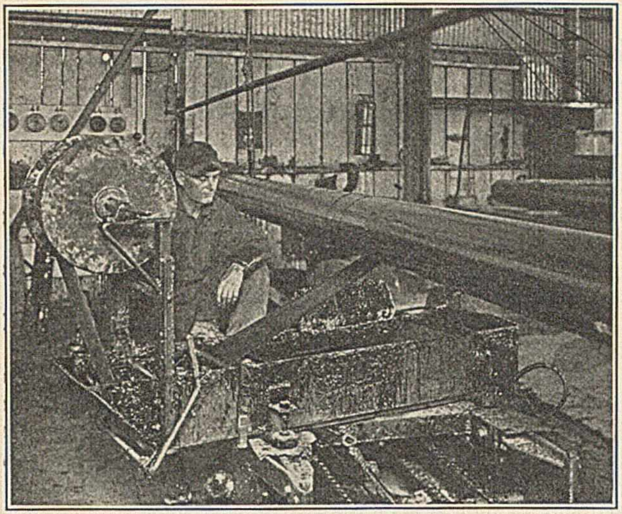
[3] *Oil Gas J.*, **26**, No. 4 (1928).



"McEverlast" Osnaburg Wrap Being Applied to 8-Inch Pipe

Coating underneath wrap consists of one coat of "McEverlast" Penetration; and two coats of Electrolysis Proof Coating.

using soil from this ditch as the electrolyte. This was done as indicated above:

Three specimens of $^1/_2$-inch pipe were painted with one coat of Electrolysis Penetration Coat and two coats of Electrolysis Cover Coat. Three days were allowed between coats for drying. These three specimens of painted pipe were used as one electrode and a battery carbon as the other electrode in a 5 per cent salt solution as the electrolyte. Current was furnished by three dry cells connected in series. The painted pipes were immersed $3^1/_4$ inches in the salt solution. The carbon ($^7/_8$ inch in diameter) was immersed $3^1/_4$ inches in the same salt solution. The distance between electrodes was about $1^1/_2$ inches. The dry cells were of a capacity of 30 amperes and 2 volts—a total potential of 6 volts for the three cells in series.

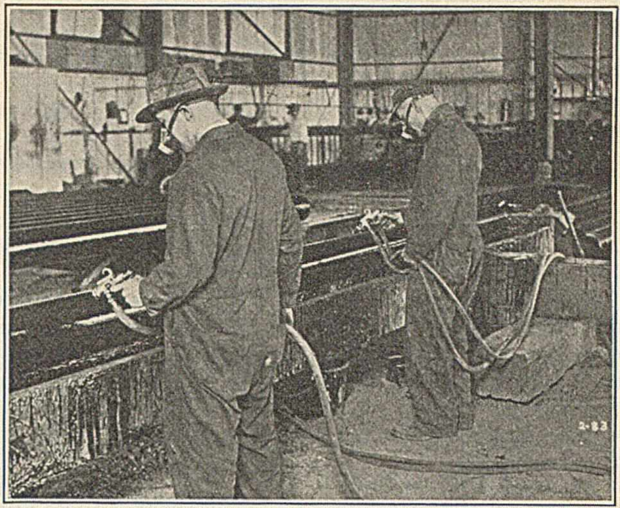
Analysis of Soil

	Per cent
Silica	45.71
Ferric oxide	5.50
Ferrous oxide	2.60
Aluminum oxide	15.30
Calcium oxide	4.76
Magnesium oxide	0.60
Manganese oxide	Trace
Alkalies (Na_2O and K_2O)	0.68
Chlorine	0.33
Sulfuric anhydride	6.10
Phosphoric anhydride	1.05
Total water	14.30
Carbonic anhydride	1.20
Ignition loss	2.00
	100.13

Analysis of Water-Soluble Salts in the Soil

	Per cent
Calcium carbonate	0.059
Calcium sulfate	1.238
Magnesium sulfate	0.974
Sodium sulfate	0.149
Sodium chloride	0.617
Sodium carbonate	None

The test was started September 18, 1927. On the 24th of October, 36 days later, there had been no passage of current, as shown by the discoloration of the solution or the failure of any of the painted test specimens.



Applying "McEverlast" Pipe-Line Coatings to 8-Inch Pipe

The three specimens of painted pipe were then (October 24) removed from the salt solution, and the same specimens were further tested by immersing them in moist corrosive soil. As in the test with the salt solution, the specimens of painted pipe were used as one electrode and a battery electrode was the other. Also the depth of immersion, distance between electrodes, and the potential (6 volts) were the same.

The corrosive soil used was some that was submitted by the Pan-American Petroleum Company, September 29, 1927, from a place from the San Pedro outer harbor district, where they had experienced much trouble from pipe corrosion.

During the first part of the test in the corrosive soil water was added from time to time sufficient to keep the soil moist. After November 8 no more water was added. The drying of the soil brought efflorescent salts to the surface. The soil, however, did not fully dry out, but remained somewhat moist, evidently owing to its claylike character and its content of saline materials.

The test specimens were examined occasionally and tests were made with a milliammeter to determine if any current was permitted to pass between the electrodes owing to the failure of the electrolysis resistant paint. Observations were taken as follows:

DATE (1927)	TIME SINCE OCTOBER 24, 1927	REMARKS
	Days	
November 5	12	No current passing. Specimens OK
November 8	15	Slight current passing. One specimen showed slight failure at junction of paint with end plug in pipe. This specimen was removed and test continued with other two specimens of painted pipe
November 14	21	No current passing. Specimens OK
November 21	28	No current passing. Specimens OK
November 28	35	No current passing. Specimens OK
December 5	42	No current passing. Specimens OK
December 9	46	No current passing. Specimens OK

America Leads the World in Copper Production

World production of copper in one hundred and twenty-seven years, or since the beginning of the nineteenth century, amounted to more than 40 million tons, according to the Bureau of Mines. In comparison, all previous production since the beginning of man's utilization of the metal, estimated by some at less than a million tons, is relatively insignificant. The increasingly important part played by the United States in supplying the world with copper is shown in an economic study of the production of copper during the nineteenth and twentieth centuries which has just been completed by the Bureau of Mines.

The United States has produced more than 19,500,000 tons of copper, or 48 per cent of the world's output since 1800, although production was negligible prior to 1850. The increase in our rate of production from 1845 to 1917 was even greater than the increase in world production during the same period. During the six decades ending with 1920 the average increase per decade in world production was 60.1 per cent. During the same period the average increase in the United States production was 145.8 per cent.

Synthetic Ammonia Plant at Ostend[1]

F. A. F. Pallemaerts

Union Chimique Belge, Brussels, Belgium

THIS plant was the first to combine the Linde system of coke-oven gas fractionation and the Casale synthetic ammonia process.

A special process had to be developed to purify the coke-oven gas in view of its use for liquefaction, and it was found necessary to make slight alterations in the liquefaction process itself during the early stages of the operation of the plant. Considerable success was secured after these changes were effected, and the plant is now producing ammonia regularly at very low cost.

The success of the Ostend plant was the signal for a rapid increase in the number of similar plants combining the Linde system of hydrogen manufacture from coke-oven gas with one of the now classic synthetic ammonia processes. At the present time about a dozen plants of this type are in operation and several others are being planned.

A type of synthetic ammonia plant is described which is being rapidly adopted in Europe. It finds its source of hydrogen in coke-oven gas and combines three processes—the Union Chimique Belge (or Semet-Solvay & Piette) gas treatment process, the Linde hydrogen extraction process, and the Casale ammonia synthesis system.

Nearly 100 million cubic feet of coke-oven gas are being treated per day by these processes, and more than 1000 tons of ammonia per day are being produced by plants of this type now in operation.

Thanks to the cheapness of the hydrogen recovered from coke-oven gas and also to the general economy of the Casale synthesis process, ammonia is produced at a very low cost, considerably below any published figures which have come to the writer's notice.

Extension of This Type of Ammonia Plant

As yet the production capacity of plants of this type does not exceed 136 tons of ammonia per day, because gas is not available from existing coke-oven plants in sufficient quantity to give larger outputs, and distillation works have not yet been systematically concentrated in Europe. However, a move is being made in this direction in Belgium, where a series of central carbonization plants is being planned, arranged for generation of power and utilization of gaseous by-products. The first of these central coking plants is to be erected in the southern Belgian coal field (Borinage) and will comprise a synthetic ammonia plant by the U. C. B. Linde-Casale systems, the first section of which has a capacity for 72 tons of ammonia a day. It is expected that a second central plant in Hainaut, Belgium, will be completed at about the same time.

Low Cost Due to Use of Coke-Oven Gas

The rapid increase in production of synthetic ammonia resulting from the new plants being built or projected cannot fail to alarm those concerned with the sale of ammonium sulfate, and experts have advanced various theories concerning the possibilities of absorption in quantities as a fertilizer.

The Adriatic conference of a few months ago might be expected to have the effect of curbing further increases in production, and although such is not yet apparent, it would seem probable. In the long run, however, the production cost of synthetic ammonia is the factor of greatest importance, and this is where, at least under European conditions, coke-oven-gas hydrogen scores, for electrolytic hydrogen is either too expensive or not available in large quantities in most European industrial countries.

It is, indeed, generally admitted that in Europe coke-oven gas, a by-product, affords the cheapest source of hydrogen. At the Ostend plant water-gas hydrogen costs twice as much as the coke-oven hydrogen.

Because of special conditions it has been decided to install, in addition to the coke ovens, a water-gas plant at Ostend on a scale sufficient for the production of 10 tons of ammonia per day. The reason is that the Ostend coke-oven plant supplies gas to the town, which has large fluctuations in demand, being a seaside resort with a seasonal population.

When it came to choosing between water gas and coke-oven gas for hydrogen manufacture in the case of the first coking plant in Belgium, the same relation in favor of coke-oven-gas hydrogen was found, and the latter was therefore chosen.

This superiority of coke-oven-gas hydrogen is not necessarily universal, and in localities where very cheap power is available, either hydroelectric or in the form of very cheap fuel, such as cheap and good lignite, the use of coke-oven gas may not be the most economical; however, according to our latest information, there is not yet a single plant where water gas for hydrogen manufacture is being produced from lignite.

The following costs are found for 1 cubic meter of hydrogen from different sources, under Belgian conditions, excluding the cost of extraction of the hydrogen from its gaseous primary material:

	Belgian Francs	Dollars
In water gas:		
From coke at 170 Belgian francs per ton	0.22442	$0.0062
From coal at 188 Belgian francs per ton	0.214	0.0059
In coke-oven gas, at 0.14 Belgian franc per cubic meter, residual gas being valued at same price per calorie as original gas	0.084	0.00234

Size of Plant

The original Ostend plant, which was really experimental as it constituted the first application of the combined Casale-Linde-U. C. B. systems, was built for an output of 16 tons of ammonia per day. It comprised three 8-ton Casale units and three corresponding Linde units, one unit of each plant being in reserve.

For the first few weeks of operation, the production was low and irregular, and improvements, bearing almost entirely on the purification of the coke-oven gas preliminary to its fractionation, had to be made. Thereafter the production rose steadily until it reached an average of 18 tons, with peaks of 23 tons, giving a regular output 50 per cent above that for which the plant was intended. Four additional Casale units have since been installed, and the hydrogen plant has

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[1] Presented at the Second International Conference on Bituminous Coal, Pittsburgh, Pa., November 19 to 24, 1928.

been increased by two large units, each with a capacity of 3000 cubic meters of hydrogen-nitrogen gas; with these the plant produces 40 to 55 tons of ammonia per day.

A plant of this size is small compared with the I. G. plant, the Billingham plant of Imperial Chemical Industries in England, or the Hopewell plant of the Allied Chemical and Dyes Corporation now nearing completion. However, it is proportional to the size of the country and, as already said, this type of plant especially lends itself to distribution and to economic operation under the conditions found in Europe. When coke-oven plants have been concentrated as is now being planned, additional units will be added and favorable results are expected from the enlarged plants.

Thanks to the cheapness of the hydrogen, and also to the general economy of the Casale synthesis process, ammonia can be produced at the cost of about 9 American cents per kilogram of nitrogen in the form of ammonium sulfate (including the cost of the sulfuric acid and total operation costs, amortization, etc.).

Genesis of the Type

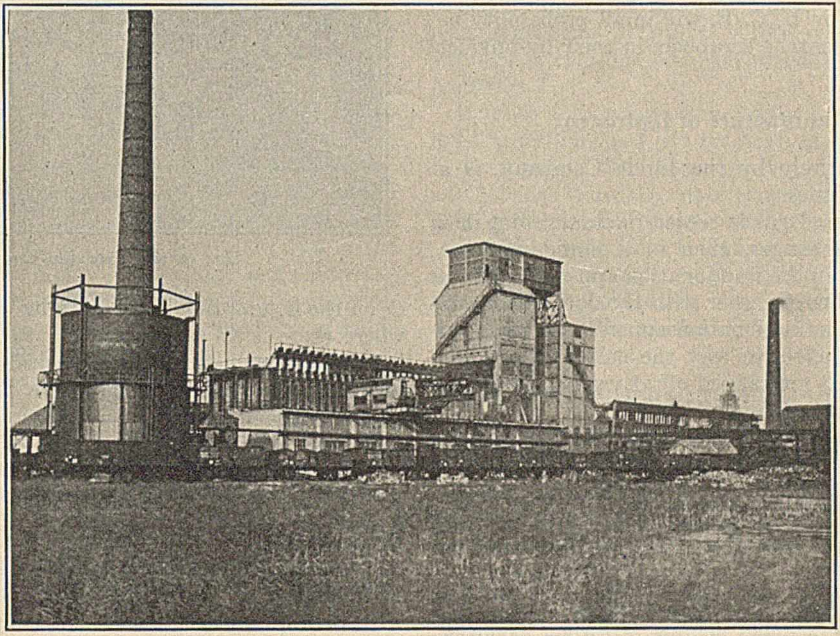
After the Semet-Solvay & Piette Company (which has since become a division of the Union Chimique Belge) decided to manufacture synthetic ammonia, the first problem was a cheap source of hydrogen. Coke-oven gas was chosen for the reasons already given.

The next question was how to obtain hydrogen from this source. Several processes were investigated—fractionation, and the iron-steam processes.

The last-named processes, which were being worked at the time by Bamag and by the Alais, Froges et Camargue Company, were carefully compared and the conclusion reached that the Alais process, which was conducted in batteries of externally heated retorts, had not been sufficiently improved. The Bamag or Messerschmidt system had been tried out on an industrial scale, but was found to require a large number of converters of small capacity, considerable labor, and to yield a rather impure hydrogen gas with a low-value residual power gas. So these processes were eliminated.

Of the fractionation processes, two were taken under consideration, both elaborated by world-famous firms; they were the Claude system and the Linde system. It would be hazardous to express an opinion as to the superiority of either of these processes over the other, as both are splendidly worked out.

The principles of each of these systems are too well known to require detailed description here. Briefly, whereas the Claude system applies expansion with external work, by releasing the compressed gaseous mixture in an expansion engine which Claude calls a hydrogen motor, the Linde process utilized the well-known Joule-Thomson effect of self-intensive cooling through expansion without external work. For certain reasons the Linde system was preferred.



Coke Ovens

The Casale system was adopted after a careful study of the three then available processes. The excellence of the choice has been proved by the fact that the Casale system has been installed all over the world in the face of competition from new processes, and has now reached a total capacity of more than 1000 tons of ammonia, equivalent to 4000 tons of sulfate, a day.

Let us now go into the details of the process.

Preliminary Treatment of Coke-Oven Gas

Such little experience as was available came from a small experimental plant situated at Oberhausen in the Ruhr district, where it had been installed with the collaboration of the Linde Company, by the originator of the coke-oven-gas hydrogen idea, Mr. Bronn, an engineer of the Rombacher Eisenhutten Company.

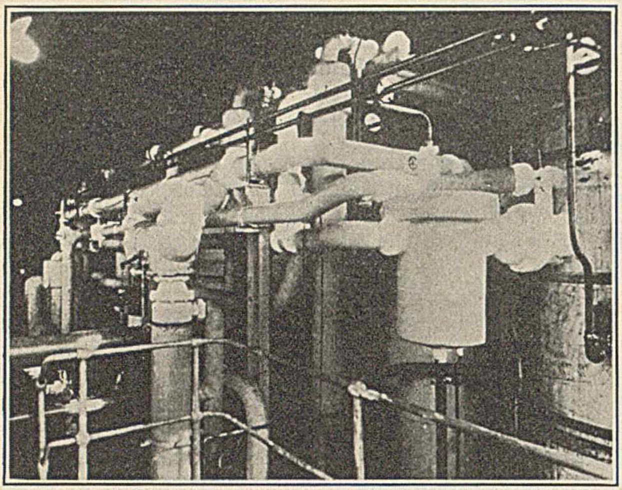
All that was known from the Oberhausen experience was that the gas had to be dry and free from carbon dioxide; also that it probably would have to be desulfurized before compression. These conditions had been effected at Oberhausen through purification of the gas in iron oxide purifiers, followed by compression, washing under pressure with water to remove carbon dioxide, a final decarbonation by means of caustic soda, and drying under pressure by means of calcium chloride.

This treatment was not considered very practical for quantity production and it was proposed to replace both desulfurization and decarbonation by an ammonia wash process, working under ordinary pressure. This was accomplished only after certain obstacles had been overcome, for the washing of gas with ammonia proved more difficult than might have been expected. The results of this treatment were excellent, the acid constituents of the gas being removed to the extent that less than 0.1 per cent carbon dioxide remained, which is better than is obtained with a pressure water wash, which leaves as a rule 0.3 to 0.4 per cent carbon dioxide.

The chemical drying of the gas was omitted and left to the refrigerating plant.

The hydrogen plant was started up along these lines, but difficulties arose from the presence of heavy unsaturated hydrocarbons in the gas; these hydrocarbons polymerized in the less cold parts of the hydrogen apparatus and caused obstructions and even local explosions. One apparatus was even partly destroyed and, as a larger unit (3000 cubic meters of hydrogen-nitrogen) was under construction, the small unit was not rebuilt. A thorough investigation of the causes of the trouble was undertaken, and it was decided to install a pressure water wash in order to remove all hydrocarbons which had a solubility coefficient higher than 1. This proved very effective, and the plant has been running smoothly ever since.

A few incidents of minor importance, however, have shown it desirable to carry the purification process still further, for the purpose of removing oxides of nitrogen and volatile nitro compounds. A simple physical treatment of the gas has been devised, of which excellent results are expected. The trouble due to the formation of explosive copper acetylide has also been eliminated.



Coke-Oven Gas Fractionation Apparatus

The ammoniacal liquor obtained in the decarbonation treatment of the gas is distilled into the sulfate saturators. This simple process will be replaced in future plants by a system in which the ammonia is regenerated for the same purpose, in order to make all the liquid ammonia produced in the ammonia plant available for uses other than sulfate manufacture from sulfuric acid.

Lately, patent applications have been made for a process replacing the whole classical treatment of coke-oven gas for the recovery of ammonia and benzene by a new simplified system combined with the synthesis of ammonia. Future coke-oven plants built by U. C. B. will in all probability be without saturators or benzene scrubbers in their by-product department.

Plant for Manufacture of Hydrogen

This plant, built entirely by the Linde Company, is a wonder of industrial physics.

The purified compressed gas is cooled in stages, first in a countercurrent cold exchanger, then in a liquid-ammonia refrigerator, and finally in the fractionation apparatus, where the Pictet cycle is applied together with the Joule-Thomson effect on nitrogen. This fractionation apparatus is arranged to utilize in the most effective way the cold contained in the condensed gases that are tapped off at various points on the gas circuit as the temperature is lowered.

The condensates which are successively removed are, in order:

(1) *Ethylene* at a temperature of about 120° A. This liquid, although called ethylene, contains only 20 to 30 per cent of C_2H_4, the other gases being propylene, ethane, methane, and some uncondensed coke-oven gas.

(2) *Methane* at temperatures of 25° to 85° A.; it contains mainly methane, with ethane, ethylene, and uncondensed gas.

(3) *Carbon Monoxide*, a liquid mixture of carbon monoxide and nitrogen, with some methane, ethylene, etc.

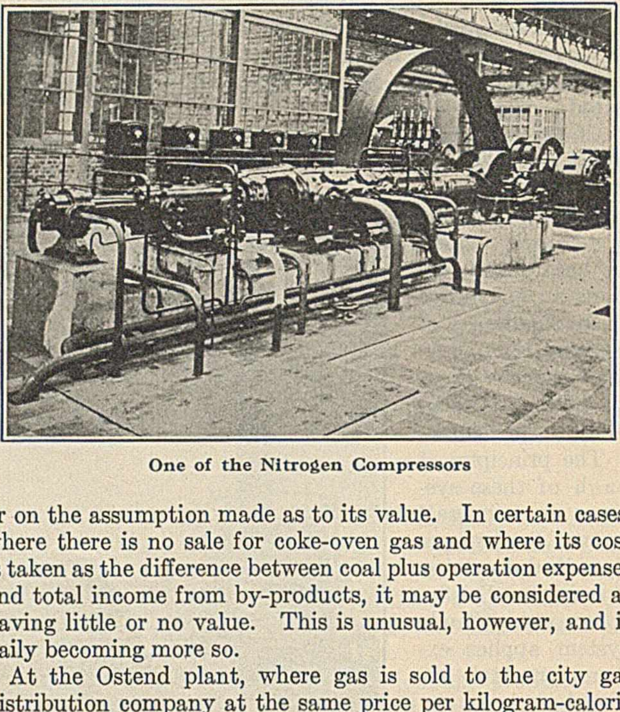
The compressed cold gas that is left is now a mixture of hydrogen and nitrogen, but still contains small quantities of methane and carbon monoxide. These impurities are almost totally eliminated by means of a liquid nitrogen wash, which removes methane entirely and leaves only 0.001 per cent of carbon monoxide. Oxygen and water vapor are also totally removed.

There is no other process, to the author's knowledge, which produces such pure hydrogen from any non-electrolytic gas. The carbon monoxide elimination is far more complete than with any chemical process, and its chemical elimination by means of cuprous solutions was abandoned by the Linde Company as soon as the liquid nitrogen wash had been applied.

This extremely important feature gives the Linde process a decided superiority over certain processes in which no attempt is made to eliminate the considerable residual carbon monoxide percentage that remains in the gas as it leaves the expansion motor. This is, however, not so great an inconvenience with the Claude synthesis process, because part of the residual carbon monoxide is converted into methanol by a preliminary catalytic treatment, and also because the large amount of methane which is formed in the ammonia catalyst tubes is eliminated with the waste gases, as there is no recirculation.

Cost of Linde Coke-Oven-Gas Hydrogen

The two main factors in the cost of Linde coke-oven-gas hydrogen are energy and the cost of the coke-oven gas itself. The energy consumption per cubic meter of hydrogen at atmospheric pressure is 0.246 kilowatt-hour. The total expenses for the production of 1 cubic meter of hydrogen (without nitrogen and at atmospheric pressure) amount to 0.141 Belgian franc ($0.00395). The cost of the coke-oven gas which is used obviously depends on the available market or on the assumption made as to its value. In certain cases, where there is no sale for coke-oven gas and where its cost is taken as the difference between coal plus operation expenses and total income from by-products, it may be considered as having little or no value. This is unusual, however, and is daily becoming more so.



One of the Nitrogen Compressors

At the Ostend plant, where gas is sold to the city gas distribution company at the same price per kilogram-calorie as coal, the cost of gas is as follows:

2.3 cubic meters of coke-oven gas at 0.14 Belgian franc per cubic meter = 0.323 Belgian franc

However, as the Linde process returns 70 per cent of the calorific power of the gas in the form of a high-calorific-power gas at 6500 to 8000 kilogram-calories per cubic meter; and when allowance is made for the income from this source, counting the hydrogen-free gas at the same price per kilogram-calorie as the original coke-oven gas, the detail is as follows:

30/100 × 0.323 = 0.0969 Belgian franc ($0.0027)

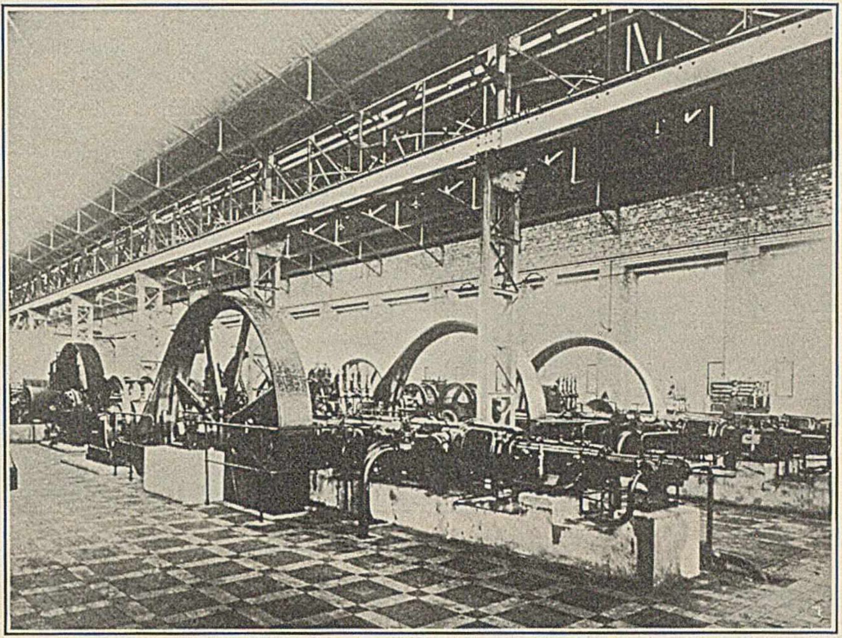
The total cost of Linde coke-oven-gas hydrogen is therefore

0.00395 + 0.0027 = $0.00665 per cubic meter ($0.1883 per 1000 cubic feet)

The author does not know of any lower cost for hydrogen.

Utilization of Residual Gas

In this calculation the residual high-power gas, which consists mainly of methane and ethylene and their homologs, with some nitrogen, has not been valued at more than the original coke-oven gas per calorie. This is a fair assumption as long as it is not used for any other purpose than coke-oven gas itself is used. But this gas is much more valuable than coke-oven gas. In the first place, it is entirely free of all sulfur compounds and other impurities, and is absolutely anhydrous. It also is particularly suited for certain industrial uses, such as the heating of special furnaces—the Libbey-Owens process for instance—and it also lends itself remarkably well to long-distance conveyance of gas which is being developed in continental Europe. A simple calculation shows that one million kilogram-calories represent 121 cubic meters of rich residual gas at 8270 kilogram-calories per cubic meter or 214 cubic meters of ordinary coke-oven gas as 4680 kilogram-calories per cubic meter. The compression of these volumes to 30 atmospheres, which is generally admitted as being suitable for long-distance distribution, will require 25.4 horsepower in the case of the former gas, as against 45 horsepower in the case of the latter. The energy economy will therefore be 43.5 per cent in favor of residual gas.



Hydrogen Plant, Nitrogen and Gas Compressors

The above advantages concern only the crude uses of the rich residual gas in the crude form. This gas, however, lends itself to even more valuable application, for its components can be collected separately and used in a whole series of chemical processes to form valuable products.

Ethylene can be converted into ethyl alcohol (this application has already been put into practice in certain European plants), diethyl sulfate, or any of the valuable halogen addition products. Propylene, which accompanies its lower homolog, can be transformed into its corresponding alcohol by the same process.

The Linde Company builds ethylene fractionating apparatus which will convert the 30 per cent "ethylene" obtained in the ordinary Linde coke-oven-gas fractionating apparatus into 80 to 95 per cent ethylene, the gas being thus rendered suitable for chemical processes requiring ethylene of high purity. The ordinary 30 per cent ethylene can be used without rectification in many processes, especially in alcohol and ether manufacture.

A Linde ethylene fractionation apparatus has been installed by the I. G., and another will soon be working at the Ostend plant of the U. C. B.

Methane has not yet found any considerable industrial use, and it is merely used for heating purposes. A certain amount, however, is compressed into tubes and used for oxy-methane steel-cutting and for the soldering of steel, lead, etc. A small quantity of hydrogen has to be mixed with the methane in order to increase the velocity of combustion, which is too slow in the case of methane alone. This use will probably never absorb the entire production of methane in coke-oven-gas hydrogen plants; but without doubt additional uses for methane will sooner or later be found, probably in the direction of its polymerization into liquid hydrocarbons.

One utilization of methane is already becoming industrial. It consists in cracking methane into hydrogen and carbon dioxide, by the action of steam and the use of suitable catalysts. This transformation, which at first may seem a degradation, is useful where a large quantity of hydrogen is required from a small quantity of coke-oven gas. Indeed, whereas 1 volume of coke-oven gas will yield 0.5 volume of hydrogen, the same quantity of coke-oven gas will give 1.7 volumes of hydrogen, or more than three times as much, if methane is converted into hydrogen. It will therefore be apparent that the advantage is considerable even without a remunerative use for methane.

It must not be forgotten, however, that in this case there is little residual gas left for heating the ovens, which have to be supplied with some other gas, such as producer gas, and this gas is usually more expensive per calorie than coke-oven gas under European conditions.

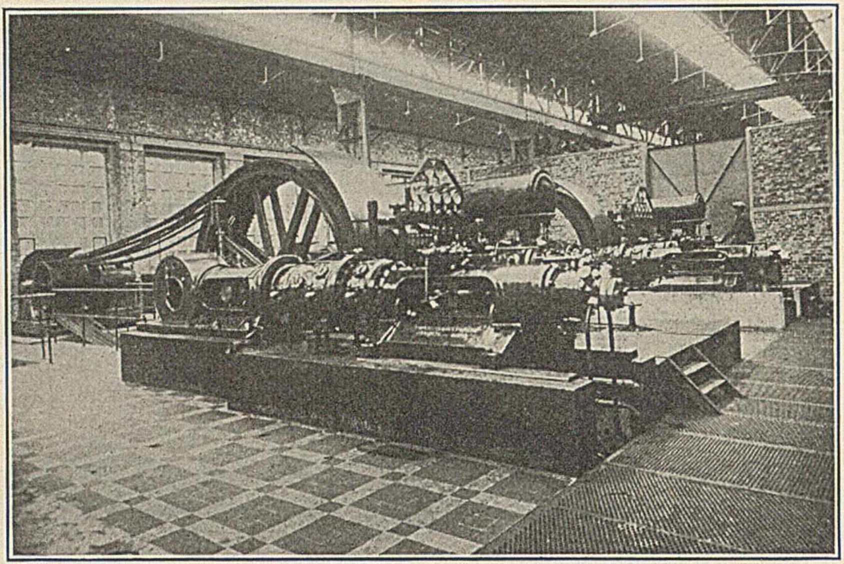
It will be seen from the above that, based on the residual gas having the same value as the original coke-oven gas, the price will probably be lowered considerably if the various constituents of the residual gas are exploited to the greatest possible advantage.

Description of Ostend Type of Coke-Oven Hydrogen Plant

Coke-oven gas from the adjoining coking plant, which has undergone the usual treatment for by-product recovery, is extracted by means of exhausters and submitted to a treatment in which it is successively washed with an ammonia solution, with water in sufficient quantity to remove the ammonia carried over, then with sulfuric acid, which eliminates the last trace of ammonia, and finally with caustic soda, which fixes any sulfuric acid or carbonic acid which might be left in the gas.

The purified gas is stored in a gasholder, from which it is exhausted by compressors which compress it in two stages to about 9 atmospheres. Under this pressure it is refrigerated by means of liquid ammonia from the synthesis plant, and in passing through a cold exchanger it is warmed again to about normal temperature.

At this temperature it is now washed with water in pressure water-wash towers, where 1 volume of compressed gas is washed with a little more than 1 volume of water. The older towers pass about 1750 cubic meters of gas per hour, the new towers, about 5300 cubic meters and the corresponding quantities of water.


Hydrogen-Nitrogen Hypercompressors

The energy of the water as it leaves the pressure towers is recovered in hydraulic turbines placed on the same shaft as the pumps and motors, each group comprising motor, pump, and turbine. The motor has to do all the work at the start, but its power consumption falls to about 40 per cent when the water is admitted through the turbines.

This water evolves gas as soon as it has passed the turbine, like soda water in a bottle when the stopper is removed. This gas is collected and returned to the residual gas from the fractionation. The "degasification gas" is not all carbon dioxide as in the case of the Haber-Bosch water wash, where a gas with 30 per cent carbon dioxide is pressure-washed. Indeed, the gas here, besides containing originally only 1 to 2.5 per cent carbon dioxide, has been very completely decarbonated in the ammonia wash. The object here is entirely different, and is to remove mainly acetylene present in the proportion of 4 parts per thousand only. It seems ridiculous to have to resort to such powerful means to remove a disagreeable gas present in such minute quantities, but the treatment is effective, besides being absolutely necessary, until some better means is brought into action. As it is, the "degasification gas" has the following composition:

	Per cent
Olefins	12
Oxygen	1
Carbon monoxide	6
Hydrogen	31
Methane	38
Ethane	2
Nitrogen	10

There is no use for this gas other than to incorporate it into the residual gas used for heating purposes.

The coke-oven gas, which is now free from benzene and amply purified, is refrigerated for the second time by means of cold exchangers and ammonia refrigerators to a temperature of about −45° C. At this temperature water vapor is removed sufficiently to avoid rapid obstruction of the fractionating apparatus due to freezing of the condensed water. The gas now enters the fractionating apparatus, and leaves it in part as a pure mixture of hydrogen and nitrogen with the desired nitrogen percentage for the ammonia synthesis and in part as various "residual" gases which at present are mixed and, after cold exchange, returned to the coking plant where the joint residual gas is used to heat the coke-oven batteries.

These coke ovens, which are of the U. C. B. (Semet-Solvay & Piette) combined type, are arranged for being heated by producer gas, rich gas, or any intermediate gas. The most varied gaseous mixtures, depending upon the demand for gas from the town gas-distribution company, which they also supply, are used successfully. Sometimes some coke-oven gas is used, but the normal supply is a variable one consisting of producer gas (from U. C. B. automatic producers gasifying coke breeze) and rich residual Linde gas. The ovens work splendidly on this variable but well-controlled mixture. They have been working for nearly four years now under these conditions.

As previously mentioned, in the original plant no provision was made for the use of the water wash, and there was some trouble with the fractionation plant, when a large quantity of benzene was collected at the ammonia refrigerators. When the water-wash plant was started, there was no longer any benzene to be seen, proving that all the benzene was dissolved by the pressure water, which acted more effectively than any oil wash. It was therefore decided to install a second refrigerator before the water wash, so that benzene was again recovered. This system of benzene recovery does not consume any energy or materials, as it consists simply of static refrigerators and cold exchangers and is run on liquid ammonia from the synthesis plant.

Since the Ostend plant has been started, the Linde Company has built a number of installations, treating daily a total of more than 2.5 million cubic meters of coke-oven gas. Besides the extensions to these various plants under preparation, or already being carried out, as at Ostend, several large new installations have been planned. The earliest plants, except for the experimental unit at Oberhausen, were built first in Belgium and then in France, but of late several large ones have been erected in Germany. It now looks as if the Germans, who apparently were at first content to rely on the I. G. process, are seriously entering the field with the Linde coke-oven-gas hydrogen process.

In all, the Linde Company has provided seven units of 1600 cubic meters of coke-oven gas per hour, and nineteen units of 5000 cubic meters per hour—all for ammonia synthesis. One unit for treating 7500 cubic meters of gas per hour is under construction, which will supply hydrogen for the Bergius process.

It is worthy of notice that the Linde hydrogen-nitrogen process does away with the expensive combustion of hydrogen in air, which is applied in certain plants in order to incorporate the necessary amount of nitrogen into the gaseous mixture. Linde nitrogen costs in power only 0.2 kilowatt-hour per cubic meter in the larger unit, and it would be necessary to secure hydrogen for nothing in order to justify using 1 volume of precious hydrogen in order to obtain 2 volumes of nitrogen.

In the hydrogen-nitrogen apparatus the nitrogen, besides coming partly from the coke-oven gas itself, is introduced by saturation of the hydrogen with nitrogen during the liquid nitrogen wash. The nitrogen proportion is ingeniously regulated by acting on the temperature of the gas, the pressure being kept constant. The temperature itself is regulated by the pressure under which liquid nitrogen is kept in the liquid nitrogen boiler, which constitutes the last stage in the cooling of the gas.

A pressure of about 0.2 atmosphere in the nitrogen boiler insures the required nitrogen percentage in the mixture, the gas itself being under 9 atmospheres.

It has been found useful at Ostend to generate hydrogen with a little less than 25 per cent of nitrogen, and to correct the mixture in each synthesis unit by means of an addition of nitrogen.

The Ostend nitrogen machines are of a size corresponding to the hydrogen units. They produce pure nitrogen of 99.8 per cent purity and at the same time pure oxygen at 99 per cent. The Linde Company builds units much larger than those at Ostend, the largest making 3600 cubic meters of nitrogen per hour (126,000 cubic feet per hour). In one plant 16,000 cubic meters (560,000 cubic feet) of nitrogen are produced per hour.

Ammonia Synthesis Plant

This is a Casale plant. The Casale system has become very widely distributed in Europe, Russia, and Japan. More than 1000 tons of ammonia a day are produced by it. This shows very remarkable development, as the first Casale unit, which produced 2 tons of ammonia per day, was started at Terni in Italy as late as the autumn of 1921. From 2 tons the capacity of the Casale unit was increased successively to 6, 20, and to 30 tons. Altogether twenty-four plants are at present in operation, distributed all over the world: ten in France, three in Japan, one in Russia, one in Spain, two in Switzerland, two in Belgium (where another large plant is being planned), three in Italy, one in England, one in the United States (originally erected at Niagara Falls but now being transferred to Belle, W. Va.).

The Casale synthesis plant runs on hydrogen from any source; nine plants run on coke-oven-gas hydrogen, ten on electrolytic hydrogen, three on water-gas hydrogen.

The equipment is standardized so that a 5, 8, 16, 24, or 30-ton a day Casale unit can be purchased complete.

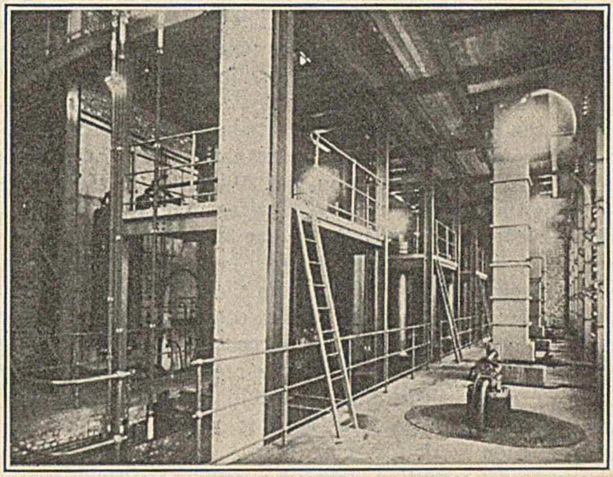
At Ostend there were at first three 8-ton units; at present there are seven. In the new plants being planned by the U. C. B. Company, 30-ton units are contemplated, although no unit of this size has yet been built. The experience with the 20-ton unit, which is in action in several plants, and which has an output of 26 to 32 tons (actually reached in one of the Japanese plants), shows that a production of 35 to 40 tons may be expected of the 30-ton unit. When the new large unit goes into operation, it will, to the best of the writer's knowledge, be bigger than any ammonia unit, including the Haber-Bosch I. G. unit.

As is well known, the Casale process works under a pressure of 750 atmospheres. Of late it has been thought in various quarters that it was advantageous to carry out the synthesis at lower pressures, 200 atmospheres or even less. In the writer's opinion, there is much to be said against this view as the use of high pressure has very decided advantages. One of the most important is that the entire ammonia output is available in the form of liquid ammonia, the latent cold content of which is extremely useful and permits very considerable energy savings in other parts of the plant, especially where coke-oven gas has to be treated. The elimination of the huge refrigerating machines, which would be required in the absence of available liquid ammonia, alone constitutes a considerable economy of energy, as has been mentioned in the description of the coke-oven gas treatment. The availability of the total output in the form of liquid ammonia also renders complete removal of benzene possible without any appreciable energy consumption, and besides, there are still other uses of this liquid ammonia in the modern ammonia derivatives plant, such as refrigeration of the nitrous fumes in the ammonia oxidation nitric acid plant, etc., which made the liquid state of the Casale ammonia an extremely valuable asset to the process.

As regards power consumption in compressing the gas, it has been repeatedly shown that there is very little difference in the energy consumed once the pressure exceeds 200 or 300 atmospheres. For instance, the ratio of the energies required for compressing an ideal gas to 729 and to 243 atmospheres is 6 to 5, so that, whereas the Casale process consumes 1.2 kilowatt-hours per kilogram of ammonia for compression, a process working under 300 atmospheres will still consume 1.05 kilowatt-hours. This difference, small as it is, is compensated by the absence of a recirculating pump in the Casale cycle, recirculation being induced in the latter system by the injection of the fresh gas, under a drop of about 50 atmospheres pressure. When the further energy savings resulting from obtaining all the ammonia in the liquid form is added, the advantage of the Casale system as regards power consumption is obvious.

The above comparison is easily made when it is remembered that the isothermal compression energy is proportional to the logarithm of the pressure.

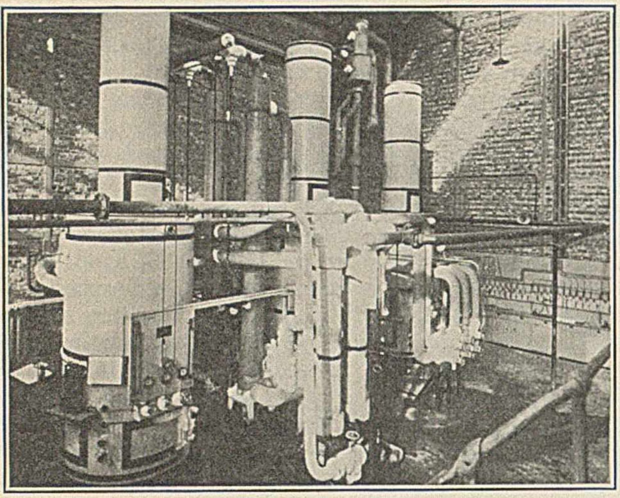
The high-pressure equipment of a Casale unit is so compact that it weighs far less than any unit of the same capacity working under a so-called medium or low pressure.



Synthesis Tubes, Ammonia Condensers and Receivers

At Ostend the hydrogen-nitrogen mixture produced in the Linde hydrogen plant is sent to a gasholder, whence it is exhausted by the compressors. These compressors (there are six of them) each compresses 1200 cubic meters of hydrogen-nitrogen mixture per hour; it must be remembered that they are the smaller type of unit. The compressed mixture is admitted as such, without any purification or desiccation, into the synthesis cycle, which comprises an oil separator, a synthesis tube, a water-cooled condenser, and a condensate receiver. At Ostend recirculation is still being effected in most of the units by means of recirculation pumps, but these are being replaced by a new injector system which simplifies the circuit considerably and does away with the upkeep and attendance, as well as power consumption, necessitated by these pumps.

Further simplifications have been brought in at the pioneer plant at Terni, which is run as an experimental plant by the Societa Italiana Ricerche Industriali Siri, this company being the research organization of the Casale Company and founded by Luigi Casale. These simplifications consist in the elimination of the oil separator (as a result of the suppression of the recirculation pumps) and the incorporation of water-cooled ammonia condenser and condensate receiver into one single apparatus. The two 5-ton units working under this system at Terni are very simple and occupy the small space of 12 × 30 feet, for the two compressors.



Nitrogen Apparatus

Compressors at Ostend have been modified in order to be able to receive their hydrogen as it comes directly under the pressure of 9 atmospheres from the Linde fractionating apparatus. This arrangement permits of a further energy saving amounting to one-third of the compression energy, so that the power requirement is reduced from 1.22 to 0.82 kilowatt-hour per kilogram of ammonia in the 6-ton units, and to 0.76 kilowatt-hour in the 20-ton units, the process becoming thus from day to day more economical.

It has been suggested that some further purification be applied to the compressed hydrogen before admitting it into the synthesis tube; but apart from the fact that any serious attempt in this direction would complicate the process, there would be little advantage in prolonging the activity of the catalyst, as its replacement is only a matter of a few hours. Besides, there is no object in prolonging the life of the catalyst beyond a year, as it is not advisable to let a catalysis tube work for more than a year without testing its mechanical condition.

The most striking part of the Casale system is the catalyst tube, which is so arranged that the pressure tube, which is very similar to a big naval gun, is kept at a temperature at least 100° C. below the temperature at which the alteration of the structure of the metal under the effect of hydrogen begins. The efficiency of the Casale design is shown by the fact that a catalysis tube, which has been in continuous action for six years, was tested at 1500 atmospheres and withstood the test.

This remarkable result is achieved by so directing the gases inside the tube that the inside surface of the pressure tube will be cooled by the incoming cold gaseous mixture, which in the course of its progress takes up part of the heat of the hot gases as they leave the catalyst. The catalyst is contained in an annular space in the core of the tube, and is thermally insulated from the inside wall of the pressure tube by the concentric heat exchanger and the cold gas which enters the tube. This arrangement, which is protected by several Casale patents, has proved exceedingly effective.

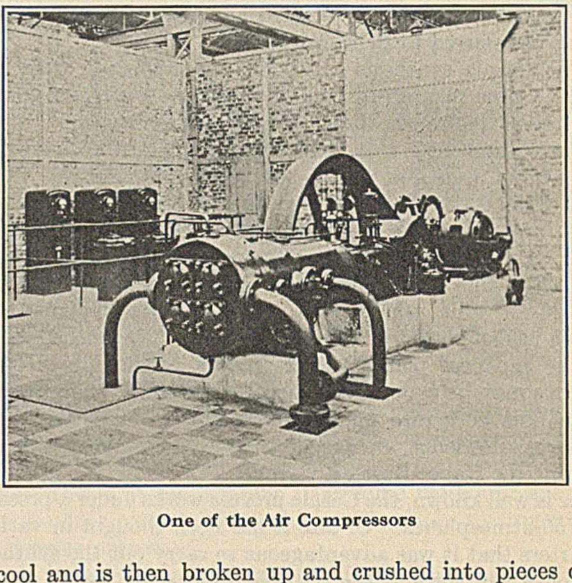
The reaction is regulated in an ingenious way. As below 750 atmospheres pressure the violence of the catalytic reaction would be such as to overheat the catalyst, there is left in the reaction mixture sufficient uncondensed ammonia to keep the system just slightly endothermal, so that it may be regulated by means of an electrically heated resistance placed in the axis of the catalyst tube, and over which the gases pass just before entering the catalyst, after they have been heated by temperature exchange with the gases which leave the catalyst. In practice the voltage and amperage are kept constant, the speed of recirculation being regulated so as to maintain temperatures and regular production. The energy consumed by the resistance is from 0.27 to 0.18 kilowatt-hour per kilogram of ammonia.

The presence of the necessary quantity of uncondensed ammonia in the gaseous mixture before catalysis is insured by simply water-condensing the reaction gases. No simpler means could be devised.

It is apparent that the system as a whole is marked by the utmost simplicity, as all special condensation arrangements are controlled with artificial refrigeration and no special purification treatment of the gas, either catalytic or chemical, is necessary.

The Catalyst

The efforts of Doctor Casale have tended toward producing a cheap and robust catalyst rather than a delicate, low-temperature catalyst. The process of manufacture, which has been patented, consists in burning steel turnings in oxygen, in the presence of certain activators which are introduced in the form of certain very cheap materials. The temperature at which the combustion in oxygen takes place is so high as to drive off any phosphorus or sulfur. When all the metal is burned and the oxide solidifies, the mass is allowed to cool and is then broken up and crushed into pieces of a proper size. The catalyst is introduced in the form of an oxide, and is reduced in the catalyst tube by means of hydrogen-nitrogen mixture.

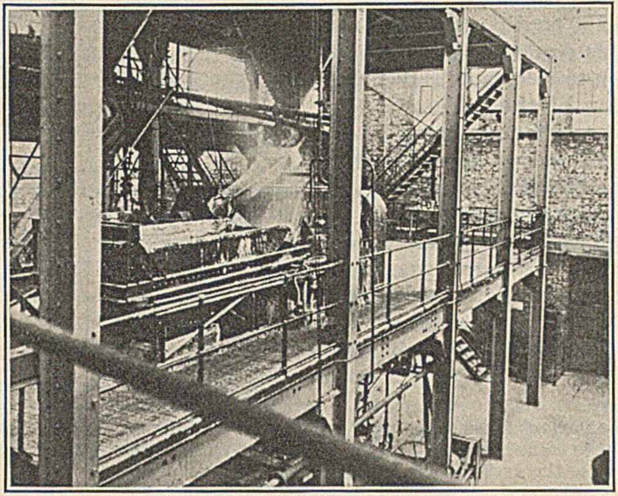


One of the Air Compressors

Catalyst which has lost some of its activity is regenerated in the same way. This catalyst, which is made of the cheapest materials, enters into the cost price of the ammonia to the extent of a few Belgian centimes only per kilogram of ammonia.

It would be wrong to think, however, that this catalyst is not very active. It is at least remarkably free from sulfur, analyses showing it to contain only one-fourth as much as a reputed specially active catalyst used in a recent American process.

The writer wishes here to pay a tribute to the originator of this simple and effective synthetic process, Luigi Casale, who, while a student at the University of Turin, undertook the study of what was then, except for Doctor Haber's work, an entirely new subject, and carried through, with the most meager financial support, to a successful conclusion its industrial application. The death of Doctor Casale, two years ago, was a great loss to the scientific and industrial world, for he no doubt would have made further important contributions to the advancement of knowledge in synthetic processes. Fortunately, however, his example inspired his disciples and collaborators, who now carry on his work so that progress has not stopped at his death, as is shown by the numerous improvements which have since been made and the synthetic methanol process now working at Terni with a production of 5 tons per day.



Part of Sulfate Plant

The Sulfate Plant

It is an easy matter to transform liquid ammonia into sulfate by means of sulfuric acid, but it is difficult to do so in a simple way without using complicated devices such as mechanical stirrers in the saturators, or blowing air or gas into them for different purposes such as has been successfully developed by the U. C. B. Company. Some difficulties with this method were at first encountered, owing partly to the high temperature maintained in the saturators and to the large production per unit capacity of the apparatus. But these troubles were overcome in a short time, and now 100 tons of sulfate are made per day in one small saturator of about 9 feet in diameter. This sulfate is centifuged and neutralized with ammonia in a special way, and is then dried in a rotary drier by means of combustion gases from a coke furnace.

This method of manufacturing sulfate will soon be replaced at Ostend by a new process similar to the gypsum process. The system, which is covered by a series of U. C. B. patents, is special in that it uses an ammonium carbonate solution made in a new way from combustion gases of a central pulverized coal boiler plant. It will be remembered that there is no concentrated carbon dioxide available in the coke-oven-gas hydrogen process as there is in the Haber-Bosch process, so that a different source had to be used. Although this sulfate process produces sulfate at a lower cost than from sulfuric acid, it is only operating on a small scale at Ostend notwithstanding that the U. C. B. Company is the largest sulfuric acid manufacturer in Belgium, because the primary material used is a valueless by-product of another industry of the U. C. B.

Another new feature, also patented, is that the evaporation of the concentrated sulfate solution, which is the most expensive item in the gypsum process, has been replaced by a simpler precipitation process.

A series of other developments are under experimental investigation at the Ostend plant, which is used as a pilot plant by the U. C. B. Company in its researches upon the new synthetic industries.

Conclusion

To summarize, a new approach to the synthetic ammonia manufacture problem has been opened up that in practice has proved remarkably satisfactory and cheap. Its development has in turn made possible a series of derived processes, mainly concerned with the transformation of the various residual gaseous by-products of coke-oven gas. Among the several new products which have been sought are those of the fatty alcohols and some of their derivatives.

Twelfth Chemical Industries Exposition

The Twelfth Exposition of Chemical Industries, which will be held at the Grand Central Palace, New York City, the week of May 6, 1929, draws together chemists, engineers, manufacturers, and others interested from forty industries which are dependent in their operations upon a chemical change in the nature of the material or are under chemical control.

A recent special study of the following of these industries

Cement and lime
Ceramics, clay, glass
Coal-tar products
Coal by-products
Electrochemical products
Explosives—cellulose
Fertilizers
Fine chemicals
Food products
Glue, gelatine
Heavy chemicals
Leather
Oils (vegetable and animal)
Paint and varnish
Petroleum refining
Pulp and paper
Rubber
Scrap
Sugar
Wood chemicals

indicates that they alone produce 17 per cent of all the products manufactured in the United States and employ 22.6 per cent of the total capital invested in manufacturing. Today these plants are producing 8 billion dollars' worth of finished products—an increase in production during the past thirty years of 6 billion dollars. The invested capital of this group is above 7 billion dollars and the average plant investment represents $843,000, while the average investment for all other industries is $183,000 per plant. The chemical process industries are among the highest capitalized; a rayon plant—in a new industry—requires a minimum of $3,500,000; an average petroleum refinery has over 3 million dollars invested, and cement plants average over 2 million.

These industries employed a million persons, ranking third in any group of American industries. They have over 2 million electric motors installed, consuming over 6 million kilowatt-hours of electrical energy. In this use of electricity they rank second in America, which is the greatest producer and user of electricity in the world. These industries consume over 98 million tons of coal per year, occupying first place in this respect.

In a study of the chemical industry made during June last, a New York banking company found that the American chemical industry, favored by its large domestic market, has grown to be the largest in the world, with an annual production of $2,278,000,000. This growth is attributed to the more numerous and prosperous population and the rapid expansion of industries in which chemicals are used. The United States is not independent of the products of other countries and while it is the second largest exporter in the world, it is also the largest importer. In 1927 chemicals imported were valued at $198,903,000 while exports amounted to $184,133,000.

Crystal Growth in Aqueous Solutions[1]

I—Theory

Warren L. McCabe

University of Michigan, Ann Arbor, Mich.

The following problem from the field of industrial crystallization is proposed: Given a saturated solution in which is suspended a known weight of seed crystals of known screen analysis, and assuming this solution to be cooled under known conditions, what will be the weight and screen analysis of the crystals at the end of the process if there is negligible formation of new nuclei?

A theoretical solution of this problem is developed. The fundamental postulates of this theory, which agree with other published researches are: (*a*) The actual yield should be very close to the theoretical yield. (*b*) The rate of growth of a face of a crystal, expressed as grams per square centimeter, is equal to the product of a specific constant pertaining to that face, and some function of the supersaturation of the solution. (*c*) The solubility differences due to particle size have a negligible effect on the growth of macroscopic crystals. (*d*) Each crystal, as it grows, remains substantially similar, geometrically, to its original shape.

It is shown that, if the above assumptions are true, geometrically similar crystals of the same material suspended in the same solution grow at the same rate if the growth is measured as the increase in length of geometrically corresponding distances on all of the crystals.

INDUSTRIAL crystallizations are often carried out, not only to obtain a maximum yield of pure solid material, as is the case in scientific work, but also to prepare crystalline particles of definite size distribution and crystal habit.

Before crystallization equipment can be rationally designed and intelligently operated, the laws that control the formation and growth of crystals must be known. Two steps are involved in the formation of macroscopic crystals from a saturated solution: first, minute crystalline aggregates, or nuclei, must form; and second, the nuclei must grow. This article is concerned with the second of these steps. The laws governing nucleus formation are not considered. The problem considered in this paper may be stated as follows:

Given a saturated solution in which is suspended a known weight of seed crystals of known screen analysis, and assuming this solution to be cooled under known conditions, what will be the weight and screen analysis of the crystals at the end of the process if there is negligible formation of new nuclei?

This problem is of importance because the more modern commercial crystallization processes are carried out by first forming nuclei and then allowing them to grow by slowly cooling the saturated solution in which they are suspended.

Previous Work

Although an enormous amount of theoretical and experimental work has been done on the symmetry, structure, habit, formation, growth, and solution of crystalline material, comparatively few researches have a direct bearing on this problem.

The work of Curie,[2] Lecoq de Boisbaudran,[3] Berthoud,[4] Wagner,[5] Marc,[6] Leblanc,[7] Wenk,[8] Valeton,[9] Campbell,[10] and Kukharenko[11] on the geometry of crystals and the rate of crystal growth is important. In spite of some disagreement among these papers, certain conclusions can be drawn that have much evidence in their favor:

1—A crystal that grows under constant external conditions remains very nearly geometrically similar to its original shape.

2—The addition of small amounts of foreign substances may profoundly affect the shape of a growing crystal and its rate of growth.

3—Different faces of the same crystal usually have different rates of growth.

4—Although the exact mechanism and the order of reaction of the growing process are not definitely known, it can be safely said that the rate of growth of any particular face in grams per square centimeter is a function of the supersaturation of the bulk of the solution in contact with that face.

5—It is very doubtful that the differences in solubility of the various faces of a single crystal, or of different size particles of the same material, are large enough to influence crystal growth unless the crystals are less than 0.002 cm. in diameter.

Work of Montillon—The only direct approach to the problem considered in this dissertation is the research carried out by Montillon,[12] who studied the growth of large numbers of seed crystals in a continuous glass crystallizer under carefully controlled conditions. A continuous apparatus was used because it could be more carefully controlled than could a batch apparatus. A large number of seed crystals were used to take advantage of the averaging effect of many nuclei.

Montillon's quantitative results were summed up in an empirical equation of the form:

$$10^{-3} \times \frac{\Delta W}{\Delta S} = ae^{b} \tag{1}$$

where ΔW is the increase in weight of the crystals during the process in grams per hour, ΔS is the increase in surface of the crystals in square centimeters per hour, Θ is the time in minutes, and a and b are constants.

Data were obtained on Glauber's and Epsom salts at various temperatures. The value of a and b in equation (1) are given in Table I.

Table I—Values of Empirical Constants in Montillon's Equation

SALT	GLAUBER'S SALT			EPSOM SALT	
Temperature	27.1° C.	29.26° C.	30.90° C.	29.25° C.	31.6° C.
a	12.57	13.90	16.26	18.52	22.13
b	0.0178	0.0178	0.0178	0.0175	0.0175

Although equation (1) is frankly empirical, it fits Montillon's data very well. However, the main advance represented

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[1] Received July 3, 1928.

[2] *Bull. soc. min.*, **8**, 145 (1885).

[3] *Compt. rend.*, **80**, 1450 (1875).

[4] *Bull. soc. Neuchatelois sci. nat.*, **33**, 122 (1904).

[5] *Z. physik. Chem.*, **71**, 401 (1910); *Z. Elektrochem.*, **17**, 989 (1911).

[6] *Z. physik. Chem.*, **61**, 385 (1907); **67**, 470, 640 (1909); **68**, 104 (1909); **73**, 685 (1910); *Z. Elektrochem.*, **16**, 201 (1910).

[7] *Z. physik. Chem.*, **86**, 334 (1914); **77**, 614 (1911).

[8] *Z. Kryst. Mineral.*, **47**, 124 (1909).

[9] *Z. Krist.*, **59**, 135 (1923); *Ber. Verhandl. K. sächs. Ges. Wiss.*, **67**, 1 (1916); *Z. Krist.*, **59**, 335 (1923); **60**, 1 (1924).

[10] *J. Chem. Soc.* **107**, 475 (1915).

[11] *Centr. Zuckerind.*, **32**, 112 (1923); *Louisiana Planter*, **71**, 211, 231 (1923); *Sucr. Belge*, **46**, 131 (1926); **46**, 107 (1926); *Chimie & industrie*, Sp. No., 589 (May, 1927).

[12] Ind. Eng. Chem., **19**, 809 (1927).

by this research was the development of a workable technic for investigating the process of crystal growth under conditions comparable to those used commercially.

Theoretical

The solution of the problem proposed depends on the answer of two questions:

1—How much material is precipitated?

2—How does the precipitating material distribute itself on the seed crystals?

The answer to the first question will determine the yield, and the answer to the second question will determine the size distribution and the screen analysis of the product.

Theoretical Yield

The first question is easily answered for most materials undergoing crystallization. Since crystallization is a slow process when nuclei do not form, and since there are a large number of crystals suspended in the cooling solution, no very great supersaturation can be expected at any stage in the process. It is true that the solution must be supersaturated to some extent or the crystals could not grow, but a very slight supersaturation will suffice. Indeed, if any considerable supersaturation should develop, a large number of new nuclei would form. This is contrary to the conditions of the problem. Therefore, it is to be expected that the solution will be very nearly saturated throughout the process and the difference in weight between the product and the seeds can be calculated from the amount of solution, the change of solubility with temperature, and the extent of cooling.

An exception to this statement occurs when the solution supports a high supersaturation without forming new nuclei, and has a high viscosity. The most important example of such slowly crystallizing substances is sucrose. For these cases the actual yield will be less than that demanded by the solubility curve, by the difference between the final and initial supersaturations.

Theoretical Screen Analysis

Consider a single crystal that is growing in a slowly cooled solution and kept in suspension by a suitable agitator. Let C denote the concentration of the bulk of the solution and C_0 the saturation concentration corresponding to the temperature of the crystal. Then the supersaturation is $C - C_0$. Each face of the crystal is, at any instant, growing at a definite rate that can be measured in grams per square centimeter per hour. The rate of growth of a face is proportional to some function of the supersaturation. The form of the function is unknown. It will be shown that the form does not have to be known. A differential equation can be written for each face. The equations for various faces are:

$$\begin{aligned} \frac{dW_1}{d\Theta} &= k_1 S_1 \, [f(C - C_0)] \\ \frac{dW_2}{d\Theta} &= k_2 S_2 \, [f(C - C_0)] \\ &\cdots\cdots\cdots\cdots \\ \frac{dW_n}{d\Theta} &= k_n S_n \, [f(C - C_0)] \end{aligned} \qquad (2)$$

where $W_1, W_2 \ldots\ldots W_n$ are the weights of material depositing on the different faces; $S_1, S_2 \ldots\ldots S_n$ are the areas of the faces; $k_1, k_2 \ldots\ldots k_n$ are the over-all reaction-rate constants of the faces; Θ is the time, and $(C - C_0)$ is the supersaturation of the solution surrounding the crystal. The total number of faces is n.

Since the crystal is growing under uniform external conditions, it is at all times geometrically similar to its original shape. If S is the total area of the crystal at the time Θ, then

$$\begin{aligned} S_1 &= a_1 S \\ S_2 &= a_2 S \\ &\cdots\cdots\cdots \\ S_n &= a_n S \end{aligned} \qquad (3)$$

where $a_1 + a_2 + \ldots\ldots a_n = 1$.

Because of the invariancy of the crystal shape, the fractions $a_1, a_2 \ldots\ldots a_n$ are constants during the growing process.

If the values of $S_1, S_2 \ldots\ldots S_n$ of equation (3) are substituted into equation (2) and the resulting equations added together, it is found that:

$$\frac{dW_1 + dW_2 + \ldots\ldots\ldots dW_n}{d\Theta} = \frac{dW}{d\Theta} = (k_1a_1 + k_2a_2 + \ldots\ldots k_na_n)\,(S)\,[f(C - C_0)] \qquad (4)$$

where dW is the total increase in weight of the crystal.

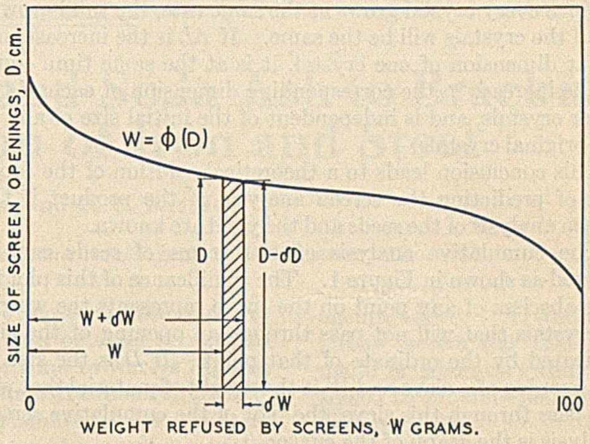

Figure 1—Cumulative Screen Analysis

If L is a linear distance between any two corners of a polyhedron, the weight and surface of that polyhedron are given by the expressions:

$$W = \rho b L^3 \qquad (5)$$

$$S = cL^2 \qquad (6)$$

where ρ is the density of the polyhedron and b and c are constants that are the equal for all geometrically similar solids provided L is the distance between corresponding points of the individual solids.

Since the crystal under consideration is growing under constant external conditions, equations (5) and (6) apply to all stages of the growth of the crystal and b and c are constants during the process.

From equation (5)

$$dW = 3\,\rho b L^2 dL \qquad (7)$$

Substituting values of S and dW from equations (6) and (7) into equation (4) the result is:

$$\frac{dL}{d\Theta} = \frac{(k_1a_1 + k_2a_2 + \ldots\ldots k_na_n)(c)\,[f(C - C_0)]}{3\,b\rho} \qquad (8)$$

Since $k_1, k_2 \ldots\ldots k_n, a_1, a_2 \ldots\ldots a_n, \rho, b$, and c are all constants, equation (8) can be written as:

$$\frac{dL}{d\Theta} = K[f(C - C_0)] \qquad (9)$$

where K is a constant and is equal to $\dfrac{(k_1a_1 + k_2a_2 \ldots\ldots k_na_n)(c)}{3\,b\rho}$

Consider, now, a second crystal of the same material, of the same geometric shape, and suspended in the same solution, but of different size than the first. If a differential equation is derived for this second crystal, it will be identical to equation (9) if the L's of the two crystals connect geometrically corresponding corners. From this fact there follows an important principle:

All geometrically similar crystals of the same material suspended in the same solution grow at the same rate, if the growth is measured as the increase in length of geometrically corresponding distances on all of the crystals.

Two assumptions are implied in the above analysis. The first assumption is that C_0 has the same value for all the crystals. The only possibility of variation of C_0 from crystal to crystal is the change in solubility with particle size. It has been stated that unless the crystals are very small such solubility differences are negligible. Experimental evidence on this point will be reported later.

The second assumption is that it is possible to maintain a number of crystals under nearly enough identical conditions so that consistent results can be obtained. Campbell[10] has shown how difficult it is to do this with two crystals. However, with large numbers of crystals an averaging effect can be expected.

Since every crystal grows at the same rate, the total growth of all the crystals will be the same. If ΔL is the increase in a linear dimension of one crystal, it is at the same time equal to the increase in the corresponding dimension of each of the other crystals, and is independent of the initial size of any of the original crystals.

This conclusion leads to a theoretical solution of the problem of predicting the screen analysis of the product if the screen analysis of the seeds and the yield are known.

The cumulative analysis of 100 grams of seeds can be plotted as shown in Figure 1. The significance of this plot is: The abscissa of any point on the curve represents the weight of crystals that will not pass through an opening of the size indicated by the ordinate of that point. If D is the size of the opening of a sieve and W is the weight of material that will not pass through this sieve, the plot of the cumulative screen analysis is the graph of the curve:

$$W = \phi\ (D) \tag{10}$$

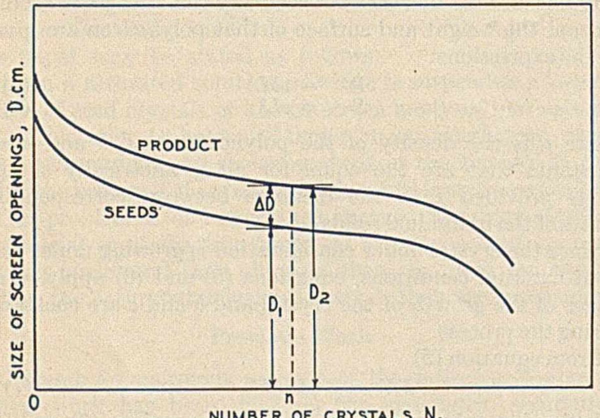

Figure 2—*N* vs. *D* Plot of Seeds and Product

There will be a definite size of crystal that will just pass through a given screen. This crystal will have a definite linear dimension, L. If all the crystals are geometrically similar, there will be a definite ratio between the value of L of any particular crystal and the size of the screen opening that will barely allow that crystal to pass. Assume that this ratio is the same for all the sieves. Mathematically, this assumption states:

$$\alpha D = L \tag{11}$$

where α is independent of D.

It will be desirable to obtain from the cumulative screen-analysis plot a cumulative plot of the number of crystals, N, against D. The abscissa of any point on this curve will represent the number of crystals that will not pass through a sieve of size opening equal to the ordinate of that point. Assume that such curves have been drawn for the seeds and the product, and that the same axes have been used for both plots. These curves are presented in Figure 2. Consider seed crystal n. It will just pass through an opening D_1 cm. on a side. After growth it will just pass through an opening D_2 cm. on a side. Let ΔD represent this increase in D. Then, from equation (11)

$$\alpha \Delta D = \alpha(D_2 - D_1) = \Delta L \tag{12}$$

But α is a constant, and ΔL is identical for all the crystals. Therefore the vertical distance between the two curves of Figure 2 is constant for all points on the curves, and if one curve and the ΔD of one crystal are known the other curve can be constructed.

The construction of the N–D curves will now be described.

Consider, first, any point on the cumulative screen plot of the seeds. This point has the coördinates W and D. (Figure 1) These coördinates mean that, of the 100 grams of seeds, W grams will not pass through a square opening measuring D cm. on a side.

Consider, next, a point very near to the point W, D. The coördinates of this second point are $W + dW$ and $D - dD$. Then, dW grams of seeds can be trapped between two screens having opening sizes of D and $D - dD$ cm. The average linear dimension of the crystals in the fraction dW is L, where $L = \alpha D$, the weight of a single crystal is ρbL^3, and the number of crystals in the fraction is

$$dN = \frac{dW}{\rho b L^3} = \frac{dW}{\rho \alpha^3 b D^3} \tag{13}$$

The total number of crystals too large to pass through a screen opening D cm. on a side is:

$$N = \frac{1}{\rho \alpha^3 b} \int_0^W \frac{dW}{D^3} \tag{14}$$

In order to obtain the arithmetical value of N, the quantity $\alpha^3 \rho b$ must be evaluated. Although the density of the crystals, ρ, is usually known, the determination of α and b is bothersome. However, for the purpose of predicting screen analyses, it is unnecessary to evaluate these constants. The plots are just as useful if N', defined by the equation

$$N' = \alpha^3 b N \tag{15}$$

is plotted against D, and equation (14) used in the form:

$$N' = \frac{1}{\rho} \int_0^W \frac{dW}{D^3} \tag{16}$$

Coördinates of points on the $N' - D$ curve corresponding to any given screen analysis can be determined by graphical or arithmetical integrations of equation (16), since the cumulative screen analysis curve gives the relationship between W and D.

Equation (16) can be written in the differential form for the seed crystals:

$$dN_s' = \frac{dW_s}{\rho D_s^3} \tag{17}$$

and for the product:

$$dN_p' = \frac{dW_p}{\rho(D_s + \Delta D)^3} \tag{18}$$

where the subscripts s and p refer to the seeds and product, respectively.

Since the same crystals form both seeds and product,

$$dN_s' = dN_p'$$

and, therefore,

$$\frac{dW_s}{D_s^3} = \frac{dW_p}{(D_s + \Delta D)^3} \tag{19}$$

it follows from equation (19) that

$$W_p = \int_0^{W_s} (1 + \Delta D/D_s)^3 dW_s \tag{20}$$

Since ΔD is independent of D_s and W_s, the value of W_p corresponding to any value of W_s can be obtained by graphical or arithmetical integration of equation (20), inasmuch as the screen-analysis curve of the seeds provides a relationship between D_s and W_s.

The steps in the calculation of the yield and screen analysis of the product on a crystal-growth process can now be outlined:

1—Calculate the theoretical yield from the ratio of seeds to solution and the solubility change of the material during the process.

2—Assume a value of ΔD and calculate the weight of the product that corresponds to this assumed value by integrating equation (20) over the range $W_s = 0$ to $W_s = 100$.

3—If the value of W_p calculated in step 2 does not check that calculated in step 1, adjust ΔD by trial and error until fair agreement is reached between the weights of product calculated by the two methods.

4—Using the correct value of ΔD, as determined in step 3, plot the integral curve of equation (20).

5—Plot W_p against D_p. This plot can be constructed from the data at hand at this point, since the integral curve plotted in step 4 gives the relationship between W_p and W_s, the screen-analysis curve of the seeds exhibits D_s as a function of W_s, and $D_p = D_s + \Delta D$.

6—From the curve of W_p against D_p that was plotted in step 5, read off the values of W_p that correspond to the sizes of the various screen openings, and convert the values to percentages of the entire product. The result is the cumulative screen analysis of the product. The differential analysis is easily derived from the cumulative analysis by subtraction.

The experimental confirmation of this theory will be described in a subsequent article.

Effect of Additions of Lime and Soda Ash to Brackish Water on the Corrosion of Iron and Steel[1]

H. O. Forrest, J. K. Roberts, and B. E. Roetheli

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

The treatment of brackish or semi-salt water to retard the corrosion of exposed iron or steel structures has been studied. Additions of lime to waters high in bicarbonate and calcium content will cause the formation of protective calcium carbonate scales. Waters containing appreciable quantities of magnesium salts require soda ash as well as lime treatment to increase the pH and supply carbonate ions before a calcium carbonate scale can be built up. A pH of 8.5 or higher is favorable to the formation of protective carbonate scales. For practical application larger scale studies are recommended to determine the minimum quantity of lime or soda ash necessary to maintain a thin protective scale on the structure.

THE use of brackish or semi-salt waters in cooling systems of plants situated along seacoasts results in appreciable loss due to the highly corrosive nature of the waters. This study was made to determine the possibilities of minimizing corrosion by building up a thin protective calcium carbonate scale on the surface of the exposed iron and steel.

The idea of the formation of protective scales by water treatment is not new. Baylis[2] successfully treated Baltimore city water by additions of calcium hydroxide in quantities sufficient to precipitate calcium carbonate on the exposed metal surface. Silicates have been added to water [3 to 6] under various circumstances to decrease corrosion probably by the formation of protective films. In these instances the water treated was fresh, containing the usual small quantities of dissolved salts. Roberts, Forrest, and Russell[7] show that additions of lime to brackish waters containing calcium bicarbonate decrease corrosion. In the case of brackish waters the relatively high salt concentrations make the use of materials such as sodium silicate of doubtful value, because of the expense involved in treating such large quantities of water.

An analysis of the problem indicated that there were three factors in the water composition which would probably influence the degree of protection obtainable: (1) the concentration and nature of dissolved salts, (2) the concentration of calcium bicarbonate, and (3) the concentration of retarding agents added. A study of these factors was therefore made in laboratory tests designed to simulate plant conditions.

Experimental Method

Samples of standard 1-inch (2.54-cm.) wrought iron and steel pipes, 4 inches (10.2 cm.) long, were tested in an apparatus as shown in Figure 1. Water was made up to correspond to the desired salt concentration and caused to flow over the outside surface of the pipes from a 20-liter reservoir as indicated, for a length of time sufficient to allow a thin film of calcium carbonate to build up. An air lift was used to recirculate as well as aerate the water. The compressed air was previously blown through a caustic soda solution to remove carbon dioxide and subsequently through sulfuric acid, water, and steel wool.

In order to study the effect of various concentrations of dissolved salts, water was made up by diluting synthetic sea water (see Table I for analysis) with distilled water. The brackish water was made up to have the salt contents as shown by the analysis in Table II. These methods were used to insure constant water composition throughout the experiments, and because of the difficulty in obtaining natural seawater samples having an average analysis. The calcium bicarbonate solution added was made up by passing carbon dioxide through a saturated calcium hydroxide solution (in contact with solid calcium hydroxide) and filtering. The filtrate was analyzed for bicarbonate content by titration to insure addition of the proper quantity to the sea water. Phenolphthalein was added to the solutions in the reservoir to note whether the pH dropped off with time.

Results

The results of this investigation are shown graphically in Figures 2 to 6 and in Table III. The corrosion rates given

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[1] Received August 6, 1928. Presented before the Division of Industrial and Engineering Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] *J. Am. Water Works Assocn.*, **15**, 598 (1926).

[3] Russell, *Am. Dyestuff Rept.*, **15**, 61 (1926).

[4] Whitman, Chappell, Roberts, *Refrigerating Eng.*, **12**, 158 (1925).

[5] Thrush, *Analyst*, **47**, 459, 500 (1922).

[6] Speller, "Corrosion—Causes and Prevention," p. 348, McGraw-Hill Book Co., 1926.

[7] *Refrigerating Eng.*, **14**, 173 (1927).

are the average values of two steel and two wrought-iron samples. The variations between the two materials under these conditions were well within the limits of experimental error in the case of untreated distilled water.

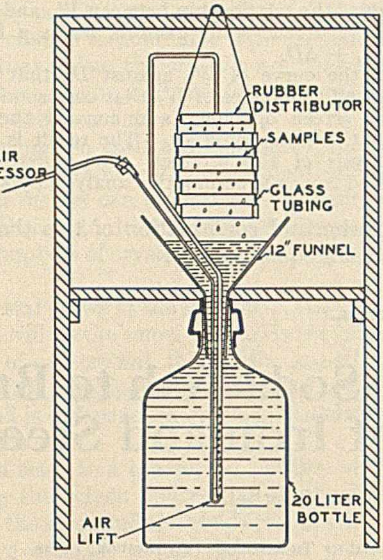

Figure 1—Sketch of Apparatus

The changes in pH caused by additions of calcium hydroxide to sea waters of different concentrations are shown in Figure 6. These values were obtained colorimetrically and are accurate to 0.2 pH units. The pH values for waters of various sea-water dilution approach the same asymptote upon addition of increasing quantities of calcium hydroxide.

Table I—Analysis of Sea Water[a]

(3.5% solids as salts)

	Per cent
NaCl	77.76
$MgCl_2$	10.88
$MgSO_4$	4.74
$CaSO_4$	3.60
K_2SO_4	2.46
$MgBr_2$	0.217
$CaCO_3$	0.345

[a] Dittmar, Van Nostrand's Chemical Annual, p. 523 (1928).

Table II—Analysis of Brackish Water[a]

(Inorganic constituents)

	P. p. m.
Carbonate (as $CaCO_3$)	None
Bicarbonate (as $CaCO_3$)	35.3
Chlorides	1550.0
Total hardness	571.0
Temporary hardness	35.3
Permanent hardness	536.0
Calcium	52.0
Magnesium	102.7
Sulfates	175.0

[a] Used by a packing plant in Montevideo.

Discussion of Results

In Figure 2 is shown the variation in corrosion rate of iron and steel in distilled water containing progressively increasing quantities of calcium bicarbonate with and without an excess of added calcium hydroxide. This figure indicates that small amounts of bicarbonate greatly accelerate corrosion, while higher concentrations of bicarbonate assist the building up of a protective calcium carbonate film. This effect is probably due to the fact that equilibrium in the reaction

$$Ca(HCO_3)_2 \rightleftharpoons CaCO_3 + CO_2 + H_2O$$

is driven to the right by evaporation of water from the thin liquid film trickling over the metal. This phenomenon is accelerated in condenser systems owing to the increased water evaporation caused by the heat absorbed by the water in the cooling process. It is obvious also that the greater the concentration of calcium bicarbonate, the greater is the tendency for the reactions to be driven from left to right.

When calcium hydroxide is added to brackish water a carbonate film may be built up in either of two ways: (1) by the reaction with free carbon dioxide or calcium bicarbonate in the solution; or (2) by absorption of carbon dioxide from the air and reaction with lime to form carbonate. In all cases except in pure distilled water containing an excess of calcium hydroxide, both methods of scale formation probably take place. The first probably predominates, however, owing to the relatively low rates of absorption of carbon dioxide from the air in the second method.

Figures 3 and 4 show the effects of adding calcium hydroxide to various dilutions of sea water varying in bicarbonate content. The same tendencies shown by the curves for distilled water may be observed here. However, in waters containing 50 per cent or more sea water the protection afforded by treatment with calcium hydroxide is relatively poor, the maximum protection being about 30 to 40 per cent. This indicates that, aside from the bicarbonate content, factors which are not prominent in dilute sea waters become significant in more concentrated waters. The sea-water analysis (Table I) shows that there are appreciable quantities of magnesium salts present, which in more highly concentrated waters probably cause the metathetical formation of magnesium hydroxide when calcium hydroxide is added. Since magnesium hydroxide does not adhere to the metal, no protective film is built up as in the case of calcium carbonate, and hence no protection is afforded. There is also the probability that the hydrolysis of magnesium chloride lowers the pH of the water sufficiently to decrease the precipitation of calcium carbonate.

Preliminary tests in a brackish water high in magnesium salt (Table II) showed that calcium hydroxide treatment was practically useless for building up a protective film, but that substantial protection could be obtained by treatment with sodium carbonate. Figure 5 shows the effect of adding various quantities of sodium carbonate to this brackish water. The function of the sodium carbonate is evidently twofold: to increase the pH of the water and to react with the calcium salts present to form an insoluble protective film.

The addition of both sodium carbonate and calcium hydroxide to this water facilitates the precipitation of protective films, as is shown in Table III. The chief function of the

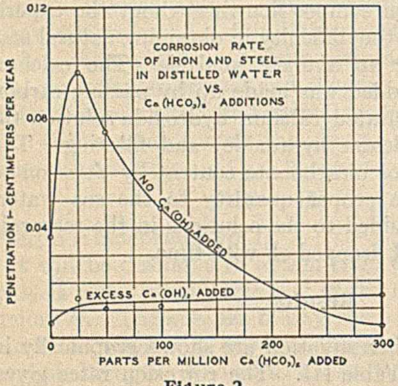

Figure 2

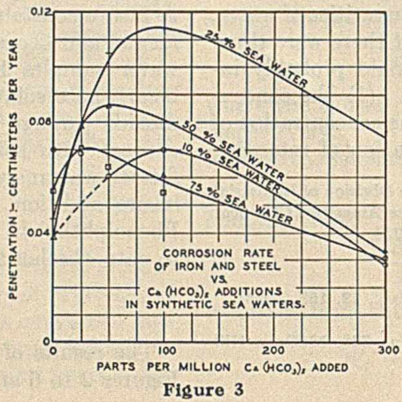

Figure 3

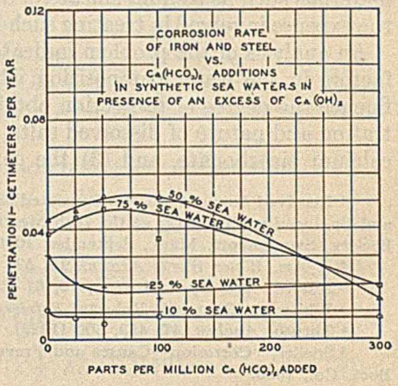

Figure 4

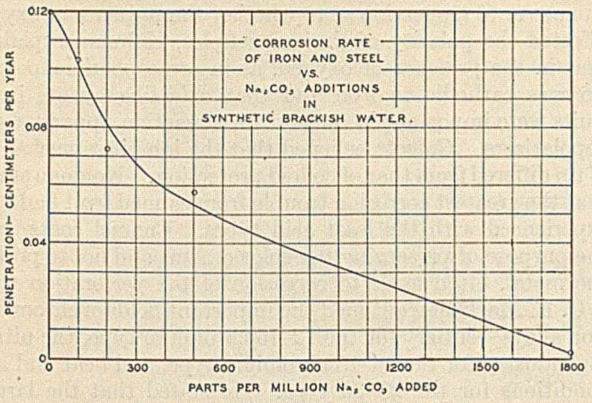

Figure 5

sodium carbonate is probably that of raising the pH while the addition of the calcium hydroxide supplies the additional calcium salts necessary to the building up of a carbonate film. The carbonate films were observed to form readily when the pH of the solution was 8.5 or higher.

Table III—Corrosion of Iron and Steel in Brackish Water

Additions	Penetration *Cm. per year*
None	0.1190
100 p. p. m. Na_2CO_3	0.1035
100 p. p. m. Na_2CO_3 and excess $Ca(OH)_2$	0.0175

The minimum quantity of lime or soda ash necessary to give protection cannot be readily determined by laboratory experiments. The results presented show the necessity of having relatively high concentrations of both calcium salts and carbon dioxide in brackish waters, if a protective scale is to be formed.

Conclusions

1—A relatively high concentration of calcium salts and carbon dioxide accompanied by a pH of 8.5 or greater will cause the precipitation of a calcium carbonate scale on iron or steel surfaces exposed to brackish water.

2—Additions of lime to waters high in bicarbonates or of soda ash to waters high in calcium salts will decrease the corrosion of iron and steel.

3—The presence of small quantities of calcium bicarbonate in distilled water accelerate the corrosion on iron and steel while larger quantities permit the formation of a protective carbonate film.

4—The addition of an excess of lime to distilled waters, and to dilute sea waters containing varying quantities of calcium bicarbonate, greatly reduces the corrosion of iron and steel in these waters.

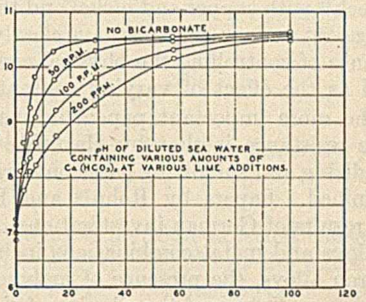

Figure 6

5—The pH values of all concentrations of sea water varying in bicarbonate content and containing 100 p. p. m. of calcium hydroxide are very nearly the same, whereas with lower concentrations of lime the pH values become considerably lower as the calcium bicarbonate content increases.

Acknowledgment

Much of the experimental work in this paper was carried out under a fellowship from the National Tube Company, directed by F. N. Speller. The authors wish to acknowledge the valuable assistance and coöperation afforded by this arrangement.

Corrosion

Round-Table Discussion[1]

R. J. McKay, Leader

IN THIS round-table discussion the subjects of inhibitors, film action and passivity, the galvanic relations between metals, corrosion testing, the effect of stress and strain on the progress of corrosion, and new developments in alloys and metal combinations for corrosion resistance were considered.

R. J. McKay, as chairman of the meeting, outlined some of the more recently published important papers on corrosion. He recalled Evans'[1,*] work on the use of alkaline and oxidizing inhibitors in natural waters to prevent the deterioration of iron, with special mention of Evans' warning that inhibitors sometimes lead to serious localized attack; the work of Speller, *et al.*,[2] in determining that the presence of an inhibitor in one case prevented the occurrence of corrosion fatigue; and the work of Chappell, *et al.*,[3] on inhibitors in steel pickling. The recent papers of McAdam[4] and Moore[5] on corrosion fatigue produced by exposure simultaneously to corrosion and stress were mentioned as opening up a new and very important phase of corrosion study. Galvanic corrosion has been treated recently in papers by Evans,[6] Kohman and Sanborn,[7] Lueck and Blair,[8] and Mantell and Lincoln.[9] Whereas in the past the progress of galvanic corrosion has been conceived to depend largely on some inherent property in the metals involved, the newer view appreciates the importance of the corroding solution and the products of corrosion as modifiers.

On the subject of passivity of chromium-iron alloys the papers of Müller,[10] Strauss,[11] Benedicks and Sundberg,[12] and Stäger and Zschokke[13] were mentioned. The mechanism of the development of the passive state in metals is in dispute. Evans[14] is among those who conceive passivity to be produced by oxide films, and he has demonstrated, at least to his own satisfaction, that iron acquires, on exposure to the atmosphere as well as to other conditions, a film of ferric

[1] Round-table discussion before Division of Industrial and Engineering Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

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

oxide. This film he has succeeded in isolating. Some other investigators do not view passivity as a result of solid films of corrosion products. Aside from passivity, Callendar[15] has measured the resistance of oxide coatings accumulating on aluminum in different exposure conditions.

Remarks on the methods of corrosion testing dealt with a recent paper by Hudson[16] describing how a close check between weight increase and electrical resistance was obtained as a measure of the atmospheric attack of wires, and the unusually thorough investigation by Vernon[17] on atmospheric corrosion, in which weight increase, change in color, and loss in reflectivity were determined. Tests by Rawdon and Groesbeck[18] with copper and nickel and the binary alloys of the two against various solutions have clearly demonstrated the importance of controlling the physical conditions of testing, as well as the effect of varying content of the metal.

One of the more important papers in the field of high-temperature resistance is that by Hatfield,[19] in which the effect of oxidizing and sulfidizing gases on various metals has been determined. Papers by Rohn[20] and Fry[21] have described the results of German investigations. New developments in alloys and metal combinations include the nickel-chromium-iron alloys, the presence of molybdenum in these and in nickel-iron alloys, and the alloying of nickel and copper with iron to make a corrosion-resisting cast iron of reasonable cost.

H. A. Bedworth described the results of an inhibitor on the corrosion of copper in salt solutions. Corrosion of deoxidized copper by calcium chloride and sodium chloride brines in 96 hours' alternate immersion exposure was lessened by one-half if 0.1 per cent caustic soda was added to the solution, but was increased three to five times if 0.1 per cent hydrochloric acid was added.

W. S. Calcott discussed an inhibitor that is practically insoluble in dilute acids and neutral aqueous solutions, yet is soluble in benzine, alcohol, etc., suggesting that the inhibitor functions only in colloidal form. An iron-zinc couple, when exposed to a solution carrying this same inhibitor, showed a reversal of polarity as compared with its usual behavior. The iron was anodic and the zinc cathodic and protected. Ordinarily zinc protects iron. It was found that 0.01 mg. of inhibitor per square inch (6.45 sq. cm.) of iron was necessary for effectiveness.

E. H. Dix described the electrochemical behavior of duralumin sheet on each side of which has been rolled a layer of pure aluminum. A difference in potential between the two on the order of 0.05 to 0.2 volt was obtained in salt solutions, with pure aluminum anodic. The significance of this lies in the fact that at sheared edges the intermediate layer of strong alloy is protected in the presence of a corrosive solution. Likewise, rivets of duralumin holding a combination sheet tend to be protected by the pure aluminum surfaces.

E. F. Kohman thought that tin salts might be viewed as inhibitors in the case of tinned cans, since a small amount of tin going into solution in a tinned can will tend to prevent further corrosion of the can. The presence of 1 to 4 p. p. m. tin salts will inhibit corrosion even in cases where tin is anodic to iron. The possibility exists that tin is present as a colloidal substance in the solution although the fact that the solutions studied were in a range of pH 1 to 4 suggests that the formation of colloid by hydrolysis was less likely to occur. The protective effect of tin is not due to its plating out on the walls of the can. The overvoltage of metallic tin itself, according to Kohman, is its reason for resistance and the iron in a tin can may not corrode because of increasing hydrogen overvoltage due to tin overvoltage. Changes in the hydrogen-ion concentration will reverse the polarity of an iron-tin contact. Tin as the stannous ion seems to be the inhibitor. In answer to a question as to whether the presence of oxygen affected the polarity of tin-iron couples, Kohman explained that in the presence of oxygen, as in atmospheric exposure, tin was cathodic to iron and that oxidizing agents in all fruits were important in the corrosion reaction apparently as depolarizers. Calcott believed that the inhibitor mechanism of tin differed from that of colloid protection. Kohman stated that the greatest corrosion trouble from canned fruit had been experienced with the least acid types. Enamel coats, with the purpose of preserving the color of fruit and not to protect the metal, often leads to corrosion of the perforation type.

C. E. MacQuigg outlined the important fields of chromium-iron alloys—cutlery for the 12–16 chromium type, the nitrating industry for the 16–18 chromium type, and heat and acid conditions for the 20–30 type. He stated that the largest development in alloys in the past year probably lay in the nickel-chromium-iron types. MacQuigg stated that the work of Müller on the passivity of metals appealed to him, and particularly that the latter's results on the rapidity with which chromium was rendered passive were significant, an oscillograph being necessary to measure this.

L. L. Statler stated that a low-chromium-iron alloy plate used as a backstop in a pickling installation was subject to continual splashing by the hot sulfuric acid pickling solution; no change in appearance had occurred after months of use. This result is significant in view of the well-recognized action of sulfuric acid on an alloy of this nature. Statler emphasized the difference electrochemically between passive and active chromium-iron alloy. It is his belief that activated metal carries on its surface a nascent hydrogen film and in the presence of an oxidizing substance this film is oxidized and the metal becomes passivated. Tin becomes anodic to iron in nitric acid.

W. H. Whitman proposed that the term "inhibitor" be restricted in its use. The present usage includes as inhibitors alkaline substances, substances for addition to acids, and substances producing colloids. Whitman also suggested that corrosion rates be expressed in some standard units, and favored penetration rates to weight-loss rates. He believed it worthwhile for corrosion rates to be given, even though the investigator realized that the conditions under which they were obtained had not been under close control. There is value in all corrosion rates.

R. M. Burns stated that a potential difference of 0.08 volt had been obtained between lead poles in oxygen-bearing and oxygen-free solutions. He said also that in many cases the current density approached zero with a definite potential difference.

Jerome Strauss believes that strained material by itself does not corrode more rapidly than unstrained; this had been shown in the case of a 14 per cent chromium-iron (low-carbon) alloy. McKay cited a case where strained metal was definitely anodic to unstrained metal in couple with it and also more corroded. Dix had found that hard rolled aluminum sheet had been more resistant than annealed, although this may have been due to the presence of oil films from the rolling process in the case of the hard rolled sheet.

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Research within an Industry Creates the Demand—and Supplies It[1]

Everett P. Partridge[2]

1440 East Park Place, Ann Arbor, Mich.

The demand for vanadium is created, and then supplied, through the work of the Research Laboratory of the Vanadium Corporation of America.

SINCE 1907, when the American Vanadium Company erected its first smelting plant, this company and its successor, the Vanadium Corporation of America, have produced ferrovanadium as the chief of their ferroalloys. Ferrovanadium is like power or money—it isn't worth much unless you can use it. Taken by itself, its intrinsic properties make it suitable for nothing much but a souvenir. Properly utilized in the making of alloy steel, however, it produces an engineering material with uniformly admirable properties.

Research was early thrust upon the manufacturers of ferrovanadium. Ordinary metallurgical processes were found inadequate for the reduction of vanadium ores, and new methods of treatment had to be derived experimentally. Even when successful production had been attained, continued extensive research was necessary to determine the fields of application of vanadium steels in order that the company might dispose of its product. Once started in this way, it was necessary for this industry to find increasing markets for its increasing production, and then, in turn, to obtain increased production for its increasing markets as the demand rose for vanadium steel in the rapidly developing automotive industry. By being called upon in these two vital capacities of creating a market and of improving methods of manufacture, research was thus established in a keystone position in the vanadium industry. As a result, the experimental laboratory of the Vanadium Corporation of America touches, at one end, ore-dressing problems, in the middle, metallurgical problems in vanadium ore reduction, and at the other end, the problems of the countless industries from automobile manufacture to sulfuric acid production in which vanadium has been or may be utilized to do good work better, or the best work more rapidly.

The range of the industries affected by vanadium will be indicated briefly in the succeeding sections of this article. The main purpose is, however, not the cataloging of applications, but rather the placing of emphasis on the practical achievements of a consistent, continuous program of research. Before doing this, a slight digression is necessary to obtain a condensed idea of the relation of vanadium to industry in general.

Importance of Vanadium

The calculated world demand for vanadium in 1930 is 2,600,000 pounds, of which 1,800,000 pounds will be consumed in the United States. This total expected consumption will be worth approximately $8,700,000 at the prices current for the past three years. As a contrast, it is interesting to note that the world consumption in 1906 was 750 pounds, all of which was used in the United States for experimental purposes. The most recent available figures on the distribution of vanadium among the industries of the country are those of 1924, which are given in Table I.[3]

Table I—Distribution of Vanadium Consumed in the United States, 1924

Field of Utilization	Consumption	
	Pounds	*Per cent*
Automotive industry—spring steel, bars, forgings, and castings	466,100	47
Motive power, railway equipment, cranes, etc.—forgings, castings, and springs	317,400	32
Tools—high-speed and other tool steels, cutting tools, drills, saws, and oil-well tools	119,100	12
Miscellaneous—forgings and castings for heavy-duty machinery, nonferrous alloys, and chemicals	89,300	9
Total consumption	991,900	

When it is realized that vanadium is used as an alloying element only to the extent of from 0.15 to 0.25 per cent in spring and forging steels, to not more than 2 per cent in ordinary high-speed tools, and only occasionally to as large amounts as 2.5 or 3.0 per cent, the amount of vanadium steel produced is seen to attain considerable magnitude.

The United States has been the pioneer in the development of vanadium. From 1906 to 1923, 75 per cent of the world's supply came from American-owned and American-operated deposits in Peru. At present over 90 per cent of the world's available supply is under American industrial control, although only 16 per cent of it occurs as mineral deposits within the United States. Next to the Peruvian source, the next most important one is located in South Africa.

The demand for vanadium is increasing at a rate which will exhaust the known resources of the world within thirty-five years, although there is some hope that additional deposits of workable minerals will be discovered. In the past vanadium used in alloy steel was not recoverable, since remelting took place largely in basic open-hearth furnaces. At present the vanadium in scrap steel is recovered in acid open-hearth furnaces, or in electric furnaces, conserving the supply of this valuable material. During the World War at least 6,000,000 pounds of vanadium were used up by the tremendous demand for high-speed tool steels and for other special alloy steels used in the manufacture of armor plate, gun parts, shell cases, and airplane and automobile parts. This vanadium,

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[1] Received October 22, 1928.

[2] Associate editor, Industrial and Engineering Chemistry.

[3] Report of Sub-Committee on Vanadium, Mining and Metallurgical Society of America, *Bull.* **175** (1925).

which was not recovered, represents 35 per cent of the total world production up to the end of 1924.

Work of the Research Laboratory

All of the experimental work conducted by the Vanadium Corporation of America is carried out in the laboratory connected with its Bridgeville, Pa., plant. Routine plant control and analytical work are completely separated from research, being placed in a separate laboratory with an entirely separate staff. The research staff consists of a permanent group of experts, one for each of the fields of work in which the company is interested, who direct research units which vary in size according to current requirements, but are maintained as continuous organizations.

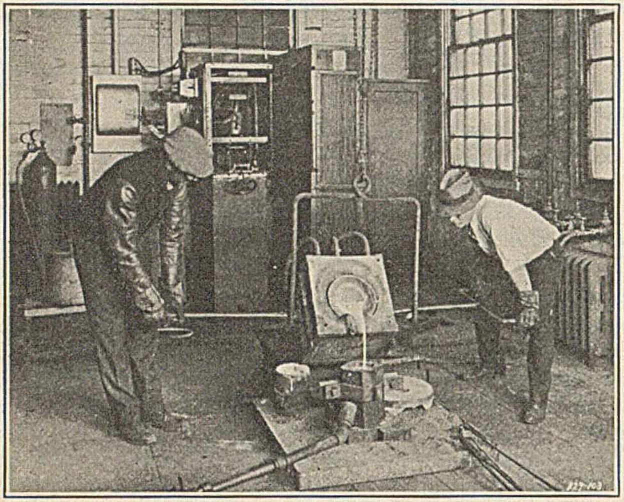

Figure 1—Corner of Metallurgical Laboratory

Pouring experimental melt from 35-kw. Ajax Northrup high-frequency furnace used for high temperature or vacuum melting.

Close contact is maintained between each research group and the plant department to which its work is related, as well as with industrial problems developed by the sales department through contact with consumers. As a result of emphasis on this point, the research units are scattered throughout the plant, the metallurgical research unit, for example, being located adjacent to the plant smelting operations.

The research work may be divided into two main parts—the first concerned with the development of the manufacturing processes of the Vanadium Corporation itself, the second with the utilization of the products resulting from these manufacturing processes. The first part is again subdivided to include, in one group, problems on the concentration of ores, and in another, problems in the metallurgical treatment of these concentrates to produce vanadium alloys, or in their chemical treatment to produce various vanadium compounds. The second of the two main fields, that dealing with the utilization of products, was until recently limited to the improvement of alloy steels and to their application in new fields. In the last three or four years, however, the scope of research has been remarkably broadened to include the application of vanadium to nonferrous metallurgy, to oxidation catalysis, and to chemotherapy.

Research on Manufacturing Processes

The real importance of the research laboratory to the continued success of this industry may best be realized by referring to some of the outstanding achievements in the various phases of the work outlined above. Probably the most valuable piece of research in the field of ore dressing was the development, a few years ago, of a concentration process for the treatment of patronite ore. This ore is mined at an elevation of 16,000 feet in the Peruvian Andes—incidentally this is the loftiest commercial mining operation in the world—and concentration at the mine is an economic necessity because of heavy transportation charges.

Patronite ore is essentially a vanadium sulfide containing some vanadium sulfate and vanadium oxide as products of weathering. Attempts at concentration of the lower grades by flotation were reported upon unfavorably by various consultants before the problem was assigned to the company's own research group. In the hands of the latter the proposition was reduced to its fundamentals. A complete mineralogical separation of the ore was made, with separate studies of the component materials, followed by some thousands of experimental flotation tests, which finally resulted in the development of a successful sequence of operations. In this case neither the application of new reagents nor new apparatus was necessary, but rather a persistent attack upon the fundamental aspects of the problem.

The metallurgy of vanadium-ore reduction presents a series of important improvements in method which have been worked out as part of the continuous program of research.[4] In the early days of the industry an electric furnace was tried, using silicon as the reducing agent, but owing to the cost of this material the process was not developed on any considerable scale. Following this, reduction with aluminum was adopted, using at first magnesite-lined iron crucibles which produced from 100 to 150 pounds of alloy per run. Over a period of years this process was continually improved, until finally the operation was carried out in small shaft furnaces, producing 125,000 pounds of alloy per run. In addition to the large increase in capacity, this development allowed the direct reduction of complex silicate mixtures, rather than requiring preliminary wet extraction of the ore to give vanadium oxide. Alumino-thermic reduction, however, shared the disadvantage of silicon reduction in that it used a relatively expensive material.

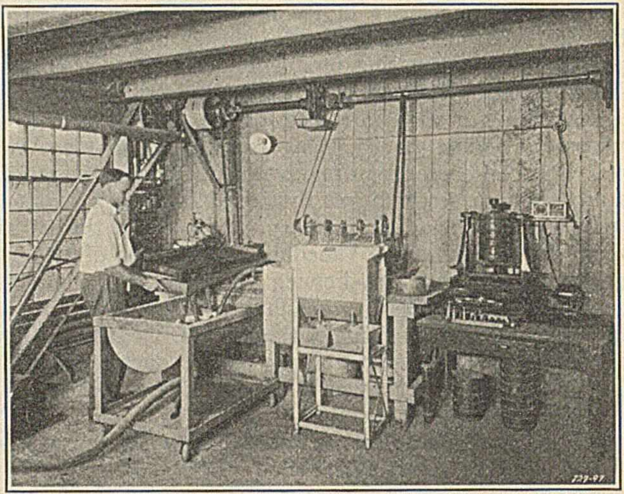

Figure 2—Part of Ore-Dressing Research Laboratory

Equipment for study of gravity concentration of ores.

Continued efforts toward the development of a less expensive method of reduction finally bore fruit, with the successful operation of a laboratory electric furnace using coke as the reducing agent. This process had been suggested by Moissan as early as 1893, but all attempts to work it out on a com-

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[4] Saklatwalla, *Trans. Am. Electrochem. Soc.*, **37**, 341 (1920).

mercial scale had hitherto failed. In 1920, following the successful work with a 750-kilowatt furnace, two 4000-kilowatt units were put in operation.

The electric smelting furnaces of the Vanadium Corporation hold the distinction of being the only continuously charged electric furnaces operating industrially in this country. Their design, described more completely elsewhere,[5] provides for the introduction at a constant rate of a mix of ore, iron turnings, coke, and flux, which is fed directly into the high-temperature zone between the tips of three 12-inch graphite electrodes, which are spaced so closely that the passage of current produces a blowpipe effect. Almost instantaneous reduction is believed to occur in this region, after which the fluid mixture of ferrovanadium and slag passes into the main part of the furnace, where separation takes place. Metal and slag are tapped off at 6-hour intervals.

Control on the furnace is maintained by an automatic device which maintains constant power input, with an ingenious device for automatically adjusting the feeding mechanism of each of the three electrodes in such a way that balance is maintained at all times in the three-phase circuit. One major requirement of the process is that the temperature of the furnace be maintained at an extremely even level. This condition is obtained by the combination of constant power and constant rate of feed of material. Furthermore, careful design of the electrical circuits has resulted in an average operating power factor of 99 per cent, and an over-all electrical efficiency of 98.5 per cent.

All of this remarkable advance in metallurgy has originated in the research laboratory of the company, where continuous work is being done in the same field. In a similar way, long-time projects in the extraction of vanadium compounds from ore by chemical means have resulted in the development of a new and efficient process for the preparation of vanadic acid on a large scale.

Research on Utilization of Products

Up to this point only the research work dealing with the improvement of plant processes has been mentioned. The other phase of the work, devoted to the utilization of the products of the Vanadium Corporation, will now be briefly described. Prior to 1924 the chief field covered by this research was the study of the various possible applications of vanadium and other alloy steels. This included work on high-speed tool steels, the introduction of vanadium steels in the manufacture of such railroad equipment as locomotive frames, side and main rods, piston rods, and locomotive and car axles; and the application of these steels in the automotive industry, both for the reduction in size and weight of chassis parts, and in the improvement of the internal-combustion engine. At the present time vanadium steels are used in automobile manufacture to the average extent of 120 pounds per unit for the entire number of cars produced.

Perhaps the most interesting recent application of vanadium steel in the automotive industry is its adoption by certain large manufacturers as the standard for crankshaft production. The story illustrates the way in which secondary factors may influence the choice of a material. It begins with the tendency toward minimizing vibration by increasing the number of main crankshaft bearings. With a plain carbon steel it is necessary to quench crankshafts to obtain the requisite properties in the finished article. Such quenching, however, produces severe strains in anything as kinky as a seven-bearing crankshaft, with resulting deformation which requires several straightening operations for correction. Residual stresses in the finished article may, moreover, release gradually over a long period of time during operation of the engine, with damage to the latter from the distortion thus produced.

Research with various alloy steels indicated that the desired properties could be obtained in crankshafts of vanadium steel in the normalized condition. While the alloy steel was more expensive than the straight carbon steel, its use would eliminate the labor and machinery charges against the straightening operations and at the same time insure a greater uniformity of product. Practical large-scale, long-period tests of vanadium-steel crankshafts showed a saving in total manufacturing costs over straight carbon steel, and the former material has accordingly been adopted.

Through the work of the research laboratory vanadium has very recently entered still another industry as chrome-vanadium steel used in the construction of apparatus for synthetic ammonia processes. Straight carbon steel used for this purpose becomes brittle, due to intergranular penetration of gases. This penetration is minimized with the alloy steel mentioned above, probably because of the increased resistance to chemical action of the material rejected to the grain boundaries of the steel during crystallization. This same resistance to intergranular corrosion has also caused the adoption of chrome-vanadium steel for the construction of oil-cracking equipment. In Germany a similar steel is being used in the manufacture of boiler plate. It would be of considerable interest to determine whether such a steel is resistant to caustic embrittlement, which is an action dependent upon intercrystalline corrosion.

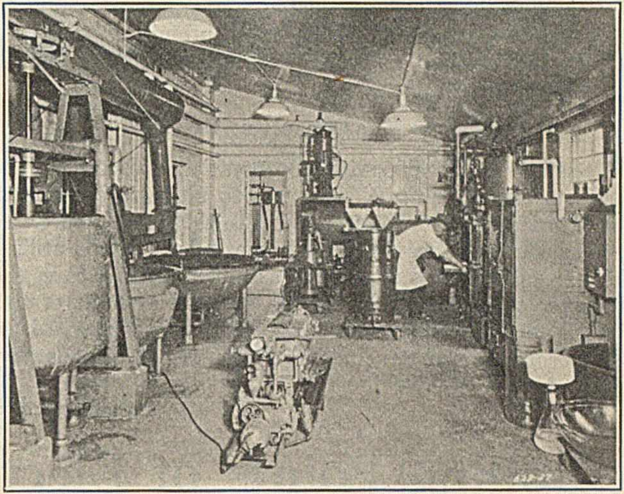

Figure 3—Laboratory for Preparation of C. P. Chemicals

Centrifugal, evaporating pans, automatic water still, filter press, and drying ovens used in production of compounds of vanadium, zirconium, titanium, uranium, and other less common metals.

In the last four years the application of vanadium to industry has taken a new turn, away from the strictly metallurgical utilization in alloy steels or in nonferrous alloys. Extensive research has developed the suitability of vanadium catalysts for various oxidation reactions, and three plants in this country are now using vanadium contact masses in the manufacture of sulfuric acid. Vanadium has the advantage over platinum of much lower cost and it is also much less sensitive to "poisoning." At the present time the efforts of the research laboratory are turned toward the fundamental problem of producing that philosopher's stone, a catalyst which can be manufactured commercially by ordinary methods, yet which will give a constant standard performance in use. The application of vanadium catalysts to various organic reactions is also being studied, particular interest being centered on the production of alcohols and organic acids.

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[5] Saklatwalla and Anderson, *J. Am. Inst. Elec. Eng.*, **42**, 775 (1923).

Still another field in which vanadium is commencing to appear is that of chemotherapy. Various vanadium compounds have been suggested in the literature for the past fifty years as being possible valuable drugs in combating various diseases. Only very recently, however, have such drugs actually been adopted. They are as yet practically unknown in the United States, but in France there have appeared several proprietary organic and inorganic compounds of vanadium for the treatment of dyspepsia, grippe, anemia, and the early stages of tuberculosis. Three of these appear, respectively, under the following names: VANUCLEOL—Solute leucosthenique injectable; VANADARSINE—Solution titree d'arseniate de vanadium au centieme; and VANADINE—D'oxide vanadique chloratee. It is also reported that vanadium salicylate is being experimented with as a substitute for salvarsan in the treatment of syphilis.

A new offshoot of the work of the research laboratory has been the preparation of a number of rare chemicals of C. P. and technical grades. Of these chemicals, one hundred and seventy have already been produced and are now available. They include inorganic and organic compounds of vanadium, molybdenum, tungsten, zirconium, chromium, titanium, colbalt, and uranium, and are, in general, not readily obtainable from other sources.

Research as Consulting Service

Inasmuch as the Vanadium Corporation does not sell its products directly as final materials to ultimate consumers, but rather as intermediate products to the manufacturers of various commodities, the research work done on the utilization of vanadium has necessarily assumed in many cases the character of a consulting service. A good example of this is work now under way to improve the riding comfort of the cars of one of the large railroad systems of the country. While the research work is actually done by the Vanadium Corporation in an effort to determine the alloy steel best suited for car springs, it involves in this effort the active coöperation of the railroad, which supplies cars for experimentation; of the manufacturers of the car springs, who are experimenting with their re-design; and of the steel manufacturers, who supply the alloy steel used in the fabrication of these springs. Such coöperation is the rule rather than the exceptional case, and an excellent spirit between the industries involved has been the general result. Any possible criticism of the research as leaning in favor of vanadium is obviated by the fact that the Vanadium Corporation, since its merger in 1924 with the United States Ferro-Alloys Company, has been active in the general ferro-alloy field.

Research as a Fundamental Industrial Necessity

An attempt has been made to show the manner in which research has entered vitally into all the phases of a particular industry. While the profit from this research has been evident in the growth of the Vanadium Corporation itself, it does not end there. Industry in general has profited largely, if indirectly, by the results of work done in the research laboratory of this company. Industry in general may profit still further by emulating the example set by this particular organization of using the research laboratory, properly manned and administered, as the agency which both creates and supplies demand.

Acknowledgment

Thanks are due B. D. Saklatwalla, vice president of The Vanadium Corporation of America, and director of the research laboratory, for assistance in the preparation of this article.

Boiling Points of Electrolytic Caustic Solutions[1]

C. C. Monrad and W. L. Badger

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

IN A previous publication by one of the authors[2] the discrepancies in the existing information on the boiling points of electrolytic caustic solutions were indicated. Shortly after that paper was written, work was begun on a redetermination of boiling points of these solutions with the hope that data could be obtained of greater accuracy and over a wider range than heretofore. In the interval Adams and Richards[3] published the results of Pink, which confirmed fairly well some of the figures used by Badger in his article. Since caustic evaporators are now in operation with working temperature drops of less than 10° C., it is obvious that an accuracy of ±1° C. is no longer within the limits of commercial requirements. The method of prediction advocated by Adams and Richards involves errors of several degrees for solutions boiling under considerably diminished pressure. The present series of data are so much more complete and of so much greater precision than anything at present in the literature that they will be presented in considerable detail.

Apparatus

Previous workers had used glass apparatus, which is open to the objection that glass is rapidly attacked by strong caustic solutions. Pink not only used glass apparatus but immersed the thermometer directly in the solution to be examined. This causes errors due to superheating and possibly smaller errors due to hydrostatic head. The apparatus used in this investigation is a modification of that described by Baker and Waite[4] and is illustrated in Figure 1. *A* is a boiling vessel made of monel with a suitable cover carrying a monel tube as a vapor pipe. Into the bottom of the bomb was inserted a closed monel tube, *A*, in the interior of which was inserted a chromel heating element wound on Usalite tubing. Over this heating element stood the modified Cottrell pumping tube, *C*, made entirely of monel. The side outlet to the bomb used for withdrawing samples was also of monel. The vapor pipe was surrounded by an iron condenser, *D*, and contained the precision platinum resistance thermometer, *E*. The glass tube which formed the casing of this thermometer was first silvered and then nickel-plated so that the solutions came in contact only with monel or nickel. A short connection led directly from the vapor space to the barometer-manometer combination, *F*, from which the absolute pressure could be read as the difference in the two mercury columns.

From the vapor pipe another glass tube led to the vacuum-producing and -regulating system. This consisted of a 12-liter flask, *H*, for damping out fluctuations in the pressure,

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[1] Received August 2, 1928.

[2] Badger, *Trans. Am. Inst. Chem. Eng.*, **18**, 231 (1926).

[3] IND. ENG. CHEM., **20**, 470 (1928).

[4] *r Tans. Am. Inst. Chem. Eng.*, **13**, Pt. II, 233 (1921).

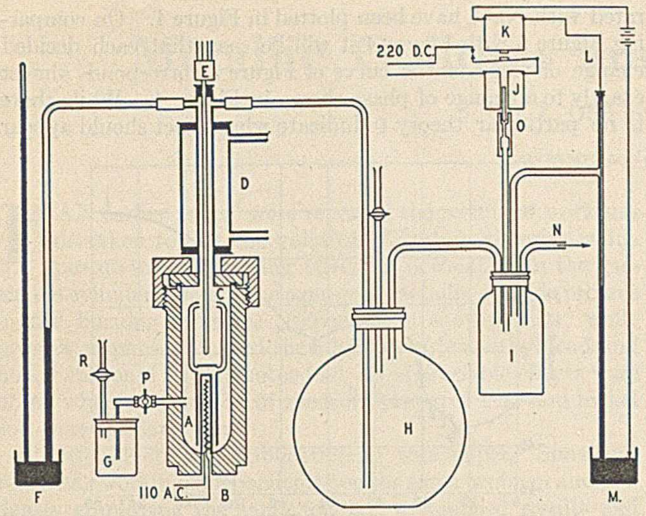

Figure 1—Apparatus for Determination of Boiling Points of Caustic Solutions

connected to a water trap, *I*, and this through *N* to a laboratory water-jet vacuum pump. The trap *I* was connected to a manometer, *M*, on the high side of which was a platinum-tipped brass rod, *L*. As the vacuum rose it made a contact between the mercury and this rod, closed a battery circuit through the relay *K*, which then closed the 220-volt circuit through solenoid *J* and opened the needle valve *O*, admitting air to the system. By means of a stop which limited the travel of the needle valve to a fraction of a millimeter, it was possible to maintain the vacuum as shown by manometer *M* constant to within 1 or 2 mm., and these fluctuations were so removed by the flask *H* that the manometer *F* showed variations of the order of 0.2 mm.

The Cottrell pumping tube kept the thermometer covered with a film of the boiling liquid in equilibrium with the vapor and prevented overheating at this point. The resulting stirring was violent enough so that the solution was thoroughly mixed and duplicate determinations check closely. The platinum resistance thermometer was calibrated against ice and steam, with the results shown in Table I.

The solutions were made up from caustic soda purified by alcohol and were saturated with sodium chloride. An excess of solid sodium chloride was maintained in the boiling vessel at all times, so that the solutions were saturated at their boiling points, as will always be the case in the commercial caustic evaporators. Since the materials used were relatively pure, these solutions differ from commercial cell liquors by containing no sulfate, chlorate, or hypochlorite. It is not believed that the presence of these compounds in commercial cell liquors will cause their boiling points to differ from those reported for these purer solutions by more than the limit of error of these determinations.

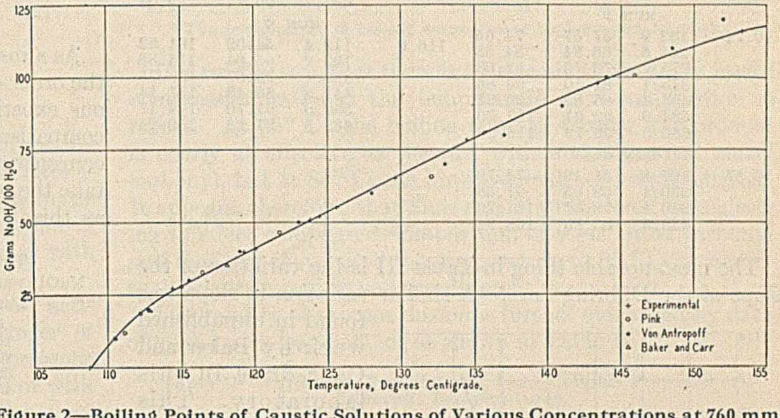

Figure 2—Boiling Points of Caustic Solutions of Various Concentrations at 760 mm. Pressure

Samples were withdrawn through the monel cock, *P*, into the closed glass weighing bottle, *G*, which was equalized to flask *H* through connection *R*. Thus, the sample was withdrawn from the boiling liquor at the boiling point. The sample was cooled to a definite temperature—in most cases 30° C., though the stronger solutions could not be cooled so far. The clear solution was carefully decanted from any sodium chloride which had separated on cooling and was then analyzed for its caustic content. The solubility of sodium chloride has been published by Hooker[5] and by Von Antropoff[6] and Sommer.[7] These two sets of determinations checked so closely that in the present work sodium chloride was not determined. From the known temperature and caustic concentration of the samples, the concentration of sodium chloride was calculated, and thus the ratio of sodium hydroxide to water was determined. For any one sample this is constant at all temperatures, irrespective of the sodium chloride content.

Table I—Thermometer Calibration

ACTUAL ° C.	CALCULATED ° C.	DIFFERENCE ° C.
98.99	98.98	0.01
52.99	53.02	0.03
78.83	78.81	0.02
92.89	92.89	0.00

It was suspected at first that at different temperatures and different rates of boiling the amount of water draining back from the condenser *D* might not be uniform. For every solution used, samples were withdrawn at three different pressures and their analyses were substantially identical. This proves that the amount of water in the vapor pipe and on the walls of the condenser did not vary enough to affect the composition of the liquid.

Accuracy of Results

It was not found possible to control the conditions during actual determinations closer than ±0.05° C. The agreement of the analyses was so close that the errors could not account for any greater fluctuation in the boiling point than this figure. Further, the boiling point of each solution was determined at a number of pressures, and in no case did these points deviate more than 0.1° C. from the best straight line that could be drawn through them. It is believed that the data here reported are accurate to within ±0.1° C. up to 50 parts caustic per 100 parts water, and to ±0.2° C. above that concentration.

Results

The original data are given in Table II and the boiling points at 760 mm. are shown in Figure 2. This figure contains for comparison the work of Pink and of Von Antropoff. It will be seen that the boiling points here reported deviate from those previously published at the high concentrations, whereas the agreement between all investigators is very good up to 50 parts NaOH per 100 parts of water.

The Dühring lines for each of the solutions were plotted and, as stated above, all the points for any one solution fell within 0.1° C. of a straight line. From these lines the boiling

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[5] *Trans. Am. Inst. Chem. Eng.*, **13**, Pt. I, 73 (1920).

[6] *Z. Elektrochem.*, **30**, 457 (1924).

[7] *Z. physik. Chem.*, **123**, 161 (1926).

point at 92.3 mm. absolute (corresponding to a boiling point of 50.0° C. for pure water) was read and the slope calculated. (Table III) A plot was made of the boiling points at 92.3 mm., and from this and Figure 2 data were read for plotting the Dühring lines for even concentrations of caustic. These data are given in Table III, and it is believed that it will be more satisfactory for the user to plot them so that they may be read at any degree of precision he desires, rather than reproducing the plot in this article.[8]

Table II—Boiling Points of Caustic Solutions at Various Pressures

NaOH per 100 H_2O *Parts*	Abs. Pressure *Mm. Hg*	B. P. H_2O *° C.*	B. P. Soln. *° C.*
	RUN A		
0	94.9	50.55	· 56.77
	224.4	69.06	76.18
	315.9	77.14	84.48
	398.1	82.85	90.68
	510.4	89.22	97.37
	613.3	94.10	102.57
	676.4	96.77	105.32
	708.7	98.06	106.68
	RUN B		
10.35	312.2	76.86	85.82
	418.7	84.12	93.22
	678.1	96.84	107.01
	RUN C		
27.07	129.1	56.91	69.00
	179.8	64.08	76.51
	251.0	71.67	84.62
	307.0	76.45	89.70
	385.8	82.06	95.57
	463.0	86.69	100.35
	543.9	90.90	104.59
	648.3	95.60	109.55
	RUN D		
27.55	119.2	55.22	67.22
	197.3	66.16	78.83
	286.5	74.79	88.14
	375.0	81.35	95.26
	463.9	86.74	100.96
	573.4	92.29	106.87
	694.2	97.47	112.10
	RUN E		
39.73	130.2	57.09	72.92
	215.0	68.10	85.10
	299.3	75.83	93.28
	396.4	82.74	100.73
	533.8	90.39	109.07
	702.9	97.83	116.91
	RUN F		
40.74	133.9	57.57	74.65
	204.5	66.84	84.53
	275.7	73.75	92.08
	373.1	81.10	99.86
	468.4	86.85	105.64.
	584.0	92.64	112.20
	680.5	96.79	116.69
	RUN G		
50.87	197.8	51.16	71.70
	230.1	69.65	91.58
	336.4	78.67	101.20
	439.5	85.35	108.24
	RUN H		
51.75	138.4	58.38	80.30
	234.9	70.13	92.44
	350.4	79.67	102.80
	475.9	87.40	111.01
	567.3	92.01	115.83
	674.4	96.69	120.76
	RUN I		
55.04	137.6	58.26	81.62
	218.3	68.45	92.55
	349.8	79.62	104.17
	468.3	86.99	111.34
	RUN J		
65.01	118.6	55.13	82.47
	254.6	72.01	100.18
	387.0	82.133	110.73
	546.1	91.00	119.14
	RUN K		
78.25	140.4	58.69	90.66
	205.4	67.06	99.67
	307.2	76.45	109.53
	418.3	84.10	117.87
	512.8	89.34	122.82
	617.9	94.30	128.49
	694.0	97.47	131.60
	RUN L		
80.46	159.3	61.41	94.96
	160.8	61.61	55.11
	385.0	82.00	116.60
	658.0	96.00	131.40
	RUN M		
97.98	147.1	59.70	100.10
	220.9	68.62	109.50
	321.8	77.51	119.30
	469.5	87.04	129.31
	667.7	96.41	139.64
	RUN N		
116.0	112.4	54.02	101.82
	193.2	65.64	114.88
	339.1	78.87	129.75
	441.8	85.48	137.14
	560.8	91.70	144.17
	688.5	97.25	150.24

The most notable thing in Table III is the variation of the slope of the Dühring lines. A similar variation in slope was found in unpublished work by Baker and Carr done in this laboratory. This slope is plotted against concentration in Figure 3, and at first sight it was thought that there must be some error because of the apparently erratic changes of slope. The work of Von Antropoff and Sommer gives the phase diagram for the system NaOH–NaCl–H_2O. From this the freezing points of NaOH solutions saturated with NaCl have been plotted in Figure 4. On comparing Figure 3 with Figure 4 it will be seen that each decided change of slope of the curve of Figure 3 corresponds almost exactly to a change of phase shown in Figure 4. While there is no particular theory to indicate what effect should appear in the properties of a solution at the temperature where a change of phase occurs in the solid, it is not unreasonable to expect some correlation between the two, and this forms at least a partial confirmation of the correctness of Figure 3 and therefore of all of the Dühring lines.

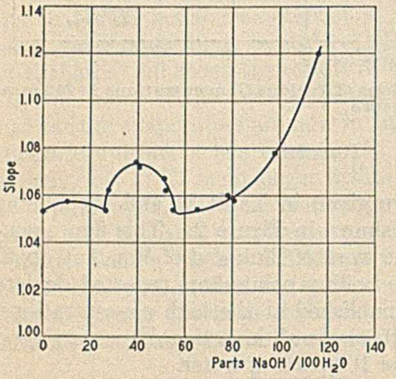

Figure 3—Slope of Dühring Lines NaOH–NaCl–H_2O

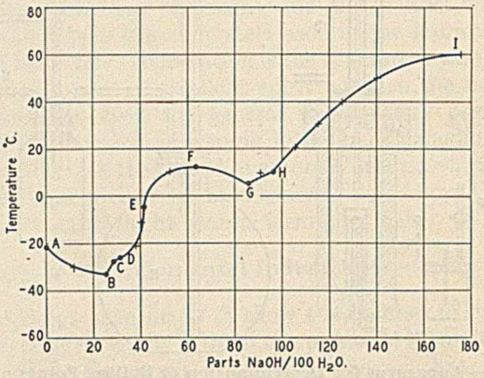

Figure 4—Phase Diagram NaOH–NaCl–H_2O

Table III—Boiling Points as Calculated from Dühring Lines

NaOH per 100 H_2O *Parts*	B. P. at 760 mm. *° C.*	B. P. at 92.3 mm. *° C.*	Slope
0	108.73	56.10	1.053
10	110.35	57.65	1.058
20	112.45	59.65	1.056
30	115.70	62.30	1.068
40	119.65	65.85	1.076
50	123.60	70.20	1.068
60	127.55	74.90	1.053
70	131.50	78.75	1.055
80	135.45	82.50	1.059
90	139.60	86.25	1.067
100	144.40	90.35	1.081
110	149.75	94.60	1.103
120	155.60	98.95	1.133

As a matter of interest, Table IV is appended, which shows the order of magnitude of the differences in the work of previous experimenters. The work of Pink is not included in this comparison, as he did not express his work in terms of even concentrations of NaOH, and the authors were not inclined to take the responsibility of interpolations for such a comparison as this.

Table IV—Comparison of Boiling Points at 760 mm.

NaOH per 100 H_2O *Parts*	Experimental *° C.*	Von Antropoff *° C.*
0	108.73	108.8
10	110.35	110.5
20	112.45	112.7
30	115.70	115.5
40	119.65	119.0
50	123.60	123.0
60	127.55	128.0
70	131.50	133.0
80	135.45	137.0
90	139.60	141.0
100	144.40	144.0
110	149.75	148.5
120	155.60	152.0

Acknowledgment

The authors wish to acknowledge their indebtedness to the Swenson Evaporator Company, who financed all of this work.

Correction

In our article on "Miscibility of Castor Oil with Gasoline Hydrocarbons" [Ind. Eng. Chem., 20, 1185 (1928)], the numbers in the last line of Table III, after the words "castor oil per gram, lower layer" should read: 0.6268—0.6278—0.6287—0.6293.

George H. Taber and Donald R. Stevens

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[8] Blue-printed charts reproducing these data on a scale that can be read to 0.1° C. can be obtained from the authors.

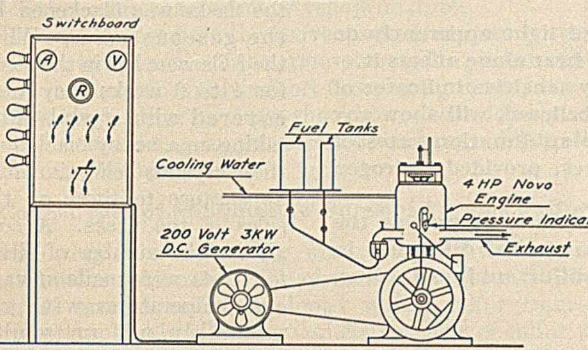
Metallic Colloids and Knock Suppression[1]

H. L. Olin and W. J. Jebens

University of Iowa, Iowa City, Ia.

IN AN earlier paper[2] were reported the results of work undertaken to test the validity of certain theories which postulated a retarding effect on detonation in the gas-engine cylinder through the agency of metallic colloids present in the burning mixture. Experiments showed that, while prompt response followed the addition of tetraethyl lead and nickel carbonyl to the motor fuel, no appreciable effects were noted when suspensions of specially prepared lead and nickel sols were similarly used.

Shortly before the publication of this paper,[2] Sims and Mardles,[3] working independently on the same problem and evidently employing the same technic, announced results and conclusions diametrically opposite to those found by Olin and co-workers—viz., that lead and nickel sols have the same antiknock activity as solutions of tetraethyl lead and nickel carbonyl containing equivalent amounts of the respective metals. It should be noted that Sims and Mardles prepared the sols by heating nickel carbonyl in boiling hexane for 40 minutes for the nickel colloid and tetraethyl lead at about 250° C. for 30 minutes for the lead.



Apparatus for Testing Motor Fuels

Because of the important bearing of this question on the solution of the general problems of the mechanism of detonation and of its suppression, the writers undertook a systematic review of their earlier work with a view to the detection of possible errors and to the harmonizing of their findings with those of the workers mentioned above.

In any study involving the preparation and use of activated colloids the obviously weak point is the danger of poisoning the active mass, either by hydrolysis in the presence of water, by oxidation, or by interaction with sulfides or with other agents of similar chemical properties. In the second series special pains were taken to avoid trouble of this kind, first by the use of calcium chloride to desiccate the gasoline thoroughly, and second by maintaining an atmosphere of dried and purified nitrogen over all solutions and sols from the time they were prepared to the time they were used. Tests of the gasoline showed the sulfur content to be practically nil.

The colloids were prepared as before by thermal decomposition of the metallo-organic compounds at various given temperatures and stabilized by the addition of small quantities of raw rubber. Working solutions of proper concentration were then made by diluting with gasoline. The tests were made in a newly designed laboratory equipped with a single-cylinder, 4-horsepower vertical engine with variable compression head which allowed a range of compression ratios from 3.75 to 9.0. This was connected by belt with a 3-kilowatt d. c. generator whose output was delivered to a switchboard and dissipated through a variable resistance made up of four 500-watt coils and twenty 40-watt lamps. A Crosby indicator supplied a graphic record of the explosion, but aural evidence of presence or absence of knock was in general the more dependable. A diagram of the apparatus is shown.

Experimental

In making a test run the engine was first operated with the original gasoline. The movable piston head was set for low compression, then gradually lowered until a light knock occurred, and finally to a point where the detonation became pronounced at intervals. This last reading was taken as the highest useful compression ratio (H. U. C. R.). The special fuel was then admitted and a new setting given to the piston head. Table I gives a summary of results obtained with nickel sols.

Table I—Antiknock Properties of Nickel Colloids Prepared at Different Temperatures

FUEL	H. U. C. R.	INCREASE IN H. U. C. R.	INITIAL CONCN. OF $Ni(CO)_4$
		Per cent	*Cc. per liter*
Straight gasoline	4.37	..	0
Gasoline with nickel carbonyl	4.70	7.54	5.501
Gasoline with nickel carbonyl heated at 69° C.[a]	4.63	5.94	5.501
Gasoline with nickel carbonyl heated at 77° C.	4.56	4.35	5.501
Gasoline with nickel carbonyl heated at 85° C.	4.41	0.92	5.501

[a] The temperature of boiling hexane, used by Sims and Mardles.

It is readily seen that there is a successive decrease in useful compression ratio as the temperature of decomposition is raised. At 69° C., the boiling point of hexane, the product is nearly as effective as the fuel with undecomposed nickel carbonyl, but at 85° C. the improvement becomes negligible. It appears, therefore, that Sims and Mardles erred in neglecting to effect complete decomposition of their nickel carbonyl and that had they raised the temperature to 85 ° C. or higher their results would have been different.

The validity of this conclusion is further evidenced by data obtained with lead colloids as shown in Table II.

Table II—Antiknock Properties of Lead Colloids Prepared at Different Temperatures

FUEL	H. U. C. R.	INCREASE IN H. U. C. R.	INITIAL CONCN. OF ETHYL LEAD
		Per cent	*Cc. per liter*
Straight gasoline	4.43	..	0.00
Gasoline with ethyl lead	5.02	13.3	1.00
Gasoline with ethyl lead heated at 250° C.[a]	4.76	7.5	1.00
Gasoline with ethyl lead heated at 275° C.	4.55	2.7	1.00
Gasoline with ethyl lead heated at 300° C.	4.44	0.0	1.00

[a] Temperature employed by Sims and Mardles.

So far as absolute proof with respect to theories postulating a catalytic effect on the part of metallic colloids is concerned, it must be admitted that negative findings leave much to be desired. It is quite possible that in the nascent state at the high temperatures of the explosion chamber their effects are radically different from those exhibited under the conditions described.

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[1] Received August 13, 1928.

[2] IND. ENG. CHEM., 18, 1316 (1926).

[3] *Engineering*, 121, 774 (1926); *Trans. Faraday Soc.*, 1926 (advance proof).

Notes on the Sublimation of Sulfur between 25° and 50° C.[1]

Roy P. Tucker

California State Department of Agriculture, Sacramento, Calif.

That sulfur sublimes as such at temperatures of 20° to 50° C. is indicated by the formation of visible crystals on the sides of flasks containing a small amount of sulfur when the flasks are kept at these temperatures for several weeks. The comparative rates of sublimation at the three series of temperatures 24–26° C., 30–35° C., and 40–45° C. has been found to be in the ratio 1:6:80.

When sulfur is mixed with lampblack to make a black mixture, direct sunlight increases the temperature of the black mass from 5° to 10° C. over that of white or yellow mixtures, and hence increases the sublimation rate.

A microscopic study of the shrinkage in area of sulfur particles and of the sulfur crystals formed at low temperatures in the flasks indicated that the former are retarded in their sublimation because of surface conditions.

Size of particle, moisture, and light apparently do not affect the sublimation rate; heat alone affects it.

Silver foil appears to be a very sensitive indicator of the sublimation rate and, it is believed, will show any material difference between the sublimation rates of various sulfurs or sulfur mixtures, provided hydrogen sulfide is not given off.

The silver-foil tests, weighing tests, as well as the microscopic study, indicate no material difference in the sublimation rates of ground sulfur, sublimed sulfur, or gas-purification sulfur.

The properties of sulfur which give it fungicidal value have been investigated by many chemists and plant pathologists. Their results have contributed much to our knowledge of sulfur. There remains, however, a demand for information on the practical application of sulfur in the control of plant diseases, pertaining particularly to the comparative values of the different kinds of sulfur on the market. Further, there appears no way of determining how far the toxic properties of sulfur extend their influence from the solid particles, a problem of great importance when fungus diseases infect plants whose foliage is susceptible to sulfur injury. With these problems in mind, the writer undertook some investigations of sulfur, the results of which are presented in this paper. All the investigations were carried out in the chemical laboratory of the California State Department of Agriculture.

Out-of-Doors Exposure

Approximately 5 grams of various commercial sulfurs and sulfur mixtures were spread over the bottom of 1-liter Erlenmeyer flasks and the flasks set out of doors in a place where they were exposed to the sun for 3 to 4 hours a day. As this work was done in September, the temperature in the flasks ranged from 40° to 50° C. during this period of the day. At the end of 2 to 4 weeks well-developed crops of crystals were found covering the upper portions of the flasks, and even in one flask kept indoors with a maximum temperature of 26° C. a visible crop of crystals formed in 2 months. These crystals resulting from the condensation of gaseous sulfur were in all cases similar. Under the microscope they appeared as nearly colorless, oblong plates with some reaching the dimensions 150 × 100 microns. The thickness was not measurable by the microscopic facilities available. They were identified as belonging to the rhombic system and when crushed made yellow masses. They were easily soluble in carbon disulfide, and gave every indication of being elemental sulfur. The formation of these crystals did not depend upon moisture, light, or oxygen, in so far as could be determined, and it appeared that the only important factor was temperature.

Although the rate of formation and size of the crystal crop varied considerably according to the temperature at which the flasks were kept, the process was entirely too slow for reliable comparative tests and it was evident that some indicator extremely sensitive to gaseous sulfur was necessary for further work.

Various indicators were tried but only one was found sufficiently sensitive for use. Pure silver foil cut into ribbons 1 to 2 inches (2.5 to 5 cm.) long and suspended in the flasks was blackened by the gaseous sulfur. When the foils were left in the flasks for 4 to 6 weeks they were covered with crystals after taking on a heavy black film; these crystals being similar in appearance to those on the sides of the flasks. A considerable number of silver foil tests were made at various temperatures with remarkably uniform results. Using 1-liter flasks with 5 grams of sulfur, the rate of blackening was as follows:

(1) 20° to 25° C., 2 days for slight film, 1 to 2 weeks for heavy film
(2) 30° to 35° C., 2 days for heavy film
(3) 40° to 45° C., 30 minutes for heavy film

That sulfur sublimes readily in boiling water is well known, and at this temperature only the slightest traces of hydrogen sulfide or oxidized sulfur compounds as dioxide, trioxide, or thiosulfates are found. As a matter of fact, negative results are usually obtained in testing for these various compounds. By dropping the temperature from 100° C. to 25–50° C. the chance of formation of these chemical compounds would be very much less. The writer therefore considers that the formation of visible crystals on the sides of the flasks kept for some time at this temperature (25–50° C.) could only come from the condensation of gaseous sulfur sublimed from the solid particles of sulfur in the flasks.

The greatly increased rate of action with succeeding rises of 10° C., as shown by the silver foil tests as well as by the microscopic work on the crystals themselves, also indicates sublimation rather than a true chemical reaction such as the formation of hydrogen sulfide, sulfur dioxide, sulfur trioxide, or other oxidized sulfur compounds.

In the control of certain plant diseases the same increase in the effectiveness of sulfur is found with successive rises in temperature. It appears safe to say, therefore, that the value of sulfur as a fungicide depends primarily upon the

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[1] Presented under the title "The Behavior of Sulfur at Summer Temperatures" at the Intersectional Meeting of the American Chemical Society at Pomona College, Claremont, Calif., June 15, 1928.

sublimation of sulfur as such, and any increase in the efficiency of sulfur as a fungicide will come from an acceleration of the sublimation rate over that which now prevails.

Various mixtures of sulfur with other materials were tried but in only one case was there any accelerating effect upon the rate of blackening of the silver foil or crystal formation; that one being a black mixture (90 per cent sulfur with 10 per cent lampblack). Sunshine had a decided effect upon this mixture because the black surface adsorbed the sun's rays and raised the temperature of the mass, the sulfur then subliming at an increased rate.

The following experiment clearly shows the effect of the direct rays of the sun on this mixture. Three small dishes were filled with the following materials: commercial ground sulfur, commercial ground sulfur and lampblack, and lampblack.

Thermometers with bulbs buried in the materials registered as follows:

	AIR	SULFUR	SULFUR AND LAMPBLACK	LAMPBLACK
	° C.	° C.	° C.	° C.
Before sun shone on dishes	21.0	22.0	22.0	22.0
Sun shining on dishes 10 minutes	29.5	30.0	46.0	47.5
Sun shining on dishes 30 minutes	42.0	42.5	51.0	52.5
Dishes in shade 10 minutes	31.5	33.5	35.0	35.0

A considerable number of tests were made and in all cases the black mixtures gave from 5° to 10° C. higher temperatures in the sun than white or yellow mixtures.

It would appear from the above results that in early spring, when the temperature of the atmosphere is low, or in localities where the sun shines only a short time during the day because of fogs, black sulfur mixtures should have considerably more effect in controlling fungus diseases, such as mildew, than white or yellow mixtures.

Comparison of Sublimation Rates of Various Sulfurs

Following this preliminary work comparative tests were made on the sublimation rate of various commercial sulfurs, such as ground sulfur, sublimed sulfur, sulfur from gas purification, and in addition, various mixtures of sulfur with inert material made in the laboratory. Two different methods were employed:

(1) Observation of area shrinkage of sulfur particles under the microscope.

(2) Comparison of the rate of blackening of silver foils exposed to the action of equal weights of the various sulfurs and mixtures spread over equal areas.

MICROSCOPIC PROCEDURE—A few particles of the various kinds of sulfur were placed on glass slides, their position, *en masse*, on the slides marked by inked circles, and the outline of a few of the particles drawn with the aid of a camera lucida. The slides were kept at definite temperatures and at intervals the same particles were redrawn. The drawings were then traced on coördinate paper and the areas calculated. This method determined the area shrinkage only. On account of the small size of the particles involved, calculations of loss of volume and weight were made from the loss of area as observed.

Only approximate results could be expected in calculating the sublimation rate from the microscopic work, for any method would be more or less arbitrary. The following method was employed: The particles were considered as cubes. The average areas of a set of particles at the beginning and end of the test were obtained. One-half the difference of the square root of each of the two average areas was considered as the depth sublimed. The weight of a mass 1 sq. cm. with this depth was then calculated, the final result being expressed in milligrams per square centimeter sublimed per 24 hours.

Example. In Table I, the original average area of sulfur crystals kept at 30° to 35° C. for 72 hours was 6000 square microns. The final average area was 3552 square microns.

$$\sqrt{6000} = 77.72\mu \qquad \sqrt{3552} = \frac{59.60\mu}{18.12\mu}$$

$$\frac{18.12 \times 24 \times 1 \times 1 \text{ sq. cm.} \times 2000 \text{ mg.}}{2 \times 72 \times 10{,}000}$$

$$= 0.6 \text{ mg. per sq. cm. per 24 hours sublimed}$$

The sulfur particles used in the microscopic study were kept under the following conditions: In Series 1 to 5 and 7 to 9 the slides were kept on the top of a drying oven and under bell jars open at the top and bottom to allow the circulation of dry air. In Series 6 moist air was passed over the slides by means of suction. In Series 10 and 11 the slides were kept in a glass case with the sulfurs used in the silver foil tests. Here they were in a humid atmosphere. Other slides were kept in an incubator with constant temperature of 39.5° C., and these sulfur particles were shut off entirely from light. Under these various conditions of moisture and light no marked difference in the sublimation rate was noted. Sulfur treated with alkali, acids, and various salts also showed no increase in sublimation rate as calculated from microscopic observation, nor could any marked difference be found when various commercial colloidal sulfurs were kept under the same conditions as indicated above.

As will be noted in the tables of Series 1 to 11, the crystals formed on the sides of the Erlenmeyer flasks kept out of doors sublimed much faster than any of the commercial samples of sulfur. Following these in sublimation rate comes lightly crushed roll sulfur. Commercial ground sulfur, according to the microscopic study, sublimed a little more rapidly than commercially sublimed sulfur, but this was not corroborated either by the silver foil tests or by the actual loss in weight. Sulfur from gas purification gave results between ground and sublimed sulfur. Amorphous sulfur made by sudden cooling of melted sulfur had the lowest rate. Crystals rapidly formed from a carbon disulfide solution saturated with sulfur also sublimed very slowly. A commercial sublimed sulfur which was 75 per cent soluble in carbon disulfide was boiled with water 8 hours a day for 1 week. At the end of this time 100 per cent of the sulfur was soluble in carbon disulfide, but, as Series 11 of Table IV shows, the sublimation rate was not materially changed. The crystals deposited on the sides of the flask above the water line gave a high sublimation rate.

A considerable number of additional slide tests were made of sulfur treated with acids, alkalies, and oxidizing agents as potassium permanganate, as indicated above, in an attempt to discover just what property of sulfur inhibits the sublimation rate of commercial sulfurs and makes it lower than that observed in crystals formed very slowly at low temperatures. No conclusive results were obtained. So far as the writer can judge, this inhibiting factor is confined to the surface of the particles. The calculated sublimation rates of the various sulfurs as shown in Tables I to IV of Series 1 to 11 were remarkably uniform throughout the experiments.

The average sublimation rate of commercial sulfurs calculated from the area shrinkage of separate particles kept in the glass case is approximately 0.05 mg. per square centimeter per 24 hours at 30° to 35° C. The actual loss in weight of fairly large masses of the same sulfurs kept under the same conditions indicates a sublimation rate fifty times smaller—namely, 0.001 mg. per square centimeter per 24 hours. In practical use it would appear that the sublimation rate from the solid particles as dusted will range between these two figures, while any crystals formed from the sulfur thus sublimed will resublime at a much higher rate—namely, 0.6 mg. (Series 3, Table I)

Table I—Area Shrinkage Observed under the Microscope of Sulfur Crystals from Sides of Flasks Kept Out of Doors. Series 1 to 4

Temperature of Crystals	At Beginning	After 24 Hours	After 72 Hours	After 96 Hours	After 260 Hours	Sublimation Rate
° C.	μ²	μ²	μ²	μ²	μ²	Mg./cm.²/24 hrs.
40–45	14,850	1413				8.426
35–38	22,273			14,862		0.683
30–35	6,000		3552			0.604
24–26	11,000				8690	0.106

Table II—Area Shrinkage Observed under the Microscope of Sulfur Particles Kept under Bell Jars on Top of Drying Oven, with Temperature Range of 30° to 35° C. Series 5, 7, 8, 9

Kind of Sulfur	At Beginning	After 72 Hours	After 168 Hours	After 216 Hours	After 344 Hours	Sublimation Rate
	μ²	μ²	μ²	μ²	μ²	Mg./cm.²/24 hrs.
Commercial ground	1500				767	0.096
Commercial sublimed	1210				1222	No loss
Fragments lump, lightly crushed	3416	2060				0.436
Lump, lightly crushed	1320		485			0.205
Ground, as check on lump sulfur above	2000		843			0.225
Crystallized from sulfur in CS_2	6428			5415		0.073

In all the microscopic studies the same temperature interval, 30° to 35° C., was maintained with the exception of those done on the sulfur crystals. As indicated in Table I, Series 1 to 4, three different sets of temperatures were used in these experiments—namely, 24–26° C., 30–35° C., and 40–45° C. The ratio of increase in sublimation rate at these three temperature intervals is 1:6:80, indicating clearly the sharp increase in sublimation rate which rise in temperature effects.

THE COMPARISON OF RATE OF BLACKENING OF SILVER FOILS BY VARIOUS SULFURS—This work was of a preliminary nature, but the results obtained appear definite enough to warrant further work along the same lines.

For comparative tests a glass case approximately 12 × 12 × 30 inches (30 × 30 × 76 cm.) was first used as one compartment, then divided into three by glass partitions so that the top and bottom spaces were of equal size, 12 × 12 × 12 inches (30 × 30 × 30 cm.). Temperature between 30° and 35° C. was controlled by electric lights, while a humid condition was maintained by beakers of water in the compartments. One-gram samples of sulfur were spread out on the bottom of Petri dishes resting on small glass cylinders. Two pieces of pure silver foil 0.5 × 1 inch (1.3 to 2.5 cm.) were placed in definite positions facing the Petri dishes for all tests. At the end of certain periods, usually 4 or 5 days, the films on the foils were compared and the foils then paraffined to protect them from the air. The Petri dishes were reweighed at the end of the test and loss was determined. For comparison, samples of the same lot of ground sulfur were placed each time in one compartment and the sulfur to be tested was placed in the other, and the same temperature maintained in both compartments.

Test 1. The case was used as one compartment. One gram of ground sulfur was spread out on a watch glass 50 mm. in diameter, which gave a ratio of sulfur surface to the surface area of the case of 1 to 500. No appreciable blackening of the foils took place in 10 days. The case was then divided into three compartments by glass partitions. The top and bottom compartments being approximately 12 × 12 × 12 inches (30 × 30 × 30 cm.).

Test 2. One gram of ground sulfur was spread out on a watch glass 50 mm. in diameter and placed in the top compartment. One gram of sublimed sulfur was placed in the lower. In neither compartment were the foils blackened in 10 days. The ratio of sulfur area to compartment area was as 1 to 250.

Test 3. One gram each of ground sulfur and sublimed sulfur was spread out in Petri dishes which were 100 mm. in diameter. In 7 days a distinct blackening of the foils resulted with no appreciable difference between the two sulfurs used.

Test 4. A duplicate experiment was run. In 5 days a distinct film was formed with no difference in the two sulfurs. The ratio of sulfur surface to area surface of the compartments was 1 to 70. The weight of ground sulfur lost was 2 mg. The weight of sublimed sulfur lost was 1.5 mg. According to the sublimation rate calculated from the area shrinkage of individual particles (0.05 mg. per square centimeter per 24 hours), the loss should have been 18 mg. No increase in acidity was noted in either sample, nor did this low loss in weight change when the beakers of water were replaced by beakers containing fused calcium chloride in later tests, which indicates that the loss in weight was not counterbalanced by gain in moisture or non-volatile sulfuric acid.

Test 5. Ground sulfur (1 gram in a 100-mm. diameter Petri dish) was placed in one compartment. Gas-purification sulfur was placed in the other. In 6 days a fairly good film was produced on the foils. The ground sulfur appeared slightly more distinct than the gas sulfur. The ground sulfur lost 3 mg. The gas sulfur lost 34 mg.

Test 6. The same two samples were used. In 5 days good films were produced with both samples losing 1.5 mg.

Test 7. New samples of the same sulfurs were used. In 5 days good films were produced with practically no difference in the two. The ground sulfur lost 2 mg. The gas sulfur lost 9.5 mg.

These tests indicate that the gas sulfur loses weight quite rapidly the first few days it is exposed to the air, but inasmuch as the foils were not blackened any more than with the ground sulfur, this loss probably comes from volatile oils.

Test 8. Ground sulfur was used in one compartment. In the other a 1:1 mixture of ground sulfur and finely ground calcium carbonate were thoroughly shaken together. At the end of 4 days the ground sulfur foils had good films while the mixture gave distinctly less stain.

Test 9. The same ground sulfur was used and a 1:1 mixture of sulfur and calcium carbonate carefully ground together in an agate mortar. At the end of 4 days the foils in both compartments were well stained with no appreciable difference between them.

These two tests indicate that a mixture of sulfur with an inert carrier does not have the effectiveness of pure sulfur. When the two are ground together, however, the sulfur apparently is ground finer, forming an almost continuous sulfur surface, thus acting like pure sulfur.

Table III—Area Shrinkage Observed under the Microscope of Sulfur Particles with Current of Moist Air Passing over Them. Series 6

Kind of Sulfur	At Beginning	After 56 Hours at 40° C. and 126 Hours at 20° C.	Sublimation Rate
	μ²		Mg./cm.²/24 hrs.
Commercial ground	3880	3489	0.140
Commercial sublimed	3222	3107	0.044

Table IV—Area Shrinkage Observed under the Microscope of Sulfur Particles Kept in Glass Testing Case with Temperature Range of 30° to 35° C. Series 10 to 11

Kind of Sulfur	At Beginning	After 168 Hours	After 240 Hours	Sublimation Rate
	μ²	μ²	μ²	Mg./cm.²/24 hrs.
Ground	2589	1925		0.100
Gas-purification	7524	6625		0.075
Sublimed	5457	5073		0.038
Ground	1794		1390	0.051
Sublimed	6000		5404	0.039
Amorphous	1036		937	0.016
Sublimed sulfur boiled 1 week in water	14,610		13,700	0.038
Crystals on flask above water	1780		1023	0.102

Following the silver-foil tests, 1-gram samples of ground and sublimed sulfur were spread out in Petri dishes (100-mm. diameter) and placed in the two compartments. Weighings were made at various intervals over a space of 50 days. These were followed by repeated weighings of 100-mg. samples spread over the same area for 195 days. The temperature was maintained between 30° and 35° C. During the run of the experiment the beakers of water were replaced by beakers containing fused calcium chloride, and later these were removed and the door of the case kept partly open. No difference in the sublimation rate was noted by the changed conditions. While these experiments were running a 1-gram sample of ground sulfur, spread out in a Petri dish (100 mm. in diameter), was kept in an incubator having a constant temperature of 39.5° C. The sulfur in this experiment was exposed to dry, quiet air with complete darkness. The sublimation rate, however, was three times that of the similiar samples in the glass case, the difference being due to the higher temperature of the oven.

The sulfurs in the glass case did not lose weight uniformly and some weighings showed a slight increase over the previous reading. Also, the sublimation curves have a tendency to flatten out. As a matter of fact, no loss in weight was shown for the last 35 days of the run.

While these experiments are not sufficient to prove the point, they indicate that sulfur loses its power of sublimation to a considerable extent at temperatures of 35° C. and less when exposed to air. (Table V)

Table V—Loss in Weight of Samples of Ground and Sublimed Sulfur on Standing in Case and in Incubator

SAMPLE	KIND OF SULFUR	WHERE KEPT	LOSS IN WEIGHT	TIME OF STANDING	SUBLIMATION RATE
			Mg.	*Days*	*Mg./cm.²/ 24 hrs.*
1	Ground	Case	4	50	0.001
2	Ground	Case	9	160	0.0007
1	Sublimed	Case	6	60	0.0014
2	Sublimed	Case	13.5	160	0.0011
3	Ground	Incubator	34	160	0.0028

The Reaction between Amino Acids and Glucose[1]

J. A. Ambler

Carbohydrate Division, Bureau of Chemistry and Soils, Washington, D. C.

The preliminary survey here reported indicates that the course of the reaction between glucose and amino acids varies under different conditions of temperature and concentration of the reacting substances. In these experiments the duration of time of heating was constant, but it is evident that the reaction becomes more complete with longer heating.

Under conditions favorable for the removal of volatile products, as in boiling either at normal pressures or under a vacuum, the loss of reducing sugars caused by amino acids may be much larger than has been supposed, amounting possibly to 10 or more mols per mol of amino acid. When the boiling point is not attained, such extensive destruction of glucose is not indicated, as a part of the amino acid is probably destroyed by condensation with the aldehydes produced by the primary reaction and thus prevented from acting on the sugar.

This survey indicates clearly progressive dehydroxylation of the glucose molecule during reaction with the amino acids, with the formation of a series of compounds of progressive complexity and probably of increasing degrees of unsaturation and polymerization, properties which must accompany dehydroxylation.

The melanoidins have a profound effect on the surface tension of the solution, causing a strong tendency to froth. In view of the fact that carbon dioxide was evolved only in the concentrated solutions of amino acid, it seems improbable that this reaction is the cause of the evolution of gas during the froth fermentation of molasses, sirups, and massecuites, as the proportion of amino acids to reducing sugars in them is much lower than that in any experiment here studied. If, however, gas is produced by any other means in such sirups, the melanoidins, by virtue of their effect on the surface tension, will be a factor contributing to the formation of froth.

There are indications that the formation of these highly colored melanoidins may be a contributing factor to the discoloration of sirups during manufacture of sugar products. Further work may reveal also that they have an effect on flavor, viscosity, filterability, turbidity, hydrolysis of sucrose, and refinability.

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THE reaction between amino acids and reducing sugars, as indicated by Browne,[2] has been considered by Lafar[3] as a possible cause of the so-called froth fermentation of molasses in the hot room, and may be considered as a contributing factor in the loss of reducing sugars shown by molasses on long standing. Although many investigators have studied this reaction, very little has been reported in regard to the amounts or proportions of the substances combining during the reaction. The present report deals with a preliminary survey of the reaction made for the purpose of determining its relationship to the spontaneous decomposition of molasses and of learning how extensive a destruction of reducing sugars may take place.

Maillard,[4] who first studied this reaction, confined his work mainly to the reaction of glycocoll, the simplest amino acid, with glucose, and reported the production of complex, highly colored "melanoidins," accompanied by a copious evolution of carbon dioxide. He stated that the other amino acids react similarly, but he gave no detailed description of the reaction when the higher amino acids were used. It is well known that the first member of any homologous series of organic compounds reacts in a manner somewhat different from the subsequent members of the series, and from new evidence, presented later in this paper, there are indications that the reaction between glycocoll and glucose differs from that between the higher amino acids and this sugar. In all his work Maillard used highly concentrated solutions—namely, 1 part of glycocoll to 4 parts of glucose in 3 to 4 parts of water. He estimated the destruction of glucose by evaporating the mixtures to dryness, and, after deducting the weight of carbon dioxide evolved, derived the weight of water lost during the reaction. This loss corresponded to 12 mols for each mol of carbon dioxide, evidence that several mols of glucose must have been involved. He made no mention of odors or aromas produced during the reaction.

Lintner,[5] who studied the reaction from the standpoint of malting, described the aromas and tastes of the resulting

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[1] Presented before the Division of Sugar Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] Paper on "The Spontaneous Decomposition of Sugar Cane Molasses" presented before the Division of Agricultural and Food Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

[3] *Oesterr.-ungar. Z. Zuckerind. Landw.*, **42**, 737 (1913).

[4] *Ann. chim.*, **5**, 258 (1916).

[5] *Z. ges. Brauw.*, **35**, 545, 554 (1912).

mixtures and reported that they were different with each amino acid used. This work was largely confirmed by Ruckdeschel[6] who studied the action on glucose of all the amino acids naturally found in malt. He noted that an excess of glucose retards the reaction and that the colored melanoidins are emulsoid colloids, which on drying lose their reversible properties, becoming insoluble, with accompanying loss of coloring power and aroma.

In 1921 Grünhut and Weber[7] reported the results of an elaborate study of this reaction, using, however, dilute solutions (0.025 *N*) of the sugars and amino acids. In these concentrations no carbon dioxide was evolved, even when the mixtures were partly distilled. They concluded that the product is a mixture of substances derived by (1) the combination of the sugar and the amino acids to produce complex amino acids, (2) a further condensation involving the amino group, (3) a loss of the carboxyl group of the amino acid by the splitting off of carbon dioxide.

During the years 1925 to 1927, various investigators, including Borsook and Wasteneys,[8] Neuberg and Kobel,[9] and Hynd,[10] reported that the reactivity and the optical activity of the sugars are, as a rule, increased by the addition of amino acids to their solutions, indicating an instantaneous combination, the extent of which is governed by the hydrogen-ion concentration of the solution. Von Euler and co-workers[11] published confirmatory evidence obtained by a study of the changes in the freezing point of sugar solutions caused by the addition of a solution of amino acid. They showed that the reaction is a combination of one mol of amino acid with one mol of sugar, probably in a glucosidic manner, which combination is increased by alkalinity and reversed or inhibited by acidity, being complete at pH 11.

Ripp[12] studied the reaction optically and chemically, using both concentrated solutions, like those of Maillard, and dilute ones, like those of Grünhut and Weber, but in both cases evaporating the solutions to dryness. He worked mainly with levulose and gave analytical results both on the course of the reaction and on the melanoidins formed. The melanoidins which he analyzed, however, were made from concentrated solutions, whereas the course of the reaction was studied with dilute solutions. There is now evidence that the course of the reaction is not the same in concentrated solutions as in dilute solution, and that the respective melanoidins are not identical.

Araboni[13] made the next and latest advance in the study of this reaction. He was interested in the aromas and investigated the volatile products formed by heating a solution or suspension of the sugar and amino acid in glycerol. He found that an aldehyde is produced and formed the hypothesis that the amino acid undergoes oxidation by the sugar, with the formation of the aldehyde of the acid containing one less carbon atom than the amino acid, the missing carbon atom having been eliminated as carbon dioxide. Thus, from alanine he obtained acetaldehyde, from phenylalanine, phenylacetaldehyde, and from leucine, isovaleraldehyde.

Experimental

The experiments here reported were carried out with two concentrations of glucose and amino acid: (1) 10 parts of glucose to 1 part of amino acid in water to make a total volume of 25 parts; (2) Maillard's concentrations,[4] that is, 4 parts of glucose to 1 part of amino acid and 4 parts of water. These concentrations are referred to as "dilute" and "concentrated," respectively. For the experiments with the dilute concentrations, a 66.67° Brix solution of glucose and a 10 per cent solution of the amino acid were made and aliquoted, so that blank experiments and comparable analyses might be made. The blank for the glucose was diluted to 25 parts by volume and heated the same length of time as the experiments. In the experiments in which Maillard's concentrations were used, the preparation of solutions was impossible, so the glucose and amino acid were weighed accurately and mixed, after which the water was added. Complete solution does not take place until the magma is heated.

In all the experiments the total time of heating was 24 hours. Two methods of heating were used: (1) The mixtures were heated over a flame to the boiling point and kept at a gentle boil; (2) the mixtures were placed in a boiling water bath.

In the experiments the following three methods of treating the volatile products were employed:

METHOD 1—The mixture was heated to boiling and then slowly steam-distilled, the volume being kept as constant as possible. The distillate was collected with an adaptor and then concentrated by slow redistillation (also with an adaptor).

METHOD 2—The mixture was heated under a reflux condenser through which a slow stream of carbon dioxide–free air was passed. The air was then passed through an absorption train for collection of aldehyde or aldehyde and carbon dioxide.

METHOD 3—The mixture was heated under a reflux condenser which was sealed from the atmosphere by a sulfuric acid trap. This method was used only once.

Carbon dioxide was determined by absorption in saturated sodium hydroxide solution in a Geisler bulb after removal of aldehyde and moisture from the gas. A calcium chloride tube was attached to this to absorb the moisture removed from the alkaline solution during the experiment. The bulb and the tube were weighed together as in determining carbon by combustion in elementary analysis.

Aldehydes were detected qualitatively with fuchsin–sulfurous acid solution. Acetaldehyde was determined by absorption in hydroxylamine hydrochloride solution and titration with alkali, according to the method given by Hoepner.[14] As a check on this method, in one experiment the aldehyde was absorbed in 0.5 *N* potassium dichromate plus sulfuric acid, and the unreduced dichromate was titrated iodimetrically. As the two methods gave similar results, the hydroxylamine hydrochloride absorbing solution was used in the rest of the experiments as being quicker and easier to handle.

Glucose was determined in the blank and in the mixtures, after clarification with neutral lead acetate and deleading with sodium sulfate, by Allihn's method. The difference between the amounts found in the blank and in the mixture represents the glucose destroyed.

Amino acids were determined by the ninhydrin method,[15] the amount destroyed being found by difference between the original solution and the mixture after heating.

As the mixtures were heated they slowly turned yellow, then brown. After about 12 hours' heating a brownish black solid began to separate, the quantity increasing with the length of time of heating. As this coloration developed in the alanine and glucose an aldehyde was liberated, which was absorbed in ice-cold water in Methods 1 and 2. In Method

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[6] *Z. ges. Brauw.*, **37**, 430, 437 (1914).

[7] *Biochem. Z.*, **121**, 109 (1921).

[8] *Biochem. J.*, **19**, 1128 (1925).

[9] *Biochem. Z.*, **162**, 498 (1925); **174**, 464 (1926); **179**, 451 (1926).

[10] *Biochem. J.*, **20**, 195, 205 (1926).

[11] *Ber.*, **59**, 1581 (1926); **60**, 992 (1927); *Z. physiol. Chem.*, **153**, 1 (1926); **155**, 259 (1926); **161**, 265 (1926).

[12] *Z. Ver. deut. Zucker-Ind.*, II, 645 (September, 1926).

[13] *Proc. Imp. Acad. (Japan)*, **3**, 672 (1927).

[14] *Z. Nahr. Genussm.*, **34**, 453 (1917).

[15] Ambler, *Intern. Sugar J.*, **29**, 382, 437 (1927).

Table I—Analysis of Products of Reaction between Alanine and Glucose

Expt.	Concn.	Method	Temp.	Alanine Used	Glucose Used	Alanine Consumed	Glucose Consumed	Carbon Dioxide	Acetaldehyde	Yield Melanoidin		Composition of Melanoidin							
												Insoluble				Soluble			
										Insoluble	Soluble	C	H	N	O	C	H	N	O
				Grams	*Grams*	*Grams*	*Grams*	*Gram*	*Gram*	%	%	%	%	%	%	%	%	%	%
1	Dilute	1	Boiling	1.00	10	0.255	1.552	....	...	4.23[a]		...	..	..	...	...	..	..	...
2	Dilute	2	Boiling	1.00	10	0.179	1.280	....	...	4.56[a]		...	..	..	...	...	..	..	...
3	Dilute	3	Boiling	1.01	10	0.331	1.468	....	...	4.87[a]		...	..	..	...	...	..	..	...
4	Dilute	2	Boiling	1.00	10	...[b]	...	....	...	5.06[c]	27.69	55.96	5.65	..	...	54.77	5.14	2.97	37.20
5	Dilute	2	Boiling	1.00	10	...[b]	...	....	...										
6	Dilute	2	Boiling	2.00	20	0.50	4.226	0.0299	0.322	61.73	80.78	59.56	5.26	3.71	31.47	56.93	4.16	2.91	36.00
7	Dilute	2	Boiling	2.00	20	0.57	4.726	0.0746	0.272	79.05	74.62	60.52	5.27	3.16	31.05	58.37	6.40	3.15	32.08
8	Dilute	1	Boiling	2.00	20	0.16	3.282	....	...	32.25	70.94	63.55	5.05	3.55	27.85	57.92	4.62	3.13	34.33
9	Dilute	2	Water bath	2.00	20	0.39	4.586	0.0000	0.087	80.4	19.11	67.80	7.06	3.91	21.23	...	..	..	...
10	Conc.	2	Water bath	2.00	8	1.12	5.080	0.1018	0.105	149.60	7.32	59.33	5.39	4.07	31.21	...	..	..	...
11[d]	Dilute	2	Boiling	1.00[e]	10	...	...	....	...	99.24	23.28	59.49	3.52	3.87	33.12	58.46	4.77	..	...

[a] Total.
[b] See text.
[c] The reaction mixtures of Nos. 4 and 5 were united for the separation of the melanoidins in order to obtain sufficient material.
[d] Products of reaction between glycocoll and glucose, heated 5$^1/_2$ hours only.
[e] Glycocoll.

3, the sulfuric acid showed marked resinification. The aldehyde solutions obtained from Methods 1 and 2 were concentrated by distillation and treated with *p*-nitrophenylhydrazine in acetic acid solution. A voluminous reddish yellow precipitate was formed, which, after crystallization from alcohol, melted at 128–129° C., indicating that the substance is acetaldehyde.[16] Quantitative results obtained by Method 2 are given in Table I.

No volatile acids were detected in the water used to absorb the soluble gaseous products.

In determining the carbon dioxide formed, the aldehyde was first absorbed in hydroxylamine hydrochloride solution, and then the gas was passed through concentrated sulfuric acid and calcium chloride to remove moisture, and finally through the weighed sodium hydroxide bulb and calcium chloride tube. All the solutions used were made with carbon dioxide-free water, and the air in the apparatus was replaced with carbon dioxide-free air before the experiment was started. After the heating had been stopped, the air current was continued for at least 2 hours, to sweep all the volatile products from the apparatus. The small quantities of carbon dioxide obtained in the first few experiments were due to small leaks in the absorption train. These were finally stopped, and the last two experiments were made with air-tight connections.

A qualitative experiment with asparagine in dilute solution showed the production of acetaldehyde. Similar experiments with glycocoll gave no indication of the formation of any aldehyde, although, if the reaction were normal, formaldehyde would be expected here.

After the reaction, the dark brown mixtures were diluted to suitable volumes, and glucose and amino acid were determined in aliquoted portions. The melanoidins were isolated from the rest of the solution by the alcohol dehydration method and analyzed.

The diluted reaction product was filtered through hardened filter paper, and the insoluble material was washed with water until the washings were colorless and free from turbidity. The residue, the "insoluble portion," was dried at 105° C. The filtrate and washings were concentrated to small volume (about 50 cc.) on the steam bath. During the concentration a further precipitation of material occurred, probably caused by a slight degree of dehydration and by a continuance of the reaction. This material, because of its scantiness, was not separated, but in further work should be investigated. The concentrated turbid filtrate was then treated with hot 95 per cent alcohol, to cause dehydration of the colloids, and filtered through hardened paper. The alcoholic filtrate was reheated and 200 cc. of hot alcohol was added to insure complete coagulation of the colloidal material. This solution was filtered hot through the same paper, and the whole was washed with hot 95 per cent alcohol. When sufficiently copious the latter precipitate should be collected separately and studied, as undoubtedly it has an elementary composition different from that of the material first precipitated from the more dilute alcohol solution. This precipitate is referred to as the "soluble portion" of the melanoidins.

After the flocculated material was completely washed, the filter paper was punctured, and the material was washed through with water. The magma so obtained was evaporated to dryness in a tared platinum dish and finally dried for 2 or 3 hours to constant weight in an electric oven at 102–105° C. After complete drying this substance is not capable of being redispersed in water.

The insoluble material is insoluble in strong alkali, even on heating. In suspension in water, or better in glacial acetic acid, it takes up bromine, indicating unsaturated carbon linkages in the molecule. The water-soluble part is partly soluble in alkali, and it also shows unsaturation toward bromine.

When there was sufficient material for the purpose, the melanoidins so isolated were subjected to elementary analysis for carbon, hydrogen, and nitrogen, the latter being determined by Clark's micro-Kjeldahl method.[17] The results are tabulated in Table I. The yields were based on the amount of amino acid taken in the experiment. A small quantity of ash (on the average, 2 mg. per 0.1 gram of sample) was found in the material. It came from the glucose used. The analytical data are calculated on ash-free organic material.

Discussion

A comparison of the data derived from Experiments 1, 2, and 3, in which the method was varied, shows that relatively smaller amounts of glucose are destroyed if the volatile aldehyde is not removed. This comparison is more easily made if the data are reduced to molecular proportions, as has been done in Table II. From this table there is little choice between the steam distillation method and the method of removing the aldehyde with a current of air. The greater destruction of alanine in Experiment 3 may be attributed to side reactions in which the amino acid is involved. Such a reaction may be that between aldehydes and amino compounds as typified by the general equation,

$$R.\mathrm{CHO} + R'.\mathrm{NH_2} = R'.\mathrm{N:CH}.R + \mathrm{H_2O}$$

The result of this side reaction would be the removal of amino acid from the sphere of activity. If the condensation products of this type were insoluble in the medium, they would be included in the "melanoidin." In this survey, no attempt

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[16] Hyde, *Ber.*, **32**, 1810 (1899).

[17] *J. Biol. Chem.*, **67**, 521 (1926).

was made to isolate these products, but that they are actually formed may safely be assumed. In Experiments 9 and 10 there is further conrfimation of this assumption. These experiments were performed by heating the reacting mixtures on the boiling water bath. The mixtures themselves did not boil. After about 12 hours' heating Mixture 10 began to swell, owing to the formation of small bubbles of gas which were unable to escape on account of the frothing of the mixture, which will be discussed later in the paper. Because of these occluded bubbles the quantities of the volatile products determined were low. The aldehyde in the bubbles was retained within the sphere of activity of the amino acid. As one would expect from Araboni's hypothesis,[13] the simplest type of the reaction seems to be indicated when the molecular proportions of aldehyde produced and amino acid consumed are 1:1, as in Experiments 6 and 7. That there is actually a different course to the reaction if the aldehyde is not removed is further indicated by the different compositions of the melanoidins in the experiments under consideration. In Experiment 9 only a slight swelling was caused by unbroken bubbles, but the aldehyde occluded in this way was sufficient in quantity to affect the molecular ratios, the composition of the melanoidins, and the yield obtained.

Table II—Molecular Proportions of Reacting Substances and Products of the Reaction between Alanine and Glucose

EXPERIMENT	GLUCOSE	ALANINE	ALDEHYDE	CARBON DIOXIDE
1	3.0	1	...	...
2	3.5	1	...	...
3	2.0	1	...	...
6	4.2	1	1.3	0.0
7	4.1	1	1.0	0.0
8	10.1	1	...	...
9	5.8	1	0.5	0.0
10	2.2	1	0.2	0.2

Carbon dioxide seems to be produced only with the more concentrated solutions. When produced, it is formed in equimolecular proportions with the aldehyde. It would be interesting to study the reaction with the concentrated solutions when the mixture is boiled. The absence of the formation of carbon dioxide from the dilute solutions confirms Grünhut and Weber's findings.[7] Because of the probable occurrence of the side reaction discussed in the preceding paragraph, it is impossible from the work so far done to estimate from the analytical data the effect of retention of the elements of the carboxyl group on the resulting melanoidins. Both phenomena probably contribute to the varying composition of these bodies.

The greater velocity of the reaction in concentrated solutions is indicated by the larger yield of melanoidin, especially the insoluble part, in Experiment 10. This confirms Ruckdeschel's statement that excess of glucose retards the reaction.[6]

The abnormally high molecular consumption of glucose in Experiment 8 is possibly explained by the fact that during this reaction a relatively large amount of steam condensed in the reaction mixture, thus making the mixture more dilute. That this experiment was otherwise abnormal is shown by the small yield and high carbon content of insoluble melanoidin. These observations warrant the assumption that in more dilute solutions there may be a greater consumption of reducing sugar per mol of amino acid than in concentrated solutions. The correctness of this can be determined only by further work along this line.

The fact that acetaldehyde is also produced when asparagine is allowed to act on glucose is in line with Araboni's rule,[13] by which one would expect the formation of the half aldehyde of malonic acid, $CHO.CH_2.COOH$. But this compound is known to be unstable, decomposing into carbon dioxide and acetaldehyde, especially under the influence of heat.[18] In this case quantitative work should reveal the fact that molecularly equivalent quantities of carbon dioxide and acetaldehyde are formed from dilute solutions, whereas from concentrated solutions there should be obtained 2 mols of carbon dioxide to 1 mol of aldehyde.

That formaldehyde is not evolved when glycocoll acts on glucose can no doubt be explained by the fact that formaldehyde condenses rapidly and completely with amino compounds, a reaction which is advantageously used in the so-called formol titration method of determining amino acids.[19] The effect of concentration of the glycocoll should be studied to determine the conditions of carbon dioxide formation by this acid.

The data on the carbon and hydrogen contents of the melanoidins agree roughly with those given by Ripp.[12] The nitrogen contents found here, however, are much lower than those he found. The higher carbon content of the insoluble part is noteworthy as indicating a progressive dehydroxylation of the sugar. More extensive fractionation of the melanoidins should show that the more soluble parts have a still lower carbon content than any reported here. Because of the unquestioned nonhomogeneous character of these bodies, any attempt to derive molecular formulas for them is at present useless.

The melanoidins have a profound effect on the surface tension of the solution. In Experiments 4 and 5 this effect caused the loss of the quantitative determinations of the products of the reaction. In every experiment there was a tendency to froth after heating a short time, which increased with the length of time of heating. In Experiments 4 and 5 the air current used to sweep away the volatile products was introduced through a tube which extended just below the surface of the solution. After the mixtures had been heated 24 hours, and the heat had been turned off, the current of air was left on as usual. But as the mixtures cooled frothing began and became more extensive with the cooling, finally causing the mixtures to froth over, through the length of the upright condenser, into the hydroxylamine solution, which itself in turn frothed over into the sulfuric acid drying bulb. This frothing was not caused by a liberation of gas from the mixture, but by the bubbles of air introduced below the surface of the solution. By raising the tube above the surface, extensive frothing of this kind was easily stopped, and in all the other experiments the apparatus was so arranged that the air swept over the surface instead of through the solution, and no extensive foaming was noticed.

At present there is no explanation, except catalysis, for the fact that the yields of melanoidin were so greatly increased when the amount of each of the reacting materials was doubled. It was expected that the relative yields would be the same as with the smaller quantities, but in every case the yields were increased from three to five times, and the quantity of glucose consumed was more than doubled, as shown in Table I. The molecular ratios of glucose and alanine consumed were increased in the same way, as shown in Table II. In future investigations of this problem, these peculiar results should be borne in mind.

Acknowledgment

Thanks and appreciation are extended to M. S. Badollet, of the Carbohydrate Division, for conducting the experimental work on the reaction mixtures and the melanoidins.

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[18] Wohl and Emmerich, *Ber.*, **33**, 2763 (1900).

[19] Sorensen, *Biochem. Z.*, **7**, 45 (1907).

Domestic Chemical Trade Service Expanded—Organization of a new phase of activity to supply a more intensive domestic commerce service has been brought about within the Chemical Division of the Department of Commerce.

The System Ferrous Oxide–Silica[1,2]

C. H. Herty, Jr., and G. R. Fitterer

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

A comprehensive survey of all previous work on the system $FeO-SiO_2$ has been given and compared with the present work.

The methods used in the preparation of the ferrous silicates, the microanalyses, and the determinations of melting points are different from those used in any previous investigation on this system.

A complete equilibrium diagram has been constructed and represented in a three-dimensional figure by plotting composition against temperature against heat content.

In a study of the deoxidation of steel with silicon it is necessary to have data on certain equilibria between silicon and iron oxide and various ferrous silicates and to know the physical properties of various types of slags composed of ferrous oxide and silica. Silicon is used in many types of steel as a deoxidizer during the process. Ferrous oxide is dissolved in the steel during steel-making, and when silicon is added for deoxidation insoluble silicates are formed which must be eliminated from the steel if high-grade material is desired. (Wrought iron is, of course, an exception; ferrous silicate slag is intentionally trapped in the metal.) If enough silicon is added to the steel for essentially complete deoxidation, SiO_2 will be the product of the reaction according to the equation

$$Si + 2FeO \longrightarrow SiO_2 + 2Fe$$

However, there is always some FeO left dissolved in the steel. This sets up an equilibrium with silica particles and some FeO is dissolved into the particles. With varying additions of silicon, various types of silicate inclusions would therefore be expected to exist in the steel. The physical characteristics of these inclusions may be determined by a combined study of the system $FeO-SiO_2$ and of the characteristics of small particles suspended in a liquid-medium—in this case, ferrous silicate suspended in steel.

This paper presents the results of a study of the equilibrium diagram of the system $FeO-SiO_2$, wherein the melting points of slags low in silica have been dealt with.

Properties of Ferrous Oxide

Melting Point—The melting point of ferrous oxide was determined by Oberhoffer[3] to be 1377° C. by extrapolation from cooling curves of samples prepared by fusing mixtures of FeO and SiO_2. Tritton and Hanson[4] also obtained cooling curves of metallic iron containing considerable FeO. Aside from the usual transformation of iron, they also found by this method that a decided deflection of the cooling curve appeared at 1370° C.; this they decided was the melting point of ferrous oxide. Prior to the work of these two groups of investigators the melting point of ferrous oxide was generally accepted as being 1420° C., the value in the International Critical Tables.[5]

Density and Atomic Arrangement—The density of ferrous oxide was determined as being 5.99 by Wyckoff and Crittenden[6] through an x-ray study of FeO prepared by saturating magnetite with iron. They concluded that FeO has the NaCl arrangement of 4 molecules in a unit cube having a side length of 4.294 Ångström units. The density of such a cube is 5.99. However, they also show the possibility that the FeO unit cell contains either 3 or 5 molecules with densities of 4.49 and 7.48, respectively.

Properties of Silica

The properties of silica have been studied at length by Sosman,[7] and no better authority on this material is to be found.

Melting Point—The melting point of silica is given as 1710° C., and is described as the melting point of cristobalite, which is the stable form of silica between 1470° and 1710° C. However, consideration must be given to the form of silica present in any sample before accurate explanations of certain peculiar phenomena occurring in silica systems are possible.

Forms of Silica—Silica has so many forms and types of transformation from one form to another that too much time cannot be spent in a study of it. This fact, however, has been discussed at length by Sosman. He shows how the various high-temperature forms of silica greatly affect a silica-containing system, because of the sluggish inversions of one form into another, and how for this reason unstable forms are nearly always present. Many times the types of silica expected and desired are not present and have not been formed because of a sluggish transformation.

Properties of Iron Silicates

Mellor[8] discusses at great length most of the previous work done on the various iron silicates. For example, mineralogists have found two definite compounds of FeO and SiO_2. The first, having the composition $2FeO \cdot SiO_2$, was found in volcanic rocks by Gmelin,[9] who called it fayalite.

Crystals of fayalite (or ferrous orthosilicate) were prepared by Gorgen, who heated a mixture of ferrous chloride and silica in a current of hydrogen charged with steam. The crystals belong to the rhombic system, and the color is said to vary from dark yellow or brown to black.

The melting point of fayalite was shown by Whiteley and Hallimond[8] to be approximately 1350° C. These investigators studied the formation of iron silicates in the slags from acid open-hearth steel furnaces, and constructed a probable equilibrium curve for the freezing points of binary mixtures of FeO and SiO_2.

No evidence has been found of the ferrous metasilicate, $FeSiO_3$, existing in any but natural rocks. This material was termed grunerite by Kenngot, as it was originally discovered by Gruner.[10]

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[1] Received August 31, 1928.

[2] Published by permission of the Director, U. S. Bureau of Mines; the Carnegie Institute of Technology; and the Metallurgical Advisory Board.

[3] Oberhoffer and Groebler, *Stahl. u. Eisen*, **47**, 1984 (1927).

[4] *J. Iron Steel Inst.*, **110**, 90 (1924).

[5] "International Critical Tables," vol. I, p. 128.

[6] *J. Am. Chem. Soc.*, **47**, 2876 (1925).

[7] "The Properties of Silica," p. 60, Chemical Catalog Company.

[8] "Inorganic and Theoretical Chemistry," vol. VI, p. 905.

[9] *Pogg. Ann.*, **51**, 160 (1840).

[10] *Compt. rend.*, **24**, 794 (1847).

Melting Points Recorded by Previous Workers

Phase equilibrium in the ferrous oxide–silica system has been considered by two main groups of workers—Greig[11] and Whitely and Hallimond.[12]

Greig studied the system from the standpoint of immiscibility of the silicate melts at high temperatures, dealing with high-silica silicates. His work determined the presence of two immiscible liquids—A, which was rich in silica, and B, which was rich in ferrous oxide. The immiscibility of B in A was determined at about 4 to 5 per cent ferrous oxide, and the immiscibility of A in B was placed tentatively between 38.5 and 40 per cent ferrous oxide, at 1700° C. The melts studied were formed by heating silica with ferrous oxalate or, in some cases, with ferric oxide. With the oxalate, decomposition at high temperatures caused the formation of FeO, whereas reduction was necessary in the case of Fe_2O_3. The determination of immiscibility was effected by micro-examination of samples quenched at 1700° C.

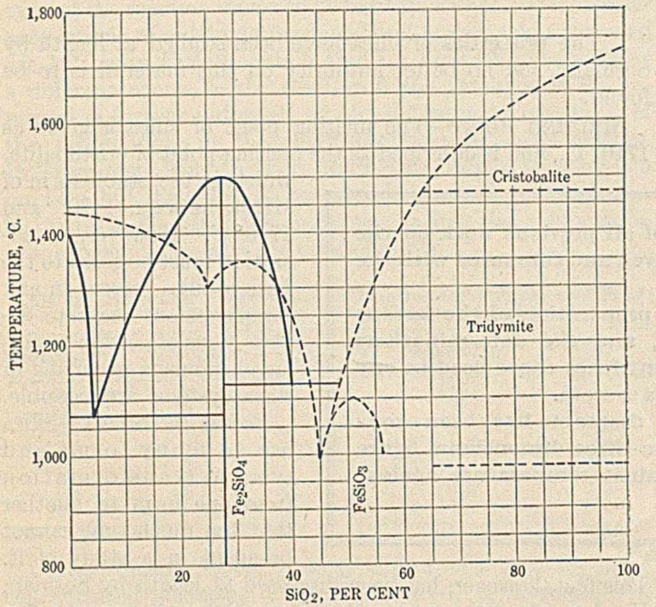

Figure 1—Freezing Points of Mixtures of Ferrous Oxide and Silica

Greig's samples contained Fe_2O_3 and belonged to the ternary system $FeO–Fe_2O_3–SiO_2$. But he realized this and extrapolated his values down to deal with binary melts. For this reason his work is relatively accurate.

Whiteley and Hallimond also studied silicate melts microscopically, but they dealt with ferrous oxide–rich materials. Their samples were acid open-hearth slags containing FeO, MnO, and SiO_2, which were relatively free from CaO and MgO. It may be stated at the outset that some erroneous results might be expected from their work, because they were unable to obtain samples free from MnO. A number of their samples contained as much as 8 to 10 per cent of this impurity. For this reason their slags were really in the three-component system, $FeO–MnO–SiO_2$, and most of the melting points determined by them should be considered in that system. These investigators accepted the then known melting point of FeO as being 1420° C., and indicated the presence of the compound fayalite ($2FeO–SiO_2$) and two eutectics, one on either side of the compound. Their phase equilibrium diagram, shown in Figure 1 (dotted lines), was drawn accordingly. The ferrous oxide–rich eutectic was indicated at 23 per cent SiO_2 and the eutectic temperature was 1300° C., whereas fayalite was shown to melt at 1350° C. and to have a composition of 29.45 per cent SiO_2 and 70.55 per cent FeO. The silica-rich eutectic (40 per cent SiO_2) was shown to have a very low melting point, 995° C., and no evidence was found to substantiate the possibility that the compound grunerite ($FeO–SiO_2$) might be in the system at 45.6 per cent silica, although the investigators indicated its presence in the diagram.

Von Keil and Dammann[13] also studied the characteristics of this phase diagram by melting mixtures of FeO and SiO_2 and obtaining the cooling curve of each. The FeO used in all melts contained about 7 per cent Fe_2O_3, and consequently their results actually represent the ternary system, $FeO–Fe_2O_3–SiO_2$. The diagram constructed from their work, shown in Figure 1 (in heavy lines), as admitted by them, is not very plausible.

Experimental Procedure

The work now under consideration was made possible by studying synthetic ferrous silicate slags prepared in various ways.

At the beginning of the investigation silicates were prepared by melting SiO_2 and Fe_2O_3 mixtures in graphite crucibles placed in a resistor-type furnace. The reduction of Fe_2O_3 to FeO was effected by the graphite crucible and any CO gas formed. The temperature reached was approximately 1600° C., which corresponds to the operating temperature of the basic open-hearth furnace. The resulting samples represented 10 per cent variations in composition, beginning with 100 per cent SiO_2 and ending with 100 per cent FeO. The ferrous oxide–rich melts were found to contain a considerable amount of Fe_2O_3 and were therefore reduced to very low Fe_2O_3 content by reheating in graphite crucibles placed in a high-frequency induction furnace. From this point on it was decided that it was better to over-reduce the Fe_2O_3, forming Fe and even Fe_3C, both of which would form large globules and are more easily separated from the FeO than are the higher oxides of iron.

The reduction and melting in the induction furnace were so successful that a number of samples were prepared by this type of melting and reduction.

Some slags were also obtained by associates studying the solubility of FeO in iron melted under a slag composed of FeO and SiO_2. These melts were made in a silica crucible placed in an induction furnace, and their Fe_2O_3 content was higher than those of melts prepared in a reducing atmosphere. They averaged about 3 per cent Fe_2O_3.

The analyses and methods of preparation, together with the melting and softening points of all these samples, are given in Table I.

Determination of Melting Points in the System $FeO–SiO_2$

One of the best known methods of studying mixtures of two or more components so as to understand their relations is to determine their melting points. With such data it is possible to predict the liquid conditions of any type of ferrous-silicate produced by a certain degree of deoxidation, and thereby to determine whether or not that type of inclusion will coalesce rapidly and form large particles. This would indirectly determine the rate of elimination of inclusions from an open-hearth furnace or from the ladle. Much information is also made available regarding the condition of the inclusion during hot-working. If the inclusion were liquid at the working temperature it would not resist deformation of the steel, but if it were solid forging or rolling of the steel would be difficult, provided enough inclusions were present.

Undoubtedly, then, these and many other advantages are to be gained by the determination of an accurate phase

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[11] *Am. J. Sci.*, **13**, 133 (1927).

[12] *J. Iron Steel Inst.*, **99**, 199 (1919).

[13] *Stahl. Eisen*, **45**, 890 (1925).

equilibrium diagram, and for this reason melting points were sought for all the samples of ferrous silicate slags on hand.

Table I—Synthetic Ferrous Silicate Slags

Method of Preparation and Sample No.	Analysis SiO_2	Analysis FeO	Analysis Fe_2O_3	Softening Point	Melting Point
	Per cent	*Per cent*	*Per cent*	° *C.*	° *C.*
Resistor furnace:					
A-1	0.24	82.9	19.35	..	..
A-2	9.04	73.5	18.65	..	..
A-3	17.24	56.5	27.20	..	1310
A-4	25.68	54.7	9.98	..	1345
A-5	40.32	47.8	1.44	..	1290
A-6	52.50	48.8	0.00	..	1400
A-7	65.82	32.4	0.00	..	[a]
A-8	77.32	22.4	0.00	..	[a]
A-9	83.88	13.5	0.00	..	[a]
A-10	92.08	5.8	0.00	..	[a]
A-1R[b]	1.10	98.9	...	1230	1355
Resistor and induction:					
A-2R[b]	11.90	88.1	...	1260	1345
A-3R[b]	22.10	77.9	...	1230	1264
A-4R[b]	33.40	66.6	...	1260	1300
Induction:					
A-20	27.55	73.0	...	1208	1330
A-21	24.26	73.5	...	1208	1310
A-22	50.34	46.8	...	..	1395
A-23	48.90	46.2	...	..	1380
A-24	32.29	66.1	...	..	1320
M-2	39.30	57.4	4.03	1240	1340
Silicate slag over liquid iron:					
M-3	40.30	56.7	2.9	..	1310
M-5	40.40	56.8	2.85	..	1310
N-2	48.90	..	...	1270	1375

[a] Above range of pyrometer.

[b] First analyzed, after which the globules of Fe and Fe_3C were removed magnetically. The analyses have been corrected for this and the melting points were made with the purified samples.

Use of Micropyrometer for Melting-Point Determinations

A Burgess micropyrometer[14] was constructed and calibrated over a wide temperature range. The samples in Table I were then melted in a nitrogen atmosphere, and each softening and melting temperature was recorded. Excellent checks were made in these determinations, and the temperatures were correlated with the compositions so as to represent an equilibrium diagram (Figure 2) which is somewhat different from that of Whiteley and Hallimond (Figure 1).

Melting Point of Ferrous Oxide

The melting point of ferrous oxide was determined by the fusion of samples A-1R (Table I). This sample contained 98.9 per cent FeO and melted at 1355° C. The melting point of FeO, then, is very close to 1355° C. With this value and the temperature of 1377° and 1370° C. determined by Oberhoffer and by Tritton and Hanson, it is safe to say that the melting point of pure FeO lies somewhere between 1355° and 1377° C., rather than at 1420° C., the value formerly accepted.

It is also possible that there was less tendency for temperature lag in the Burgess type of melting-point determination than in the methods employed by either Oberhoffer or Tritton and Hanson. Moreover, there is the presence of Fe_2O_3 in Oberhoffer's samples, which would tend to raise the melting temperature, whereas in Tritton and Hanson's determination there is a possibility that the point measured was the melting point of some solution, such as iron in FeO or FeO in iron. The elimination of all of these conditions would tend to bring the temperature nearer the 1355° C. point just determined. At any rate, the temperature range is narrowed, so that the accuracy would be little affected if either the higher or lower values were accepted.

Melting Points of the Ferrous Silicates

If we now consider samples containing more and more silica, several interesting changes in the melting points throughout the system may be noticed.

With 11.9 per cent silica (sample A-2R) the liquidus drops below that of the previous sample or to a temperature of 1345° C. Likewise, with 22 per cent silica (sample A-3R) the melting point was dropped to 1264° C. However, with a sample containing 24 per cent silica (sample A-21) the melting point has been raised to 1310° C. This is immediately followed by a continued rise in sample A-20, which contained 27.5 per cent silica and melted at 1330° C.

At this time it should be pointed out that all of the samples had approximately the same softening temperature, 1240° C., and a reconsideration of these melting and softening points indicates the presence of one eutectic between the compositions of 0 and 29.45 per cent silica.

Various publications of Whitely and Hallimond's diagram differ somewhat in these softening temperatures. For example, the *Journal of the British Iron and Steel Institute*[12] shows a softening point of 1240° C., whereas Mellor[5] shows 1300° C. for samples containing up to 29.45 per cent SiO_2. Although there is some discrepancy in these two publications, our work agrees as to the type of curve given by them for this part of the diagram.

The softening and melting points of silicates containing more than 29.45 per cent SiO_2 were also determined. Two samples (A-4R and A-24) having 32.4 and 32.29 per cent SiO_2, were found to melt at 1300° and 1315° C., respectively, and to soften at 1260° C.

The samples next considered, those containing approximately 40 per cent SiO_2, should have an eutectic composition

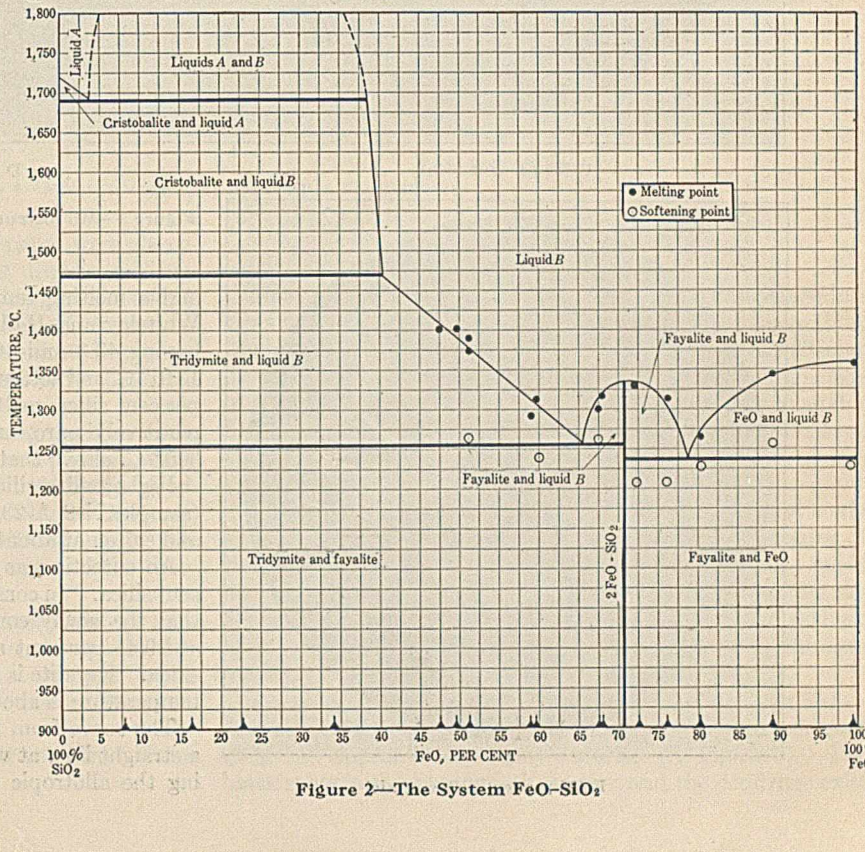

Figure 2—The System FeO–SiO_2

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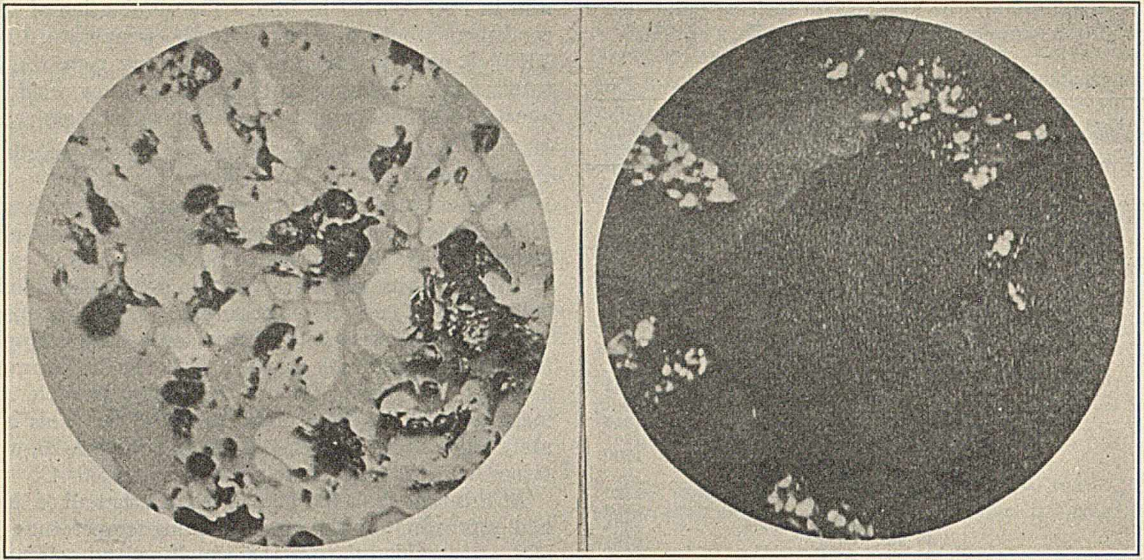
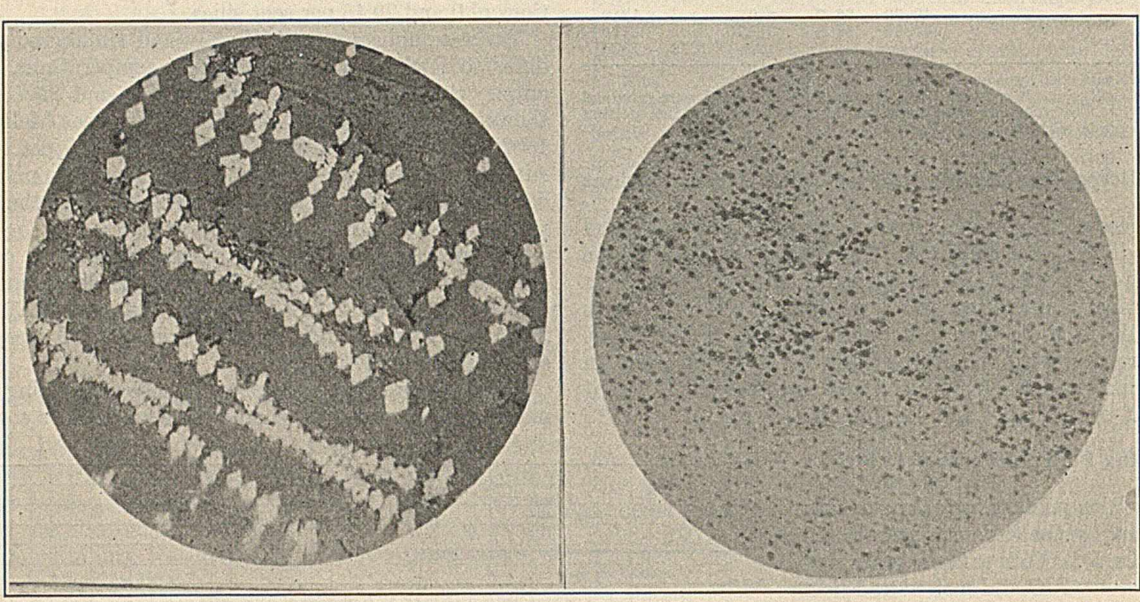
[14] Burgess, Bur. Standards, *Bull.* **3**, 345 (1907); Fieldner, Selvig, and Parker, Ind. Eng. Chem., **14**, 695 (1922).



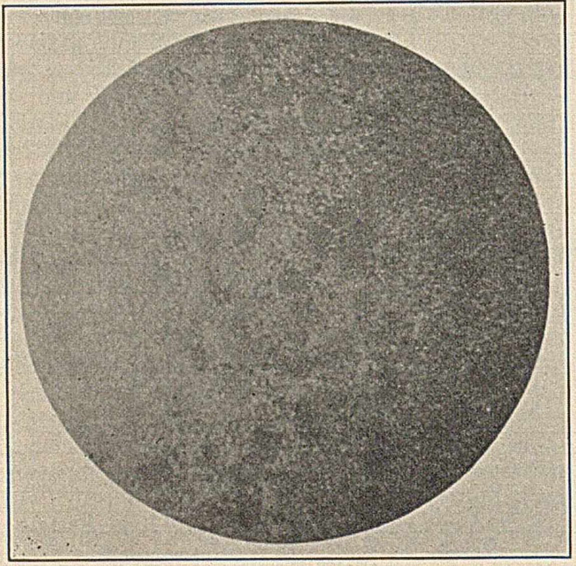
A (10 per cent SiO_2)

B (22 per cent SiO_2 eutectic)



C (25 per cent SiO_2)

D (40 per cent SiO_2)



E (35 per cent SiO_2 eutectic)

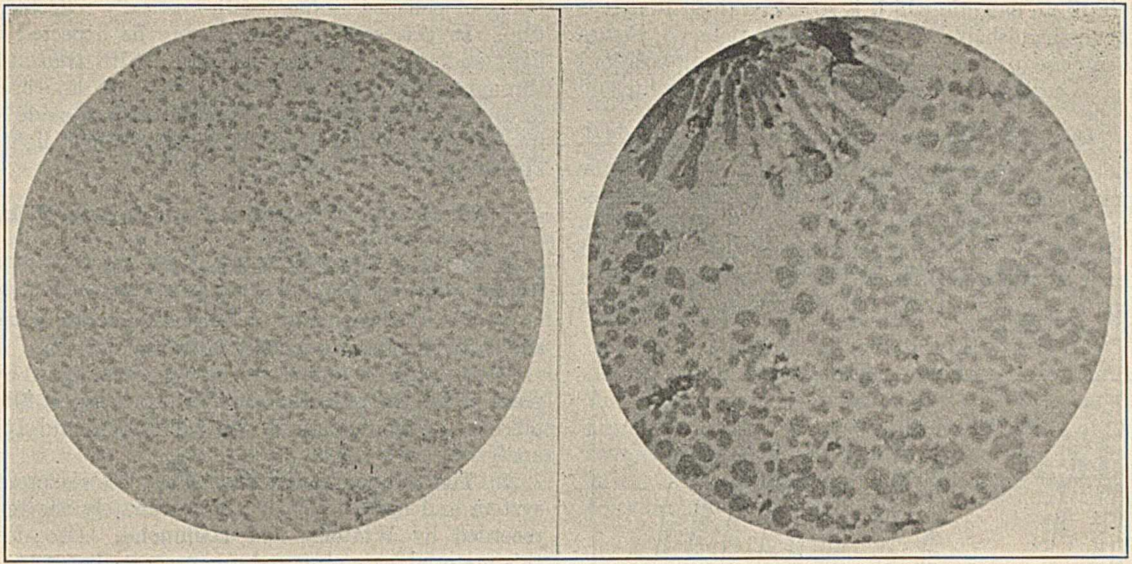
Figure 3—Microstructures of High FeO Ferrosilicates. 300 ×

and a melting temperature of about 995° C., according to Whiteley and Hallimond. However, samples M-3 and M-5, having 40.3 and 40.4 per cent silica, were found to melt at 1310° C. and soften at 1240° C; also sample A-5, having 40.32 per cent silica, melted at 1290° C. These samples were comparatively pure, and their melting points are shown to be 300° C. above that recorded by Whiteley and Hallimond.

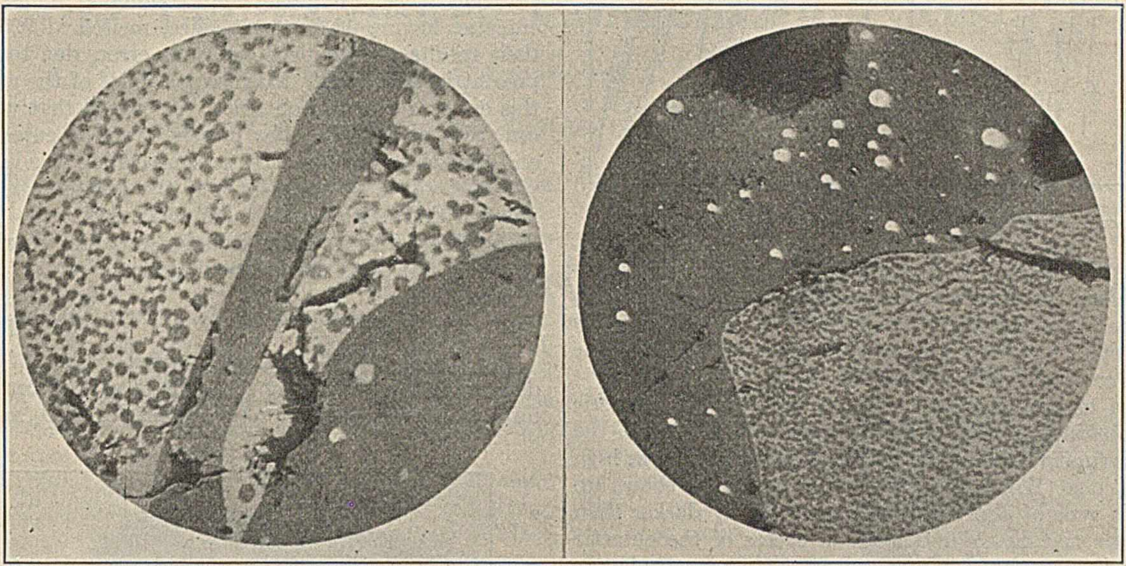
Higher silica silicates, ranging from 48 to 55 per cent silica (samples N-2, A-23, A-22, and A-6), melt at 1375° to 1400° C., and soften at about 1260° C.

An eutectic was previously shown to be present at 22 per cent silica. In considering the points just discussed it is found that the newly constructed curve (Figure 2) shows fayalite at 29.45 per cent silica and another eutectic at 35 per cent silica. Fayalite is found to melt at 1335° C., and the eutectic temperature is about 1260° C.

The curve from this eutectic to 60 per cent silica is nearly a straight line, at which point it intersects the line representing the allotropic transformation of silica from cristobalite



A (52 per cent SiO_2) B (66 per cent SiO_2)



C (77 per cent SiO_2) D (83 per cent SiO_2)

Figure 4—Microstructures of High-Silica Ferrosilicates

to tridymite. Although the samples as prepared were glassy (amorphous), the extremely small samples used in melting determinations evidently went through the changes from tridymite to cristobalite upon heating, thus causing a distortion of the diagram. According to Mellor,[8] this effect has been found in other silica systems, resulting in similarly distorted diagrams at this point.

The remainder of the system is that of Greig,[11] whose work on the high silica end of the diagram was accepted as being correct and combines nicely with our work. Although good samples in this range of composition were obtained, no attempt was made to check Greig's work, both because of the difficulty of working at such high temperatures and the time available.

Aside from the tridymite-cristobalite transformation and its effect upon the equilibrium diagram, no changes in the solid state were considered. For example, it was not determined whether or not there were eutectoid transformations at the eutectic compositions.

The entire equilibrium diagram as reconstructed from these determinations is shown in Figure 2.

Microstructure of the Iron Silicates

Most of the samples used in the melting-point determinations were prepared and examined by methods similar to those used on steel samples. This involved the use of reflected light instead of the transmitted light used in the examination of thin sections. Time and equipment were not available for this latter type of observation. However, it is believed that sufficient data were obtained for the purposes of this investigation.

Few of the allotropic transformations of silica, if any, could be expected to have taken place in these samples because of the sluggish inversions in such silica systems and the rapid cooling rate employed. However, enough characteristics are available to determine their relative positions in the system. This will then serve as a structural check upon the equilibrium diagram just constructed from melting-point data.

FERROUS SILICATE CONTAINING ABOUT 10 PER CENT SiO_2—In samples of ferrous silicate containing about 10 per cent SiO_2, FeO appears as light gray dendrites (A, Figure 3). The black spots in this photograph are pits, and the dendrites exist in a matrix of an eutectic which is so fine-grained that it is just barely distinguishable at 1000 magnifications (B, Figure 3). This eutectic (or eutectoid having the same composition) was judged to consist of alternate laminations of fayalite and ferrous oxide.

FERROUS SILICATES CONTAINING ABOUT 24 PER CENT SiO_2—Ferrous silicates containing about 24 per cent SiO_2 have the microstructure shown in C, Figure 3, and contain dendrites which are probably the compound fayalite ($2FeO.SiO_2$). This sample appears on the opposite side of the 22 per cent silica eutectic from the position of the last sample (having a 10 per cent SiO_2 composition), but the matrix is the same eutectic in both samples.

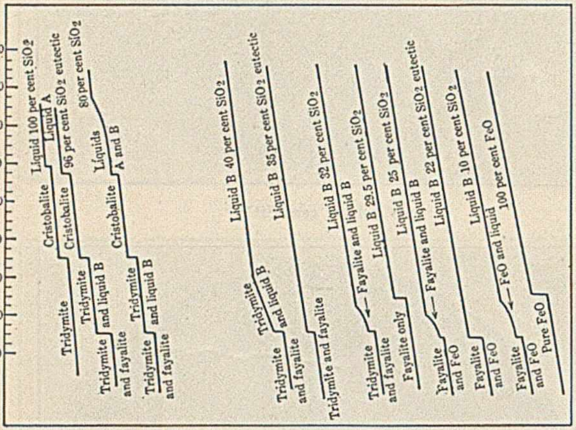


Figure 5—Probable Cooling Curves in System FeO–SiO_2

FERROUS SILICATES CONTAINING ABOUT 40 PER CENT SiO_2—The structure of ferrous silicates containing 40 per cent SiO_2 (D, Figure 3) has changed to consist of numerous dark round dots (or spheres) embedded in a matrix of a new eutectic judged to consist of silica and fayalite.

An idea of the appearance of the silica-fayalite eutectic may be obtained by studying E, Figure 3. Here again the eutectic is fine-grained and can be distinguished only at high magnifications (1000 ×). Pure silica in excess shows up under this type of illumination as spots faintly darker than the eutectic matrix. The spheres in excess of the eutectic were found to consist of silica as vitreous glass (amorphous). This was determined by the fact that they showed no "birefringence" or double refraction when studied under a petrographic microscope. Although these samples were slowly cooled, relative to metallic solidification, their cooling rates were not slow enough to cause the transformations from liquid glass to cristobalite to tridymite and then to quartz. Such allotropic transformations would require many hours of heating at the various inversion temperatures, so that the ferrous silicates, either as inclusions in steel or as the synthetic melts, can be expected to contain only the amorphous type of pure silica phase.

FERROUS SILICATES CONTAINING MORE THAN 40 PER CENT SiO_2—As we progressively increase from 52, 66, 67, and 83 per cent silica (A, B, C, D, Figure 4) it is evident that a gradual increase in the amount of excess silica occurs, as would be expected from the standpoint of the newly constructed equilibrium diagram (Figure 2). A large excess of pure silica is shown as the dark constituent in C and D, Figure 4.

The series of photomicrographs in Figure 4 shows the typical structural changes, with gradual change in composition throughout the system. It must be kept in mind during the study of these photographs whether the particular material in question will absorb or reflect light. The pictures were taken of polished surfaces with vertically reflected illumination. In this case pure silica may be expected to absorb light and appear as dark spheres. With transmitted light through a thin section of this material the same spots would, of course, be transparent. Likewise ferrous oxide and fayalite, having very low absorption, reflect direct light rays and appear as white or gray areas.

Summary of Properties of the Ferrous Silicates

In regard to the melting point and microstructure of the ferrous silicates, the following conclusions may be drawn:

(1) The melting point of ferrous oxide lies between 1355° and 1377° C., but is probably nearer to 1355° C.

(2) At 22 per cent silica an eutectic is indicated by melting-point data, the eutectic temperature being 1240° C. The presence of the eutectic is also definitely found upon microanalysis.

(3) The compound fayalite ($2FeO.SiO_2$) is present in the system and melts at 1335°, approximately the temperature recorded by Whiteley and Hallimond. Also dendrites of this material were observed microscopically.

(4) A second eutectic, melting at 1260° C., is found at 35 per cent silica. Whiteley and Hallimond found that this eutectic, having 40 per cent silica, melted at 995° C., but their results are unquestionably in error, due to the MnO present in thin slags. Microscopic proof of the existence of this eutectic was also obtained; it showed that with 40 per cent SiO_2 excess silica was present over the eutectic matrix and that therefore the eutectic composition was less than 40 per cent silica. This point was the greatest disagreement found with Whiteley and Hallimond's work.

(5) The transformation from cristobalite to tridymite is found to noticeably distort the diagram.

Heat Content in the System FeO–SiO_2

The usual two-dimensional representation of a binary diagram is far from being sufficient to explain certain transformations occurring within the system FeO–SiO_2, and a clearer picture is highly desirable. It is possible to express the diagram just constructed to a little better advantage by means of a method described by Tammann.[15] He suggests a three-dimensional diagram for the representation of a binary system, and constructs such a diagram by plotting composition against temperature against heat content. Although actual losses of heat content are not known, their relative positions can be determined and clearly represented.

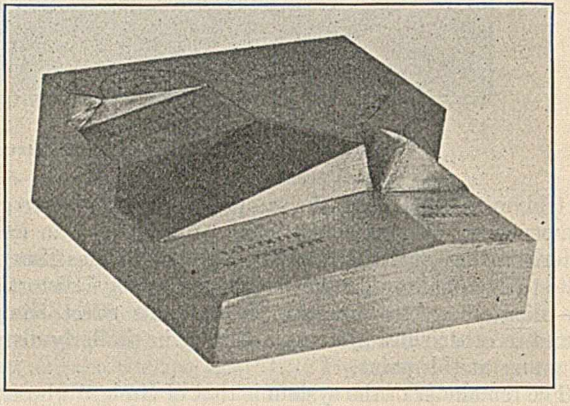


Figure 6—Solid Representation of System FeO–SiO_2. Heat Content–Temperature–Composition

In other words, if actual cooling curves had been obtained

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[15] "A Textbook of Metallography," p. 149.

and used in the construction of this diagram, they would probably appear as those in Figure 5 and would depict a solid representation, such as is shown in Figure 6. Only latent heats of transformation are represented by this solid figure, and, if changes of heat content in the various stable states were shown, the diagram would become very complicated.

A model of the type shown in Figure 6 aids the interpretation of the system in a clear-cut manner. For example, pure silica would cool from the liquid to the solid state (as cristobalite) at 1710° C., with a loss of heat as shown by a drop to a lower plane in the solid figure. The cristobalite so formed loses some heat down to 1470° C., where the change from cristobalite to tridymite is shown as a drop to a still lower level of heat content; another drop, which is not shown here, would occur at the transformation of tridymite into quartz. The high and low forms of these various stable types of silica as discussed by Sosman would make this side of the solid figure extremely complex.

Pure fayalite and ferrous oxide would drop directly from high to low levels of heat content upon solidification. Intermediate compositions would drop to lower levels in various manners. Also, solid fayalite would have a higher heat content than either pure solid silica or ferrous oxide, and it is thus shown.

The diagram, the probable cooling curves, and the solid representation have all been constructed under the assumption that the most stable phases of silica exist at their various temperatures. Equilibrium cannot be otherwise expressed.

With pure silica, cristobalite is shown to exist between 1710° and 1470° C., where the transformation to tridymite occurs, and tridymite is the stable phase from 1470° to 870° C. At 870° C. tridymite changes to the quartz phase, which is the stable form at room temperature. These transformations are only possible through prolonged heating at the various temperatures, and, although they probably do not all occur in the ferrous silicates under discussion, they do represent equilibrium.

A Light-Colored Condensation Resin[1]

H. A. Gardner, C. A. Knauss, and A. W. Van Heuckeroth

Gardner Laboratory, Institute of Paint and Varnish Research, Washington, D. C.

During the last few months several new synthetic resins of the "phthalic" type have made their appearance. According to some of the patent claims, these resins are produced by the condensation of molecular proportions of glycerol and phthalic anhydride, together with certain organic acids, such as butyric, succinic, malic, citric, fumaric, oleic, linseed, and tung oil acids, or with castor oil. We have prepared resins in which the glycerol has been replaced by another polyhydric alcohol. Such alcohol has been condensed with phthalic anhydride and aliphatic hydroxy mono- and dibasic acids.

By the elimination of two molecules of water from three molecules of glycol, a polyglycol, known as triethylene glycol, is formed. This compound, which has the formula $HOCH^2—CH^2—O—CH^2—CH^2—O-CH^2—CH^2OH$, has a boiling point of 278° C. It apparently possesses several desirable properties for a resin base. It has two hydroxyl groups with a long chain separating them so that if formed into a resin it should possess good plasticity. It also has a comparatively high boiling point, so that the reaction of formation may take place at a relatively high temperature without danger of loss by evaporation.

Triethylene glycol prepared as above was heated with phthalic anhydride and tartaric acid. A soft liquid resin was produced. Combining this with cellulose ester gave a lacquer which formed durable films without any added plasticizer. Apparently resinous products of the type produced by these reactions act as both resins and plasticizers when used in cellulose ester lacquers.

Method of Preparation

One mol (148 grams) of phthalic anhydride and one mol (150 grams) of triethylene glycol were heated together at 110° C. for a half hour. The temperature was gradually raised to 175–180° C. and held until evolution of gases had ceased. Then the temperature was raised to 200–210° C., and 1 mol (140 grams) of tartaric acid was added. A temperature of 185–200° C. was maintained for several hours. If the resin is allowed to cool after heating for about 3 hours, it is of a pale amber color and is in the form of a viscous solution soluble in acetone, alcohol, and chloroform, but insoluble in toluol. It is quite compatible with nitrocellulose solutions.

If the heating is continued for 15 to 18 hours, a dark amber plastic mass is produced, which is incompatible with nitrocellulose solutions but compatible with cellulose acetate solutions. During this continued heating the acid number is not materially decreased, so that the change must be one of polymerization rather than of condensation.

These resins will not form solids either by baking for several hours or by heating under pressure. Apparently they are true liquid resins.

It will be noted that the resin may be produced in a form that is compatible with cellulose acetate or in a form that is compatible with nitrocellulose. As very few resins are compatible with cellulose acetate, this resin might prove especially desirable for use in cellulose acetate lacquers. In an exposure test on nitrocellulose or cellulose acetate, lacquers containing as high as equal parts of the resin to the cellulose ester used were exposed upon iron panels for several weeks with fairly satisfactory results.

Figure 1—Illustration of Clarity of a Light-Colored Resin

Printing upon paper placed at bottom of a friction can cover is readily discerned through a layer of resin about 5 mm. in depth.

Regulation of the use of spray painting by compressed air machines, by common carriers, and employees of Federal agencies is proposed in a bill (H. R. 15,385), which was introduced in the House of Representatives December 14 by Representative Zihlman and referred to the House Committee on Labor.

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[1] Received August 31, 1928.

Composition and Use of Ferric Hydroxide as a Coagulant[1]

Edward S. Hopkins

BUREAU OF WATER SUPPLY, BALTIMORE, MD.

Practical operating data governing the use of ferric hydroxide floc as a coagulant and the maximum removal of turbidity by it, as well as a discussion of its theoretical composition.

AS IT was believed that information on the maximum precipitation and turbidity removal value of ferric hydroxide floc is of interest to the water plant operator, such a study, using Gunpowder River water, was made. It is realized that results with a given water do not necessarily apply to water from other sources, but it is possible to establish values which may be used for guidance. The buffer characteristics of the water, using data compiled from plant records for 1927–28, are given in Table I.

Table I—Composition of Gunpowder River Water

	pH	Alkalinity	Soap Hardness	CO_2	Fe	Mn	Turbidity
		P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
Average	6.9	25	35	5.5	0.8	0.14	13
Maximum	7.2	37	48	11.0	3.4	1.10	800
Minimum	6.6	21	31	1.7	0.3	0.02	6

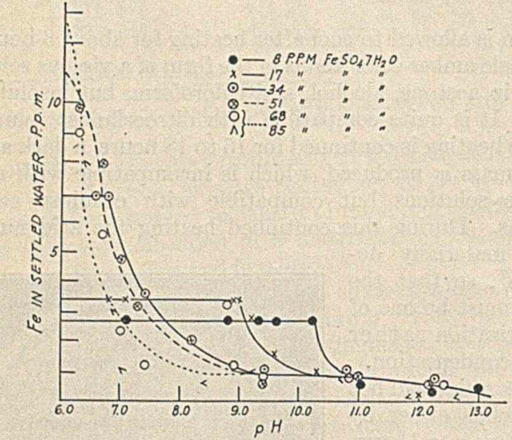

Figure 1

Previous investigations have been made on the formation of ferric hydroxide floc, but no data on its use as a coagulant or on the economical pH value for the control of the mixing basin when it is used are available. This study was undertaken to place water-plant operation on a more accurate control basis similar to that described by Baylis[2] for alum.

Experimental Procedure

The practicability of duplicating plant operating conditions with laboratory appliances is generally recognized. The method of procedure[3] used consisted in treating liter samples of the river water in beakers with a given quantity of the coagulant, rapidly mixing with a stirring rod, and then stirring with a rotary mechanical agitator at 100 r. p. m. for 15 minutes. Upon completion of the agitation the samples were allowed to settle for 30 minutes, pH values were determined colorimetrically as soon as sufficient clear water was available. At the end of the settling period the supernatant water was decanted from the precipitate and used for the determination of suspended floc and turbidity removal. Lime was used to produce the desired alkalinity below a concentration of 150 parts per million, above which sodium hydroxide was substituted. Check determinations proved that both bases gave the same analytical results.

Iron Removal

The iron present in the supernatant water was determined by the permanganate titration method, after dissolving in sulfuric acid and reducing with a Jones reductor, or, if in small quantity, by the thiocyanate color method in hydrochloric acid solution.

As the amount of coagulant present in the supernatant liquid will be inversely proportional to that precipitated, a curve showing these figures will be comparable to one showing maximum precipitation (Figure 1). Therefore the point showing the minimum amount of iron in suspension is also the point giving maximum removal of coagulant (ferrous sulfate) from the water. Table II summarizes the pH values of maximum removal for various concentrations of ferrous sulfate containing 7 mols of water of crystallization.

Table II—Maximum Precipitation of Ferric Hydroxide Floc

$FeSO_4 \cdot 7H_2O$ (p. p. m.)	8	17	34	51	68	86	171	428	1710
pH value of maximum precipitate	12.2	12.0	12.2	12.2	12.6	11.8	9.0	8.7	7.0

As this high alkalinity will produce a taste, and possibly physiological conditions, precipitation at a lower pH value is necessary. Inspection of the curve will show the possibility of obtaining a quantitative removal of floc at pH 9.4 for all concentrations of coagulant, thereby establishing an economical operating point. These results are in agreement with Miller's statement[4] that "ferric hydroxide does not redissolve at higher pH values." Regardless of the initial concentration of iron, not more than 1 p. p. m. will be found in the supernatant liquid, as floc precipitation at or about pH 9.4 gives an efficient removal of coagulant. With plant operating conditions these particles are usually of insufficient density for settling and compose the floc formed on the filter beds.

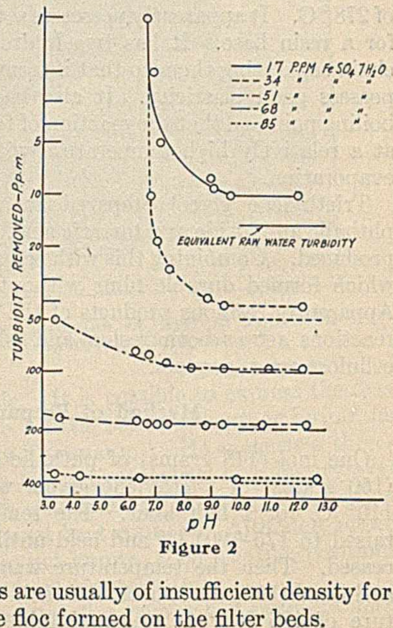

Figure 2

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[1] Received August 20, 1928. Presented before the Division of Water, Sewage, and Sanitation at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

[2] *J. Am. Water Works Assocn.*, **10**, 365 (1923).

[3] Hopkins, *Ibid.*, **12**, 405 (1924).

[4] U. S. Pub. Health Service, *Pub. Health Rept.* **40**, 1413 (1925).

Turbidity Removal

Various methods have been suggested to obtain a true picture of conditions in the settling (coagulating) basins. The suspended solids determination, using either porous cup or paper, and centrifuging the settled water to obtain total suspended matter or dispersion of the mass, with subsequent turbidity reading, include an estimation of the quantity of floc present and do not give the amount of insufficiently coagulated turbidity. It is admitted that the amount of floc present at the maximum precipitation point is small, as shown on the curve (Figure 1), but if the raw water turbidity is very low a difference of 1 or 2 p. p. m. will cause a decided change in the efficiency of the basin. It is believed that an accurate portrayal of the suspended floc can be obtained by dissolving the coagulant with acid and estimating the resultant turbidity either by the bottle method[5] or by diluting and using the Baylis turbidimeter.[6]

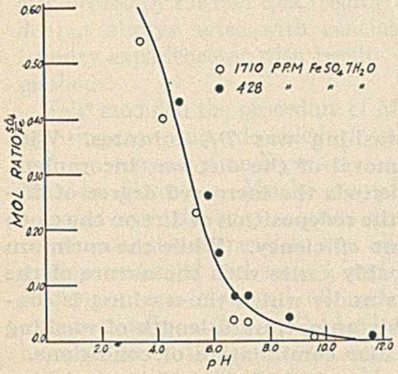

Figure 3

Turbidity determinations were made in conformity with the foregoing procedure on the liter samples of settled water obtained as explained in the first part of this article. These turbidities were artificially prepared in the laboratory, and the particles produced Brownian movement. Therefore they may be considered of colloidal dimension, about 5 mμ in diameter. This procedure gave comparable precipitation reactions for all gradients of turbidity. Table III shows the amounts of suspended turbidity found when these waters with sufficient concentration of coagulant to assure proper floc formation in accordance with plant practice were used.

Table III—Suspended Turbidity in Settled Water

Turbidity of raw water	15	50	100	200	400
Minimum turbidity of settled water	5	8	8	5	1
pH value minimum of settled turbidity	9.6	9.4	9.4	8.9	8.4

The minimum pH value is above 8.4 with 9.4 as the point for average turbidities. Turbidity removal being inversely proportional to that in suspension, deduction of the latter from the initial raw water content will give the amount removed. These results, plotted logarithmically in relation to turbidity in order to present clearly the reduction obtained for the various raw waters, are shown in Figure 2. The minimum removal pH value decreases as the amount of coagulant increases, thereby proving the effect of the positive ions. Using 17 p. p. m. and 34 p. p. m. of $FeSO_4 \cdot 7H_2O$, about the usual operating dosage, the maximum turbidity removal is at pH 9.5, which is the point of maximum ferric hydroxide precipitation. Therefore good removal of turbidity may be expected at economical plant operating pH values.

Composition of Floc

Ferric hydroxide floc obtained from the maximum experiment was washed free of sulfates "by centrifuging and subsequent decantation with water, care being taken to break up the floc at each washing."[3] Adsorption of sulfate did not occur with normal operating concentration of ferrous sulfate; 17 to 170 p. p. m. floc produced under these conditions may be considered as simply $Fe(OH)_3$. At increased concentrations, 428 and 1710 p. p. m. definite adsorption of sulfates were obtained. Figure 3 gives the mol ratio of SO_4 to Fe, plotted against the pH values. This ratio being in direct proportion to the sulfate content, the curve shows that adsorption is a function of pH value. Sulfates are present in floc found at an initial pH of 3.4–4.8 for these concentrations of iron, decreasing in regular order until above the point of maximum precipitation (9.4). Plotting the SO_4 to Fe ratio against the mols of NaOH added per mol of Fe to produce floc, sulfate adsorption practically disappears when 3 mols, or the theoretical amount of alkali to give complete reaction, is added (Figure 4). The alkalinity of the water and that of the lime were calculated to NaOH, so as to give an equal value for all alkali present. In general agreement with the work on alum,[3] it may be definitely stated that "when a quantity of NaOH in excess of that required to react with the ferric ion according to the equation $Fe + 3OH = Fe(OH)_3$ is present the precipitate can be washed free of sulfate." A definite basic sulfate is not formed with $Fe(OH)_3$ in these concentrations, as occurs with $Al(OH)_3$, for, upon calculating possible formulas, as was done by Williamson[7] for alum, it was found that the relation of Fe_2O_3 to SO_3 varied irregularly as a function of the pH value. These data support Buswell's[8] contention that the reaction is an adsorption phenomenon rather than a solid solution of SO_4 in OH and confirm his statement that "the floc as found in coagulating basins may be considered only as the hydroxide."

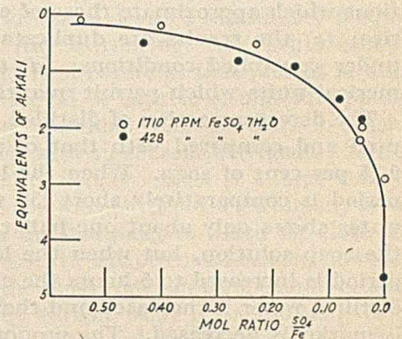

Figure 4

Miller[4] used solutions of ferric sulfate, potassium alum, and ferric chloride with oxygen excluded, working in an atmosphere of nitrogen, for a similar study. This work is not comparable with plant operation using ferrous sulfate. He also used concentrations equivalent to 0.01 mol Fe, and normal coagulating concentrations are from 0.000061 to 0.0003 mol Fe. A comparison of the sulfate adsorption results obtained by him with those presented in this paper, using the mol ratio SO_4:Fe curves indicates that they are in general agreement, sulfate adsorption being found in definite pH zones, which appear at lower values and narrow as the concentration of Fe is increased. Absence of sulfate when stoichiometric quantities of alkali have been added is also noted.

A paper[9] published in 1926 duplicates in part the work of previous investigators giving results of sulfate adsorption from alum as a function of pH value, and another article,[10] published in 1928, assumes that the decline in adsorption is caused by a reversion of the electric charge affected by the OH ion in the solution, using trisodium phosphate as the adsorption phase. All of this work confirms the older belief of Weiser[11] that the ion with an opposite charge may be adsorbed and stabilize the colloid.

The maximum pH precipitation value of ferric hydroxide floc is close to that obtained for absence of sulfate adsorption. This would indicate that the theory of a "solution link" advanced by Thomas and Frieden[12] would be applicable, with the SO_4 ion as the soluble portion of the floc, for their iron

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[5] American Public Health Assocn., "Standard Methods for Examination of Water and Sewage," p. 4 (1925).

[6] IND. ENG. CHEM., **18**, 311 (1926).

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

[8] "Chemistry of Water and Sewage Treatment," pp. 164, 176.

[9] Krause, *Roczniki Chem.*, **6**, 45 (1926).

[10] Stollenwerk and Von Wrabgel, *Z. Elektrochem.*, **33**, 501 (1927).

[11] *J. Phys. Chem.*, **25**, 742 (1921).

[12] *J. Am. Chem. Soc.*, **45**, 2522 (1923).

oxide hydrosol had a hydrogen-ion concentration of 10^{-4}, or pH 5. It is believed that this theory has considerable merit although Sorum[13] indicates that such an assumption may be in error. However, as he gives no information relating to the pH value of the ferric hydroxol obtained, the "solution link" theory is submitted as the most plausible explanation of sulfate adsorption in ferric hydroxide floc.

[13] Sorum, *J. Am. Chem. Soc.*, **50**, 1263 (1928).

The Detergent Action of Soap[1]

F. H. Rhodes and S. W. Brainard[2]

CORNELL UNIVERSITY, ITHACA, N. Y.

A satisfactory method for the quantitative determination of detergent power is described. This test fulfils the following requirements: (*a*) It measures detergent power directly and not some other property of the cleansing agent which may or may not be related to detergent power; (*b*) the measurements are obtained under conditions which approximate those of ordinary laundry practice; (*c*) the results are duplicatable and are obtained under controlled conditions; (*d*) the results are in numerical units which permit quantitative comparison.

The detergent action of distilled water has been measured and compared with that of a solution containing 0.25 per cent of soap. When the length of the washing period is comparatively short (30 minutes) the distilled water shows only about one-half the detergent effect of the soap solution, but when the length of the washing period is increased to 5 hours the cleansing action of the distilled water is increased and that of the soap solution is markedly decreased. The pronounced decrease in the detergent action of the soap with increase in the length of the period of washing is probably due to an increase in the degree of dispersion of the dirt.

Variations in the temperature at which the washing is conducted have comparatively little effect between the limits of 20° and 60° C.

With the conditions obtaining in the test, the maximum detergent effect was produced when the time required for each individual washing was 7 1/2 minutes. With shorter periods the removal of the dirt was incomplete. With longer washing periods the increased degree of dispersion of the dirt and the redeposition of dirt on the cloth decreased the detergent efficiency. While the optimum period of washing probably varies with the nature of the dirt and the conditions under which the washing is conducted, there is probably an optimum length of washing period for every particular combination of conditions.

Increasing the concentration of soap in the solution above 0.25 per cent produces little further change in detergent effect. Solutions containing 0.05 and 0.1 per cent of soap remove about the same amount of dirt in five washings as do the more concentrated solutions, but the rate of removal in the first few washes is slightly lower. Solutions containing only 0.01 per cent of soap are distinctly less efficient.

Soap solutions 24 hours old show about the same ultimate efficiency as do freshly prepared solutions, although the rate of removal of dirt during the first few washes is slightly lower when aged solutions are used.

The detergent powers of a few typical soaps have been measured and compared.

A formula has been developed which translates the experimental data of the tests into numerical indices which express the detergent characteristics of the soaps used.

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IN VIEW of the great practical importance of soap as a cleansing agent, it is but natural that attempts should be made to develop a satisfactory quantitative method for measuring and comparing detergent power. The first methods which were suggested were based not upon the direct measurement of detergent action, but upon the determination of some physical or physical-chemical property which was supposed to bear a direct relationship to detergent power. For example, measurements were made of the surface tensions of soap solutions against air or against oils and the results thus obtained were taken as criteria of the cleansing powers. In other cases the amounts of froth produced by soap solutions under specified conditions, the ability of the soaps to emulsify oils, or the protective action (gold numbers) of various soaps were used as bases for the comparison of detergent power. Experience has shown, however, that there is no constant and direct relationship between detergent power and any one of these other readily measurable properties. It may be that in certain special classes of soap the ability to remove dirt is qualitatively parallel to the ability to lower surface tension or to produce lather or to stabilize colloidal gold, but such relationships are not quantitative or universal. Detergent power cannot be determined quantitatively by measuring some other characteristic of the soap.

Previous Work

McBain, Harborne, and King[3] developed a method for determination of detergent power which is based upon the measurement of the amount of carbon which can be retained in stable suspension in a solution of the soap. Carbon black was shaken with a soap solution of known concentration under definite conditions, the resulting suspension was filtered to remove undispersed carbon, and the amount of carbon passing through with the filtrate was determined. The detergent power of the soap solution was assumed to be directly proportional to the amount of carbon in the filtrate.

This method is not entirely satisfactory. In order to get consistent results the filter paper used must be of standard and uniform texture. Even slight variations in the size of the pores may cause appreciable error. To obtain filter paper of such constant and closely duplicatable texture is difficult. Furthermore, the amount of carbon carried through depends upon the pressure applied in folding, so that very careful manipulation is required. The volume of filtrate obtainable in a single experiment is not more than 10 cc.; larger portions require so long for filtration that changes in the suspension may occur. The amount of carbon suspended in this volume of filtrate is so small that it cannot be determined accurately by gravimetric methods, since even a very small absolute error in weighing causes a relatively

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[1] Received June 26, 1928.

[2] Du Pont Fellow in Chemistry at Cornell University.

[3] *J. Phys. Chem.*, **28**, 1 (1924).

large error in the apparent detergent power. Colorimetric methods for estimating the concentration of suspended carbon may be used, but here again the possible errors are of considerable magnitude. Finally, there is no necessary and exact parallelism between the ability of a soap solution to *retain* carbon black in suspension and the ability to *remove* dirt from cloth. That the method of McBain does not always give quantitatively correct measurements of detergent power is indicated by the fact that results obtained by this procedure do not always agree with conclusions drawn from actual laundry experience or with results obtained by more refined methods.

Fall[4] modified the procedure of McBain and his co-workers by using manganese dioxide instead of carbon black as "dirt" and by removing undispersed material by settling rather than by filtration. Finely ground manganese dioxide was agitated with the soap solution under definite and specified conditions, the suspension was allowed to stand until any undispersed solid had settled, and a portion of the colloidal suspension was siphoned off and analyzed for manganese volumetrically. This method eliminated many of the disadvantages of the procedure suggested by McBain, but is still not entirely satisfactory. Manganese dioxide is not an important component of the dirt that ordinarily occurs in soiled clothes, and it is not permissible to assume that the behavior of different detergents toward manganese dioxide will be the same as or exactly parallel to their behavior with ordinary dirt. Furthermore, there is no necessary quantitative relationship between the ability of a substance to retain manganese dioxide in suspension and its ability to remove dirt from cloth.

The obvious way to measure the ability of soap to remove dirt from cloth is to wash dirty cloth with a soap solution of known concentration under controlled conditions which approximate as closely as possible the conditions existing in normal laundry practice and then to measure the amount of dirt removed.

Such methods have been suggested by various investigators. Ehukov and Shestakov[5] soiled cotton cloth by immersing it in a mixture of lanolin, lampblack, and benzene, and then washed under controlled conditions. The efficiency of washing was judged by the appearance of the washed samples. These investigators found that the most efficient washing was secured when the solutions contained between 0.2 and 0.4 per cent of soap. Stericker[6] made actual washing tests on batches of greasy overalls. He made only a few tests and his results have little general or quantitative significance. Heermann[7] developed a rather elaborate washing test which did not give quantitative results. Bergell[8] made washing tests on woolen cloth soiled with charcoal, fat, and ether. The amount of dirt removed was determined by weighing. The results are of a qualitative significance only. Hirose[9] made washing tests in which the cloth was soiled with lanolin and indigo. He attempted to correlate the detergent power of a soap with some of its other properties, such as surface tension, lathering power, etc.

Objections to Previous Methods

Most of the methods hitherto suggested for the direct determination of the cleansing power of soap have been subject to one or more of the following objections:

(1) The soil used in dirtying the cloth did not approximate the composition of ordinary dirt.

(2) No satisfactory quantitative method for measuring the extent of cleansing was available, so that the results were comparative and qualitative only.

(3) In some cases the conditions under which the washing was effected were not comparable with those obtaining in normal laundry practice.

Method for Determining Detergent Power

Any satisfactory quantitative test for detergent power should meet the following requirements:

(1) It should measure detergent power and not some other property of the soap which may or may not be directly indicative of detergent power.

(2) The measurements should be obtained under conditions which approximate those of ordinary laundry practice.

(3) The results should be duplicatable and should involve the smallest possible amount of variation due to the personal equation of the operator.

(4) The results should be obtained in numerical units which permit quantitative comparison.

Method of Soiling Cloth—In the development of such a test, the first problem was to devise a satisfactory method of soiling the cloth. Any satisfactory soil should contain material of the same general nature as that present in ordinary dirt on cloth, it should be capable of uniform application, and it should be removable from the cloth in a comparatively few washings with an efficient detergent. "Dirt" is a very indefinite term; it may consist of a large number of different substances and the nature of the dirt in any given case will depend upon the treatment to which the cloth has been subjected. If we leave out of consideration, however, iron rust and stains, the most common components of ordinary dirt are probably carbon (soot or lampblack), fatty substances (from perspiration and grease), and oils. It is probable that any detergent which will remove these substances will remove most of the dirts met with in ordinary laundry practice. The most obvious way of securing uniform and duplicatable soiling is to apply the dirt by dipping the cloth in uniform suspension or solution of the soil in a readily and completely volatile liquid.

A number of different soils were tried. It was found that the one suggested by the Detergents Committee of the American Oil Chemists' Society most completely fulfilled the requirements. This is prepared as follows:

Lampblack	2 grams
Lubricating oil	5 grams
Tallow	3 grams
Carbon tetrachloride	2000 cc.

The cloth used in this work was cotton sheeting with a thread count of 58–68. Any sizing was removed by boiling 5 minutes with an approximately tenth-normal solution of hydrochloric acid, rinsing several times with distilled water, boiling 5 minutes with an approximately tenth-normal solution of sodium hydroxide, rinsing several times in hot water, boiling 10 minutes in 0.5 per cent solution of soap flakes, and finally rinsing several times with hot distilled water and drying. The final dry cloth was ironed smooth.

The soil was applied to the cloth as follows: The stock solution was shaken to insure uniform distribution of the suspended carbon black and 100 cc. were poured out into a shallow porcelain evaporating dish (36 cm. diameter). The clean and size-free cloth, cut in a strip 25 cm. long and 10 cm. wide, was held at the ends and passed through the solution several times until soiled to the proper degree. It was then held by the upper corners with the long axis inclined at about 20 degrees from the horizontal and allowed to drain until the excess solution ceased to flow in a continuous stream from the lowest corner. The drained cloth was laid flat on eight thicknesses of cheesecloth, covered with a similar pack of cheesecloth, and pressed out well with the hands. This

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[4] *J. Phys. Chem.*, **31**, 801 (1927).

[5] *Chem-Ztg.*, **35**, 1027 (1911).

[6] Ind. Eng. Chem., **15**, 244 (1925).

[7] *Z. deut. Ol.-Fett. Ind.*, **44**, 361, 378, 391 (1924).

[8] *Seifensieder Z.*, **51**, 627, 647 (1924).

[9] *J. Soc. Chem. Ind.* (*Japan*), **30**, 734, 742 (1927).

blotting removed excess solution and insured even soiling. The blotted cloth was dried in an electrically heated oven at 80 degrees for exactly 1 hour and then aged in the room for 11 hours. It was found that any marked variation in the temperature at which the cloth was dried had a very considerable effect upon the ease with which the soil was removed in subsequent washing. For this reason care was taken to keep the temperature of drying constant. Freshly soiled and dried cloth also washed somewhat more readily than cloth that had stood for several hours after drying. To eliminate possible errors due to differences in aging, all samples were aged for 11 hours. In every experiment the cloth was soiled to a brightness of about 30 per cent. With some experience it was possible to duplicate the degree of soiling very closely.

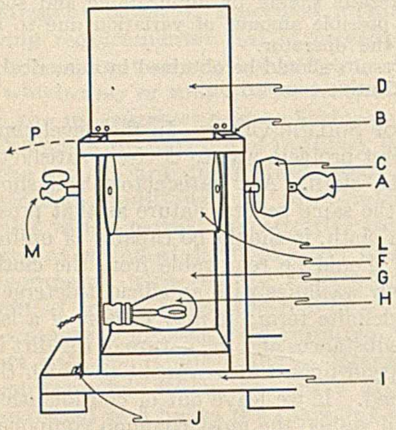

Figure 1—Diagram of Washer

A, thistle tube; *B*, slot to admit trunnion bearing; *C*, friction gear; *D*, hinged cover; *F*, washing cylinder; *G*, glass front; *H*, incandescent bulb; *I*, wooden base; *J*, hinge for tilting frame in direction *P*; *L*, trunnion bearing; *M*, brass stopcock.

METHOD OF WASHING—In developing a washer for this work, the following requirements were to be met:

(1) The apparatus should give results comparable with those obtained in laundry practice.

(2) With a good detergent the soil should be removed practically completely from the cloth in a comparatively few washings.

(3) It should be possible to control and duplicate conditions during washing.

(4) Neither large amounts of cloth nor large quantities of soap solution should be required for a single test.

After a considerable amount of experimentation an apparatus and a procedure for washing the cloth were developed which gave satisfactory results.

Apparatus. The apparatus consisted essentially of a glass cylinder which was revolved horizontally and which contained a cylindrical cage of rubber-covered metal bars. The glass cylinder itself was 13.3 cm. long and 12.7 cm. in internal diameter. It was prepared by cutting the top and bottom from a bottle of suitable size and grinding the edges smooth and parallel.

This cylinder was mounted between circular brass plates, the joints between the cylinder and the plates being made tight by annular rubber gaskets (0.3 cm. thick) set in recessed rings in the end plates. The ends were held firmly against the cylinder by six spiral springs as shown in the drawing. Through the center of each end plate was soldered a brass tube (1.3 cm. outside diameter), which tubes served as trunnion bearings. Through one of these bearings was inserted a glass thistle tube (*A*, Figure 2), held in place by a rubber stopper. This served as an inlet tube during filling. A small opening (*C*) near the end of the brass tube acted as an air vent. The opposite bearing served as an outlet when the machine was emptied, and was closed by a brass stopcock. Within the outer cylinder was a cage made by fastening six brass rods (0.45 cm. diameter) through circular disks of aluminum. These rods were so placed that the distance from the wall of the glass cylinder to the center of a rod was 0.9 cm. The disk at the inlet end contained a central circular opening 5 cm. in diameter; the opposite disk was provided with several circular holes (0.6 cm. diameter) to permit rapid draining when the apparatus was emptied. Each of the brass rods of the cage was covered by a snugly fitting length of rubber tubing, 0.8 cm. outside diameter. The cage was held firmly in the outer glass cylinder by means of sections of rubber tubing, split lengthwise and placed around the edge of each aluminum end plate.

This cylinder, with its cage, was mounted horizontally in a wooden case fitted with glass front and hinged cover. (Figure 1) This case was hinged at one edge, as shown, so that it could be tilted until the cylinder was vertical, for filling or emptying. When in the running position the cylinder was revolved about its horizontal axis by the friction gear, *C*, which was operated through a motor-driven gear train. An incandescent bulb below the washing cylinder served to maintain constant temperature during washing.

Procedure. After a strip of the cloth (25 by 10 cm.) had been properly soiled, dried, and aged, it was folded once in the middle and a strip 2.5 cm. wide was cut from each end to remove any portions which might have been irregularly soiled. It was then sewed around the edges to form a closed bag 10 cm. square. Just before the bag was sewed shut 100 grams of solid glass beads (0.3 to 0.6 cm. diameter) were placed in it. Two such bags, prepared from duplicate cloths, were placed together within the cage in the machine and the washing cylinder was assembled, closed, and placed in its supports. The current in the heating bulb was turned on for a few minutes until the apparatus itself was brought to the temperature at which the washing was to be made. The case was then tilted until the axis of the cylinder was vertical and 500 cc. of a freshly prepared soap solution of known concentration were introduced. (This amount filled the cylinder almost half full.) The soap solution was brought to the desired temperature of washing before being put into the cylinder. The frame was turned back to the "running" position and the motor which revolved the cylinder was started. The time of washing was taken from this instant. The speed of revolution was constant at 80 r. p. m. unless otherwise noted. The temperature of the solution was controlled by raising or lowering the sliding glass front of the case.

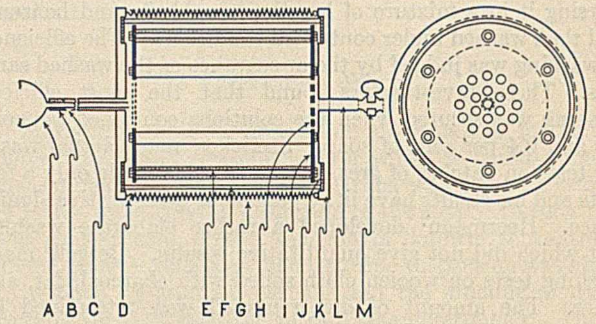

Figure 2—Detail of Glass Cylinder in Washer

A, glass thistle tube; *B*, rubber stopper; *C*, air vent; *D*, hook for holding springs; *E*, rubber-covered brass rod; *F*, glass cylinder; *G*, steel spring; *H*, openings at discharge end of cage; *I*, aluminum end plate; *J*, rubber gasket; *K*, brass end of washing drum; *L*, trunnion bearing; *M*, brass cock.

RINSING—At the end of the washing period the frame was again tilted, the outlet cock opened, and the soap solution drained. The drum was removed and disassembled and the bags (still containing the glass beads) were removed. The two bags, held by corners with crucible tongs, were rinsed by dipping together five times in each of the following rinsing solutions: (1) soap solution of the same composition and concentration as that used in washing; (2) distilled water; (3) distilled water; (4) dilute acetic acid (0.05 *N*); (5) distilled water. The amount of each rinsing solution used was 500 cc. and the temperature was that of the soap solution used in washing.

In outlining this schedule, soap solution of the same concentration as that used in washing was selected as the first rinse, because it was suspected that if the clothes still containing some dirty wash water were rinsed directly in distilled water some of the dirt in the adhering wash water might be reprecipitated on the fabric. The first rinse left the bags wet with practically clean soap solution. The second and third rinse eliminated most of the soap, while the fourth rinse in very dilute acetic acid neutralized any possible adsorbed alkali and thus prevented any yellowing on drying. Acetic acid was selected for this purpose, because it is so weak that it should not injure the fabric and also because it is readily volatile. The final rinse left the cloth wet with distilled water only.

DRYING—After the last rinse the bags were opened at one end, the beads were poured out, and the double thickness of washed cloth was pressed flat between clean filter paper and dried in an oven for 60 minutes at 80° C. When the drying was complete the brightness was measured.

MEASUREMENT OF BRIGHTNESS—The same samples were washed, rinsed, and dried as many times as desired. By measuring the brightness of the cloth after each cycle, data were obtained from which a "washing curve" could be drawn for the particular detergent under a specified set of conditions. It was found that in most cases five washings served to bring the brightness to almost the maximum attainable value.

This procedure gives results which are at least comparable with those of ordinary laundry practice. The washing is uniform and comparatively efficient. The conditions can be so closely controlled that duplicate experiments give practically identical results. The tests can be made fairly quickly and require but little material.

The measurement of the brightness or "whiteness" of the washed or partially washed cloth has troubled a number of investigators. Attempts have been made to compare the washed cloths with arbitrary standards—papers of various degrees of whiteness (or grayness), painted surfaces, pastes, etc. This method is not satisfactory. The standards were more or less arbitrarily chosen so that the measurements were not in any definite rational units. The standards were often difficult to duplicate and were not always permanent in shade. The comparison between the washed cloth and the standard was rendered difficult by slight differences in tint and in texture of the surface. Finally, comparisons depended so much on the personal equation that different observers often got widely different values for the same sample.

In selecting a method for measuring the brightness or "cleanness" of the cloth, the following requirements were kept in mind:

(1) The results should be in rational numerical units—in terms of true reflecting power or "percentage brightness." On this scale a perfectly white surface should give a reading of 100 per cent and a perfectly black surface should give a reading of 0 per cent.

(2) There should be involved no comparison with standards which might be impermanent or difficult to reproduce or which might differ from the sample in tint or in texture.

(3) Any personal bias of the observer should not affect the results.

Apparatus. These requirements were met by the use of an integrating photometer. This instrument was patterned after the one described by Taylor.[10] It consists essentially of a hollow copper sphere 15.2 cm. in diameter, provided with three openings, as shown in Figure 3. To one opening, *P*, is attached a lighting tube which is so arranged that it may be rotated to direct a beam of parallel light either upon the test surface, *H*, below the opening, *G*, or into the top of the sphere itself. This lighting tube is provided with a 32-candlepower automobile headlight bulb, *B*, the back of which has been silvered to reflect as much as possible of the light into the sphere. This bulb is operated at approximately 15 volts and is closely controlled through a slide-wire resistance. A set of lenses, *C*, gives a beam of approximately parallel light of small diameter and free from scattered rays. Through a diaphragm at the opening, *E*, is inserted the photometer tube of a Macbeth illuminometer, which is focused on a small spot at the opposite side of the sphere. A small screen, *F*, prevents light from being reflected from the test sample directly to this observation spot. The opening, *G*, below which the test sample was placed was 5 cm. in diameter and was surrounded by a flange faced with felt to prevent the entrance of light between the sample and the instrument. The entire inside of the sphere was painted with a special white photometer paint of very high light-reflecting power, prepared by suspending 4 parts by weight of zinc oxide in 4 parts of cellulose lacquer diluted with alcohol and turpentine.[11]

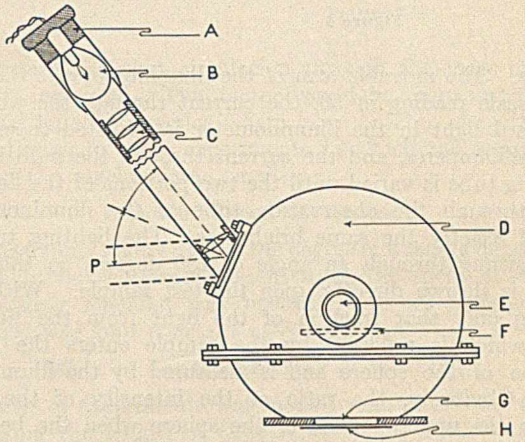

Figure 3—Photometer for Measuring Brightness of Cloth

A, hard-rubber base for socket; *B*, 32-candlepower bulb, silvered on back; *C*, upper lens system of tube; *D*, spun copper sphere; *E*, opening for telescope of illuminometer; *F*, small screen on inner surface; *G*, opening for sample; *H*, test surface; *P*, position of lighting tube when beam is directed into upper part of sphere

Procedure. Four thicknesses (two test-piece bags) of the sample of dry cloth are placed on a circular wooden disk 6.8 cm. in diameter, drawn flat and held firmly in place by a leather ring slipped over the edge of the disk. This is then placed on a cam-operated table below the observation opening of the reflectometer and raised until the cloth fits snugly against the flange around the opening. By using four superimposed layers of cloth in this way, any possible error due to the porosity or lack of opacity of the fabric is eliminated; the top layer is backed by three other layers of substantially the same brightness. With the sample in position, the lighting tube is turned so as to throw the beam against the inside of the top portion of the sphere. With this setting *all* of the light from the lighting tube enters the upper portion of the

[10] Bur. Standards, *Sci. Paper* **405** (1920).

[11] Taylor, *Trans. Illum. Eng. Soc.* (*N. Y.*), **16**, 587 (1922).

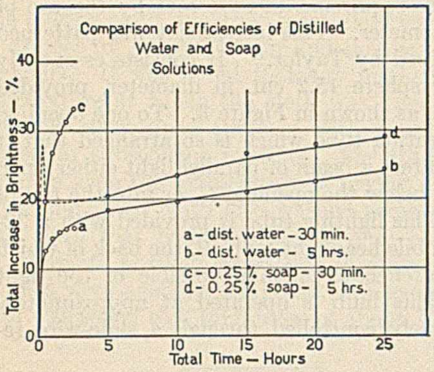

Figure 4

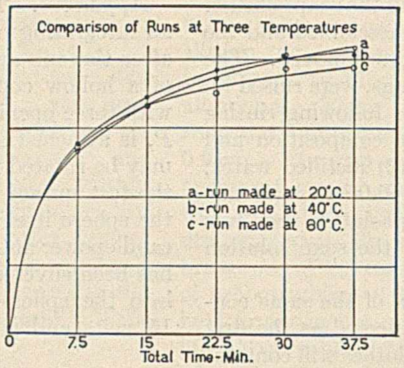

Figure 5

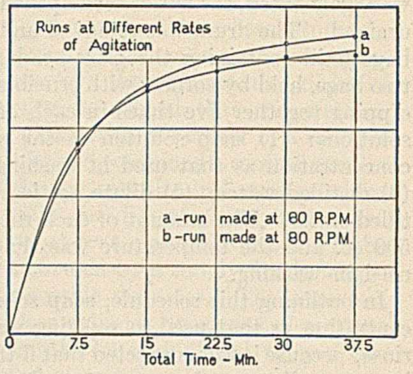

Figure 6

sphere. The movable arm of the illuminometer is then set at a scale reading of 50, the current through the working standard light in the illuminometer is adjusted to exactly 225 milliamperes, and the current through the bulb in the lighting tube is varied until the two portions of the field, as seen through the observation tube of the illuminometer, are of exactly the same brightness. The lighting tube is then swung through an angle of 180 degrees so that the beam is thrown directly upon the test sample. With this setting only that fraction of the light from the lighting tube which is reflected by the sample enters the upper portion of the sphere and is measured by the illuminometer. Obviously, the ratio of the intensity of the light within the upper portion of the sphere when the beam is first reflected from the sample to the intensity of the light in the upper portion when the beam enters the upper portion directly is equal to the reflecting power or brightness of the sample. When the beam is directed on the sample, the arm of the illuminometer is lowered until the two portions of the field again match, and the reading of the scale on the illuminometer arm is noted. This reading, multiplied by 2, gives the brightness of the sample. The positions of the two test samples on the observation block are then interchanged and the observation repeated. Three readings are made on each sample and the average of these three results is taken as the brightness. In few cases is the maximum deviation between individual readings on the same sample greater than 2 per cent. In most instances the agreement is better than this. The probable error of the final average value for the brightness of the cloth is considerably less than this maximum error.

Summary of Procedure for Tests—In making a complete washing test, the cloth is freed from sizing and dried and its brightness is determined. The sample is then soiled, dried, and aged, and the brightness of the soiled fabric is measured. The cloth is then put through a series of washing cycles, brightness determinations being made after each cycle.

Soap Solution—In all the experiments which were made to determine the effect of the various conditions upon the extent and progress of the detergent action a flake soap of a widely used commercial brand was used. This soap was selected, not because it is better or worse than others, but for the following reasons:

(1) It is readily obtainable in quantity.
(2) The moisture content is rather low (1 to 2 per cent) and the determination of moisture presented no analytical difficulties.
(3) It is easily pulverized, so that large portions can be uniformly mixed.
(4) The powdered flakes are readily soluble in water.
(5) It is free from addition agents and fillers, so that the effects of fillers can be studied separately.
(6) It is assumed to be approximately representative of a rather large number of good commercial soaps.

In preparing the soap solution for use in a test, sufficient of the powdered soap was weighed out to give 1 liter of a solution of the desired concentration. (All soaps were analyzed for moisture before use, and all concentrations were calculated on the basis of the percentage of dry soap in the solution.) The soap was then dissolved in distilled water at slightly above the temperature at which the solution was to be used. A portion (500 cc.) of the soap solution was immediately measured out and transferred to the washing cylinder containing the sample bags and the washing was started at once. The remainder was reserved for use in rinsing.

Preliminary Experiment

Effect of Washing on Cloth—A few preliminary experiments were made to determine whether or not the cloth itself is darkened or discolored by the soap used in washing or by the contact with the metal in the washing machine. Samples of unsoiled cloth were washed for 1 hour in 0.25 per cent soap solution at 40° C. and the brightness of the washed fabric was measured. The original clean cloth had a brightness of 78.4 per cent; the brightness of the washed cloth was 79.5 per cent. It is evident that there is no discoloration due to the soap used in washing or to the accumulation of dirt from the washing machine. The apparent slight increase in brightness is probably due to the removal of a small amount of coloring matter from the cloth itself, although it is within the possible maximum error in measurement.

Time of Drying—Other preliminary experiments showed that complete drying of the cloth after the washing and rinsing is secured in less than 45 minutes, and that drying for longer than 45 minutes does not affect the brightness of the sample. In order to avoid any possibility of error from incomplete drying, all samples in the subsequent work were dried for 60 minutes.

Effect of Washing with Distilled Water Alone—To determine the detergent effect of water alone, samples of soiled cloth were washed in distilled water at 40° C. In one series of experiments the washing period was 30 minutes; in the other it was 5 hours. The results are shown graphically by curves *a* and *b* of Figure 4. It is apparent that distilled water alone has an appreciable detergent action. The removal of dirt is rather complete in the first few washes but decreases as the washing is continued.

Comparison of Detergent Action of Distilled Water and Dilute Soap Solution

In order to compare the detergent action of distilled water with that of dilute soap solution, two parallel series of experiments were made in which the cloth was washed with a solution containing 0.25 per cent of commercial soap flake at 40° C. The washing periods were 30 minutes and 5 hours, respectively, as before. The results are plotted as curves *c* and *d* of Figure 4.

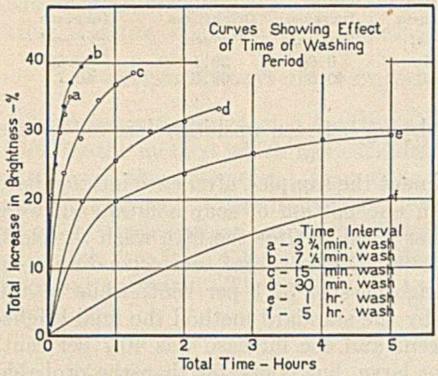

Figure 7

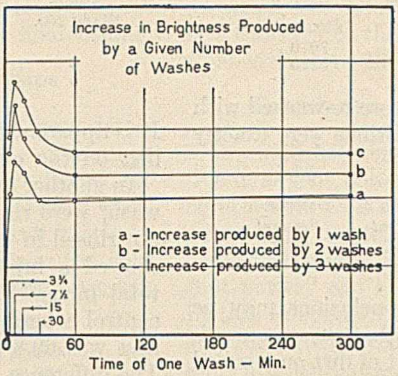

Figure 8

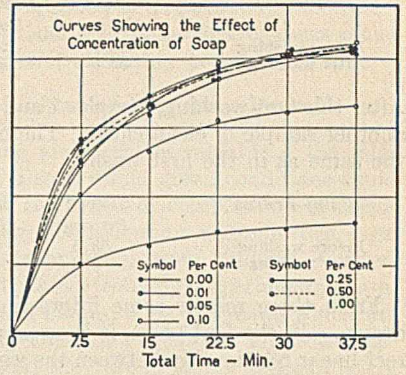

Figure 9

The detergent effect of the dilute soap solution, when used in 30-minute washes, is very much more pronounced than that of distilled water alone. On the other hand, there is very much less difference between the soap solution and the water alone when the washing interval is increased to 5 hours. The decrease in the apparent efficiency of the soap with increase in the length of the period of washing may be due to changes which take place in the soap itself during the longer washing periods. McBain and others have shown that on long standing the molecules and the ions present in a solution of soap tend to agglomerate with the formation of colloidal aggregates or micelles, and that this agglomeration is accompanied by a decrease in the detergent power. Experiments which will be described below have shown that this change in the structure of the soap is not the principal cause for the observed decrease of efficiency with increase in the washing period. Furthermore, later experiments have shown that a solution which contains only 0.1 per cent of soap is almost as effective as one containing 0.25 per cent, so that the aggregation of over one-half the molecules or ions originally present in the freshly prepared solution would not account for the observed decrease in efficiency. The decrease may also be due to changes in the character of the surface of the cotton. On long-continued agitation in weak soap solution the cotton may become partially hydrated or otherwise changed so that it adsorbs the dirt more firmly and retains it more tenaciously. This is probably not the true explanation of the observed phenomenon, since later experiments have shown that this decrease in detergent effect with increase in the length of the period of washing appears in even such a short time as 30 minutes. It is not probable that any appreciable degree of hydration of the cotton would occur in this short time under the conditions obtaining during washing operation. A third possible hypothesis is that on continued agitation with the soap solution the dirt becomes increasingly finely divided so that it is adsorbed more firmly by the cloth and coats it more effectively.

Effect of Temperature

The detergent action of dilute soap solution, as determined by the method described, was found to be practically independent of the temperature within the limits of 20° to 60° C. Three series of washings made with a 0.25 per cent solution of commercial soap flake at temperatures of 20°, 40°, and 60° C., respectively, with a $7^{1}/_{2}$-minute washing period, gave practically identical results. (Figure 5) In all subsequent experiments a standard temperature of 40° C. was used.

In actual practice the use of the higher temperatures is probably advantageous for several reasons. The soaps dissolve much more rapidly in warm water than in cold and the viscosity of the solution is considerably less at the higher temperatures, so that circulation through the mass of the fabric is improved. This factor would be more important in actual laundry practice where large batches of cloth are handled than in these experiments in which the weight of cloth in the machine was small.

Effect of Speed of Washer

It was found (Figure 6) that the degree of washing depended to a slight but noticeable extent upon the speed at which the washing machine was operated. In all experiments the speed was kept constant at 80 r. p. m.

Effect of Length of Time of Washing

A series of experiments was made to determine the effect of varying the length of time taken for a single washing period. These washings were made with a 0.25 per cent solution of commercial soap flake at 40° C. In each case five successive washings were made, the brightness being determined after each wash. Six sets of experiments were made with individual washing times of $3^{3}/_{4}$, $7^{1}/_{2}$, 15, 30, and 60 minutes and 5 hours, respectively. (Figure 7) In Figure 8 the increases in brightness produced by a given number of washes are plotted against the lengths of the individual washing periods.

It will be observed that in every case increases in brightness produced by a given number of washes is greater with a washing interval of $7^{1}/_{2}$ minutes than with one of $3^{3}/_{4}$ minutes, and that increasing the length of the interval beyond $7^{1}/_{2}$ minutes gives progressively smaller increases in brightness. In $3^{3}/_{4}$ minutes equilibrium between the dirty cloth and the soap solution is not reached and the washing action is still incomplete. With washing periods longer than $7^{1}/_{2}$ minutes equilibrium appears to be reached, but some change takes place in the soap, in the cloth, or in the dirt which displaces the apparent equilibrium and renders the cleaning of the cloth more difficult. This same phenomenon was observed in the experiments described above under Effect of Washing with Distilled Water Alone. In the discussion of these results were given the reasons for believing that the observed results were due to changes in the condition of the dirt.

Other experiments, the results of which need not be given in detail here, indicated that increasing the length of the washing period from $7^{1}/_{2}$ minutes to $11^{1}/_{4}$ minutes lowered the efficiency of the detergent action. Inasmuch as the maximum cleansing was attained with $7^{1}/_{2}$-minute periods, this period was adopted as standard in all subsequent experiments.

Redistribution of Removed Dirt upon Prolonged Washing

Two samples of soiled cloth and one of clean cloth were washed together for 5 hours in a 0.25 per cent solution of commercial soap flake at 40° C.

BRIGHTNESS	SAMPLE 1	SAMPLE 2	SAMPLE 3
	Per cent	*Per cent*	*Per cent*
Before washing	36.6	34.7	79.0
After washing	53.5	53.7	52.5

After this first washing, samples 1 and 2 were re-washed with another sample of clean cloth. The conditions were exactly the same as in the first wash.

BRIGHTNESS	SAMPLE 1	SAMPLE 2	SAMPLE 3
	Per cent	*Per cent*	*Per cent*
Before washing	53.5	53.7	78.7
After washing	57.3	56.0	63.4

From these results some interesting conclusions may be drawn. In the first place, it is apparent that there is no direct linear relationship between the weight of dirt on a soiled sample and the difference between the brightness of the sample and the brightness of the original cloth. In other words, the ratio of change in brightness to change in concentration of dirt is not constant. In the second washing the total amount of dirt removed from both soiled samples was equivalent to a total increase in brightness, for a single sample, of 6.1 per cent; yet even a portion of this dirt when redeposited on the clean cloth was sufficient to reduce the brightness 13.3 per cent.

In the second place, the experiments show that on long-continued agitation with soap solution the dirt tends to become actually fixed on the cloth. In the first washing practically complete equilibrium was reached. The unsoiled sample adsorbed soil from the solution and the soiled sample gave up dirt to the solution, so that at the end of the washing period all three test pieces were of the same brightness.

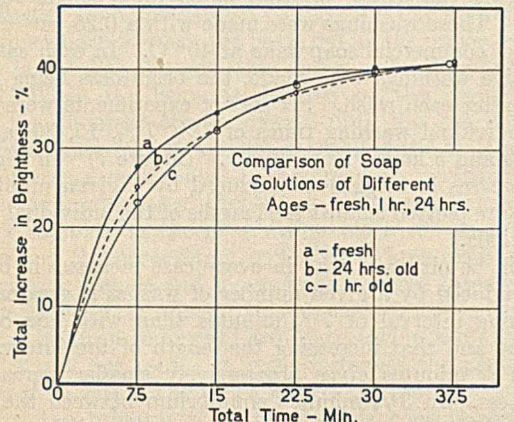

Figure 10

In the second washing there was a very slight increase in the brightness of the soiled cloths and no very large decrease in that of the unsoiled fabric. Equilibrium was not reached. It is evident that during the original treatment the unremoved soil was so firmly fixed on the cloth that it could not be removed even by long-continued washing.

Effect of Rinsing and Drying

It is possible that the dirt left in the cloth after any particular wash may become fixed on the fabric during the subsequent drying and may be thus rendered more difficultly removable in subsequent washings. To determine the extent to which such fixation occurs, a series of washings was made in which the cloth was not dried after the rinsing but was put back in the machine for re-washing while still wet. In preparing the soap solution for every wash except the first, allowance was made for the distilled water (about 50 grams) remaining in the wet rinsed sample. All washings were made for 7$^1/_2$ minutes in a 0.25 per cent solution of commercial soap flake at 40° C. The results were as follows:

AFTER WASH NO.	WITHOUT DRYING		STANDARD METHOD	
	Brightness	Increase	Brightness	Increase
	Per cent	*Per cent*	*Per cent*	*Per cent*
0	28.5	0.00	29.1	0.00
5	69.0	40.5	69.8	40.7

It is apparent that drying between washings does not fix the dirt on the cloth.

In another experiment the samples, after each intermediate wash, were rinsed in one portion of soap solution but were not rinsed in water or dried. After the fifth wash the cloth showed a brightness of 67.6 per cent, corresponding to a total increase in brightness of 37.1 per cent, while in the control experiment by the standard method the final brightness was 69.8 per cent and the increase was 40.7 per cent. The difference is not large, but is greater than the probable error of the experiment. It would appear that all the dirty wash water is not removed by the rinse in soap solution and that some of the soil is taken out by the rinses in water.

Effect of Concentration of Soap in Washing Solution

Samples of soiled cloth were washed with soap solutions of the following concentrations: 0.00, 0.01, 0.05, 0.10, 0.25, 0.5, and 1.0 per cent. In each case five washings were made, the soap used was the commercial flake soap, the temperature was kept at 40° C., and the length of the individual washing period was 7$^1/_2$ minutes. (Figure 9) The detergent power increases with the amount of soap in solution, rapidly at first and then more slowly, until the concentration reaches 0.25 per cent. Further increase in concentration produces little, if any, further increase in detergent action. For laboratory work in which close control of the conditions is possible, a standard concentration of 0.25 per cent was adopted.

In all these experiments the soap was dissolved in distilled water. If tap water had been used, larger quantities would have been required because some of the added soap would have been precipitated and removed by the calcium and magnesium salts. It is possible that somewhat different results might have been obtained if the water had contained small amounts of sodium chloride or other salts of the alkali metals. Experimental work on the effects of dissolved salts on detergent action is now under way.

Previous investigators have also accumulated data as to the relationships between concentration and detergent power as measured by various methods. McBain[3] found that solutions containing about 4.5 per cent of soap showed the maximum peptizing effect on carbon. This concentration is much higher than is used in laundry practice. Fall,[4] from his work with suspensions of manganese dioxide, concluded that solutions containing 0.25 to 0.45 per cent of soap were the most efficient.

Effect of Age of Soap Solution

It is known that when a solution of a soap is allowed to stand for a considerable time some of the ions and the molecules originally present agglomerate to form aggregates or "micelles," and that under certain conditions this agglomeration is accompanied by a decrease in the peptizing power of the soap. Comparative tests were made using a freshly prepared solution and solutions which had been allowed to age for 1 hour and for 24 hours, respectively. The results (Figure 10) indicate that the age of the soap solution has but little effect upon the detergent power. The total amount of dirt removed in five washes is almost exactly the same in all cases, but the rate of removal during the first few washes is a little less rapid when the solution is allowed to age. Any slight decrease in detergent power, as thus indicated, appears to take place rather quickly and to be almost complete in 1 hour. In all tests on detergent action the soap solution used was freshly prepared, so that any slight change during standing could have no effect on the final results.

Detergent Powers of a Few Typical Soaps

The detergent powers of a few typical soaps were determined by the method which has been described. The soaps tested were the commercial soap flake, a potash–coconut oil liquid soap, a powdered olive castile soap, a tallow soap, and a commercial potassium oleate. These were all relatively pure soaps, free from filler and containing water as the only important impurity. The amounts of water present were as follows:

	Per cent
Commercial soap flake	1.97
Potash-coconut oil liquid soap	67.99
Powdered olive castile soap	1.06
Tallow soap	3.08
Potassium oleate	50.6

In all the tests the following conditions were constant:

Time of washing interval	7½ minutes
Concentration of dry soap solution	0.25 per cent
Temperature	40° C.
Brightness of unsoiled cloth	80.4 per cent

The results are shown in Table I and Figure 9.

Table I—Brightness of Soiled Cloth after Washing with Typical Soaps

After Wash No.	Sample 1	Sample 2	Average	Total Increase
	Per cent	*Per cent*	*Per cent*	*Per cent*
		COMMERCIAL SOAP FLAKES		
0	28.7	29.5	29.1	00.0
1	56.5	57.2	56.9	27.8
2	63.7	63.7	63.7	34.6
3	67.5	67.4	67.4	38.3
4	70.3	69.3	69.8	40.7
5	69.4	70.1	69.8	40.7
		POTASH–COCONUT OIL LIQUID SOAP		
0	26.6	27.7	27.2	00.0
1	55.8	54.3	55.0	24.9
2	62.3	61.3	61.8	34.6
3	64.1	62.3	63.2	36.0
4	65.3	63.7	64.5	37.3
5	67.0	65.1	66.1	38.9
		POWDERED OLIVE CASTILE SOAP		
0	30.5	29.6	30.1	00.0
1	55.6	54.4	55.0	27.8
2	65.4	65.7	65.5	35.4
3	67.7	68.4	68.0	37.9
4	68.5	70.5	69.5	39.4
5	69.3	71.8	70.5	40.4
		TALLOW SOAP		
0	29.3	28.1	28.7	00.0
1	53.3	53.8	53.5	24.8
2	60.5	62.0	61.3	32.6
3	64.1	64.8	64.5	35.8
4	64.7	65.5	65.1	36.4
5	66.5	66.8	66.7	38.0
		POTASSIUM OLEATE		
0	28.5	29.2	28.9	00.0
1	54.5	52.9	53.7	24.8
2	62.3	62.7	62.5	33.6
3	66.3	66.3	66.3	37.4
4	67.7	67.9	67.8	38.9
5	68.1	69.2	68.7	39.8

The tests do not indicate any very marked differences in detergent power. On the basis of the slight variations which are displayed, we may divide the five samples into three not very distinct groups:

(1) Commerical soap flakes and powdered olive castile soap, which show a rather high rate of removal of dirt and a high final removal.

(2) Potassium oleate, which shows a high final removal of soil but a somewhat low detergent action during the first few washes.

(3) Potash–coconut oil soap and tallow soap, which show both a low initial rate of cleansing and less detergent power after the fifth wash.

The results obtained with the freshly prepared solution of potassium oleate were somewhat similar to those obtained with an aged solution of commercial soap flakes of the same concentration. Inasmuch as the potassium oleate used in preparing the solution contained a large amount of water, it is conceivable that the soap had undergone changes somewhat similar to those which ordinarily occur in aging.

Calculation of "Indices of Detergent Power"

It would be interesting and perhaps valuable if the relative detergent power of a soap under given conditions could be expressed as a simple coefficient or combination of coefficients. In the following discussion an attempt has been made to derive a formula by which such "indices of detergent power" can be calculated from the experimental data. In this calculation certain assumptions are made which are not based upon direct experimental evidence. These assumptions are justifiable in that they are probably approximately true and that from them we can arrive at a formula which appears to apply fairly well to the experimental results.

In the following calculations the brightnesses are expressed as the ratio of the brightness of the sample to the brightness of the original cloth. For example, if the unsoiled cloth had a brightness of 80 per cent and the sample at a given stage during the washing had a brightness of 40 per cent the relative brightness of the soiled sample would be 0.5.

If we assume that when one (unspecified) unit weight of dirt is applied to the clean cloth the brightness of the cloth is reduced by the fraction R, the brightness of a sample containing one such unit quantity of dirt would be $(1 - R)$. The addition of a second unit weight of dirt would further the brightness by $(1 - R)R$, so that the total reduction would be $R + (1 - R)R$ and the brightness would be $1 - 2R + R^2$ or $(1-R)^2$. Similarly, cloth containing X_n unit weights of dirt would have a brightness of $(1-R)^{X_n}$, or

$$B_n = (1 - R)^{X_n} \tag{1}$$

$$\log B_n = X_n . \log (1 - R)$$

$$X_n = (\log B_n)/(\log (1 - R))$$

$$X_n = k \log B_n \tag{2}$$

in which

$$k = 1/\log (1 - R) \tag{3}$$

The general equation correlating the surface concentration of material adsorbed on a solid substrate with the contraction of the same material in a solution in equilibrium with the adsorption compound is:

$$X^y = Kc \tag{4}$$

in which X = concentration on the adsorbing solid
c = concentration in the solution
y and K = constants for any particular set of conditions

We may assume that a similar relationship applies to the distribution of dirt between the cloth and the soap solution. In this case the total amount of dirt in the solution is equal to the difference between the weight of dirt on the cloth before the particular wash and the weight on the cloth after the wash. If we work with constant volumes of solution, we have

$$c = k'(X_{n-1} - X_n)$$

in which X_{n-1} = weight of dirt on cloth before wash
X_n = weight of dirt on cloth after wash

Equation (4) becomes, therefore,

$$X_n^y = Kk'(X_{n-1} - X_n) \tag{5}$$

or

$$y \log X_n = \log K + \log k' + \log (X_{n-1} - X) \tag{6}$$

$$= C + \log (X_{n-1} - X_n)$$

If in this equation we substitute the values for X as defined by equation (2), we have

$$y \log (k \log B_n) = C + \log (k \log B_{n-1} - k \log B_n) \tag{7}$$

or

$$y \log (k \log B_n) = C + \log (k \log B_{n-1}/B_n) \tag{8}$$

In this equation k is defined (equation 3) as $1/\log(1-R)$, where R is the fractional reduction in brightness caused by the application of the first unit weight of soil. The exact weight of the unit quantity of soil has not been specified. The formulas given above apply regardless of the exact magnitude of this unit. We can, therefore, take as the unit weight of dirt that weight which, when applied, to clean cloth, will reduce the brightness of the cloth 1 per cent of its original value. In this case R becomes equal to 0.01 and $(1-R)$ is 0.99. Therefore k is 1/log 0.99 or -229, and the equation becomes:

$$y \log (-229 \log B_n) = C + \log (-229 \log B_{n-1}/B_n) \quad (9)$$

Since B_n is the ratio of the brightness of the soiled or partly washed cloth to that of the unsoiled cloth, it is always less than 1, and its logarithm is negative in sign. Similarly, the brightness of the cloth before a given wash is less than its brightness after that wash, so that the quantity $B_n - 1/B_n$ is fractional and its logarithm is negative. Therefore, all logarithms involved in equation (9) are logarithms of positive quantities.

It follows, therefore, that if we plot, on logarithmic graph paper, the values of $(-229 \log B_{n-1}/B_n)$ against the corresponding values of $(-229 \log B_n)$ for any particular series of washes made under similar conditions, a straight line should result. The intercept and the slope of this line should afford information as to the detergent characteristics of the particular agent under the conditions obtaining during the washing.

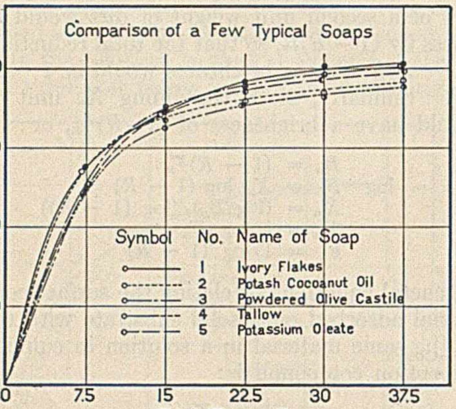

Figure 11

In the method for testing detergent power which is used, the soiled cloth has an original brightness of about 30 per cent. The cloth before soiling has a brightness of approximately 80 per cent. Therefore, the relative brightness of the original soiled cloth (B_0) is about 0.375. If we plot the values of log $(-229 \log B_0/B_n)$ against log $(-229 \log B_n)$ for various values of B_n we get the curve shown as a dotted line on the accompanying graph. The ratio of the ordinate of the point of intersection of the graph for a particular detergent with this curve to the abscissa of this point of intersection is an index of the initial cleansing action of that detergent, while the magnitude of the slope of the graph is an index of the continued cleansing action in later washes.

The results obtained in a few series of washing tests are shown by Figure 12. These graphs represent:

(*a*) Standard soap flakes, 0.25 per cent concentration, 7$^1/_2$-minute intervals
(*b*) Tallow soap, 0.25 per cent concentration, 7$^1/_2$-minute intervals
(*c*) Standard soap flakes, 0.25 per cent concentration, 300-minute intervals
(*d*) Distilled water, 30-minute intervals
(*e*) Distilled water, 7$^1/_2$-minute intervals

It will be observed that in series (*a*), (*b*), and (*e*) the points representing the results of the first washing fall on or very close to the theoretical line, while in those series in which the washing was continued for a relatively long time (runs *c* and *d*) the points fall below this line. These discrepancies are evidently due to the change which takes place in the particle size of the dirt on continued agitation with the detergent solution. In the runs made with the 5-hour periods with the dilute soap solution the change in the character of the dirt is also evidenced by the abrupt break in the graph after the first washing. For the three series of experiments made under similar conditions the value of the ratios of the coördinates of the points of intersection of the detergency graphs with the theoretical curve for the first washing are:

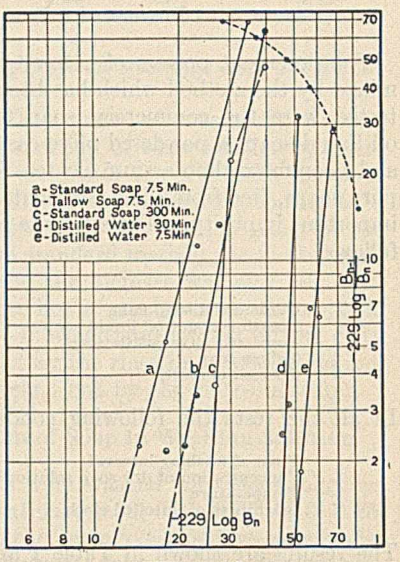

Figure 12

(*a*)	Commercial soap flake	1.117
(*b*)	Tallow soap	1.104
(*c*)	Distilled water	0.785

The values for the slopes of the curves are:

(*a*)	Commercial soap flake	3.8
(*b*)	Tallow soap	5.07
(*c*)	Distilled water	10.76

It is therefore evident that this treatment of the experimental data gives simple numerical values which may be taken as indices of the detergency of the soaps under test and that these data are capable of being referred to similar data obtained from tests made on some pure soap taken as a standard.

Synthetic Organic Chemical Manufacturers Elect Officers

The seventh annual meeting of the Synthetic Organic Chemical Manufacturers Association was held on December 14 at the Hotel Commodore, New York, N. Y. The executive meeting of the association was held in the morning, at which the following officers were elected for the coming year:

President: August Merz (reëlected)
Treasurer: Albert J. Farmer
Vice Presidents:
  Ralph E. Dorland (reëlected)
  W. F. Harrington (reëlected)
  E. H. Killheffer (reëlected)
  A. Cressy Morrison
Board of Governors:
  E. A. Barnett, John Campbell & Company
  J. W. Boyer, Monsanto Chemical Works
  A. S. Burdick, Abbott Laboratories
  R. W. Cornelison, Peerless Color Company
  Ralph E. Dorland, Dow Chemical Company
  A. J. Farmer, Pharma-Chemical Corporation
  W. F. Harrington, E. I. du Pont de Nemours & Company
  Glenn Haskell, U. S. Industrial Chemical Company
  E. H. Killheffer, Newport Chemical Works
  E. H. Klipstein, E. C. Klipstein & Company
  August Merz, Heller & Merz Company
  A. Cressy Morrison, Carbide & Carbon Chemicals Corporation
  Wm. S. Weeks, Calco Chemical Company
  S. W. Wilder, Merrimac Chemical Company
  F. G. Zinsser, Zinsser & Company

Solid Solutions of Lime and Arsenic Acid[1]

A. T. Clifford and F. K. Cameron

UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.

SMITH[2] has shown that in the system calcium oxide, arsenic acid, and water at 25° C., monocalcium arsenate, $CaH_4(AsO_4)_2$, is the stable solid phase in contact with liquid solutions containing more than 518 grams arsenic oxide, As_2O_5, per liter, while a diarsenate, $CaHAsO_4.H_2O$, is the stable solid in contact with more dilute liquid solutions, down to a concentration of 25 grams arsenic oxide per liter. At yet lower concentrations of the liquid phase a more basic solid is stable, and it appears that this has generally been regarded as a mechanical mixture of calcium hydroxide or calcium oxide with a hypothetical tricalcium arsenate.[3] That the latter exists cannot be assumed on the basis of the evidence so far offered; while the existence of a series of solid solutions of calcium oxide and phosphoric acid in contact with solutions of low concentration of phosphoric acid, as shown by Cameron and Bell,[4] suggested that a similar series of solid solutions of calcium oxide and arsenic acid would be found to be stable in contact with liquid solutions of arsenic acid. It is probable that the calcium arsenates of commerce, now widely used as insecticides and in combating weevil infestations, are such solid solutions. They are sometimes precipitated at considerably higher temperatures than 25° C. and may not be in final equilibrium with their mother liquor, since the attaining of such equilibrium has been found to be a matter of weeks or months rather than hours. But the writers know of no evidence that they are different in any essential from the precipitates they studied.

Experimental

The lime and the arsenic acid used were C. P. grade obtained from the Baker Chemical Company. The arsenic acid was shown to be free from arsenious acid on testing with iodine and starch paste.

A series of Winchester quart or acid bottles were nearly filled with a saturated solution of calcium hydroxide, and varying quantities of a solution of arsenic acid (250 grams As_2O_5 per liter) were added to the several bottles with continued stirring. A fluffy, non-crystalline precipitate formed in each case. Six of these bottles, occasionally shaken, were kept for 2 months in a large water bath at approximately 25° C. Because of the low concentrations in the liquid phase and the analytical difficulties involved, the standard "indirect" methods of analysis could not be reliably employed and the procedure followed was to determine the ratio of As_2O_5 to CaO in the solid phases. The solid phases were separated from the mother liquors by centrifuging, the very small amount of mother liquor remaining being negligible since very dilute. One-liter portions of the mother liquor were withdrawn from the bottles through cotton-wool plugs in such a way as to prevent absorption of carbon dioxide in the operation. Solutions 1, 2, and 3 were basic to phenolphthalein. Solutions 4 and 5 gave no color reaction with either phenolphthalein or methyl orange. The other solutions were plainly acid in reaction.

Another series of bottles of 250 cc. capacity was prepared but with concentrations of arsenic acid sufficient to insure precipitation of calcium diarsenate as solid phase. Fifty cubic centimeter portions of the mother liquor were withdrawn for analysis.

Calcium was determined by adding sufficient nitric acid to insure complete solution. Then, after neutralizing with ammonia slightly acidified with acetic acid, ammonium oxalate was added. The precipitated calcium oxalate was taken up with sulfuric acid and the mixture titrated with standard solution of permanganate. Arsenic in the liquid phase was precipitated as silver arsenate from solutions slightly acid from acetic acid. The silver arsenate, after washing, was dissolved in nitric acid and the silver precipitated and weighed as silver chloride. Arsenic in the solids was determined by bringing the solid into solution with nitric acid, adding potassium iodide, and then strongly acidifying with hydrochloric acid. The liberated iodine was titrated with a standard solution of thiosulfate. Blanks showed the effect of the nitric acid used to be negligible. The amounts of arsenic in solutions 1, 2, and 3 were too small to be determined by the method described. It was shown to be present by the Reinsch test.

Discussion of Results

The results obtained are given in Table I. The data for solutions 8 and 10 in contact with dicalcium arsenate are in good accord with those of Smith. The data for solution 9 are taken from Smith's paper.[2]

Table I—Concentrations in the System $CaO-As_2O_3-H_2O$ at 25° C.

SOLUTION	LIQUID PHASE		SOLID PHASE
	As_2O_5	CaO	Ratio As_2O_5:CaO
	Grams per 1000 grams solution		
1	Trace	0.909	1.083
2	Trace	0.735	1.117
3	Trace	0.598	1.213
4	2.13	0.684	1.364
5	6.42	0.240	1.414
6	8.82	0.732	1.569
7	1.372	0.956	
8	23.4	6.2	
9	27.8	7.2	
10	40.0	9.9	

The ratio As_2O_5 to CaO for the solid phases in contact with solutions 1, 2, 3, 4, 5, and 6 varies continuously from 1.08 to 1.60. Consequently, these solids are members of a series of solid solutions. The ratio of arsenic acid to lime in the hypothetical tricalcium arsenate is 1.367, corresponding to a solution near No. 4 in the series tested. If this salt actually exists, we then have two series of solid solutions intersecting, instead of one series. The analytical methods available are not sufficiently delicate to determine which alternative is correct. A plot of these results shows that the isotherm for the liquid solutions in contact with the solid solutions has a minimum point. There can be, therefore, a liquid solution in equilibrium with a solid solution in which the arsenic acid–lime ratio in the liquid phase is the same as in the solid phase. The plot indicates that it probably lies very close to the point where the solid phase has the ratio corresponding to tricalcium arsenate. Continued leaching

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[1] Received June 28, 1928.

[2] *J. Am. Chem. Soc.*, **42**, 259 (1920).

[3] Robinson, *J. Agr. Research*, **13**, 281 (1918); Haywood and Smith, U. S. Dept. Agr., *Bull.* **750** (1918); Tartar, Wood, and Hunter, *J. Am. Chem. Soc.*, **46**, 804 (1924); McDonnell, Smith, and Coad, U. S. Dept. Agr., *Bull.* **1115** (1922); Smith and Hendricks, IND. ENG. CHEM., **16**, 950 (1924); Reedy and Haag, *Ibid.*, **13**, 1038 (1921).

[4] *J. Am. Chem. Soc.*, **27**, 1512 (1905).

of this complex will give solutions with a constant ratio of arsenic acid to lime, which has misled previous investigators to consider the complex a definite compound. There seems to be no evidence that tricalcium arsenate can be formed from aqueous solutions, nor persist in contact with them. Analytical methods purporting to separate it from other calcium compounds should be viewed with caution.

Tricalcium arsenate may be formed, as in the Cullen process, where calcium oxide and arsenic trioxide are heated in a current of air. As far as the writers know, the products so obtained are not crystalline, and one may well hesitate to express a positive opinion. That any one of them will, in contact with water, form two solutions, one solid, the other liquid, is reasonably certain.

Deterioration of Soap-Nicotine Preparations—II[1]

C. C. McDonnell and J. J. T. Graham

Food, Drug, and Insecticide Administration, U. S. Department of Agriculture, Washington, D. C.

Commercial soap-nicotine preparations decrease in nicotine content on storage. This loss is shown to be due to volatilization of nicotine and, in the case of soaps made from drying oils such as fish oil, to oxidation which results in a condensation product between the nicotine and the fatty acids. The work here reported shows that this decomposition can be prevented by packing the soaps so that they are completely protected from the air and that such products can be produced and marketed so as to retain their nicotine content for at least two years.

In our work in connection with the enforcement of the Insecticide Act it has been found that most of the commercial soap preparations containing nicotine, especially those in cake form, contain less nicotine than the manufacturer claimed to be present. Several years ago an investigation to determine the cause of this shortage was begun. In a previous paper McDonnell and Nealon[2] reported that hard soaps made from sodium hydroxide, menhaden fish oil and nicotine solution lose nicotine rapidly on storage regardless of the type of package, and that potash soaps (soft soap) and soft soda soaps containing nicotine retain practically their original nicotine strength for a period of four years. In other words, whether or not nicotine is lost depends upon the physical condition of the product. It was further reported that any loss of nicotine was due, not to volatilization, but to chemical changes, whereby it was converted into an insoluble, non-volatile, polymeric form or a condensation product, probably the latter, as the decrease in nicotine was accompanied by a decrease in the fatty acids of the soap, indicating a reaction between the two.

The present paper reports the results of additional work on this subject, including that with soaps made from different types of oils, both drying and non-drying.

Preparation of Samples

Soda and potash soaps were prepared with the following oils and fatty acids: menhaden fish oil, cottonseed oil, linseed oil, red oil, and stearic acid. Nicotine was added in the form of a water solution of the "free" alkaloid.

Note—Soaps containing nicotine sulfate solution, which is the most common form of commercial nicotine preparations, would no doubt act in the same way. Since alkali or soap sets nicotine free from nicotine sulfate, its use would have liberated fatty acids and added an additional factor in making it necessary to provide for more alkali in order to produce a neutral soap.

The saponification values of the oils and fatty acids were determined, and the exact amount of alkali solution (prepared practically free from carbonate) required to form a neutral alkaline or superfatted soap as desired was added. Saponification was accomplished in a jacketed steam kettle equipped with an agitator, the ingredients being added to the hot kettle and heated somewhat below 100° C. until the soap attained a pasty consistency, when it was transferred to a shallow, flat, enameled pan to cool. Small quantities of water and nicotine were lost during saponification, but complete analyses of the finished soaps were made.

Fish-oil soaps were used in most of the work. They were prepared in three types—neutral, alkaline, and superfatted soda soaps (both in cake and paste form), and neutral and alkaline potash (soft) soaps. The cottonseed oil, red oil, and stearic acid soaps were prepared only in the neutral form. The formulas are given in Table I.

Soft soda soaps were prepared from portions of the hard soaps A, B, C, I, and K by adding a sufficient quantity of water to convert them to the consistency of a thin jelly and then enough nicotine solution to make the total nicotine content approximately 3 to 4 per cent. These were designated D, E, F, J, and L. All the samples were packed in glass jars fitted with rubber rings and tightly closed. The hard soaps were cut into cakes about 4 × 4 × 10 cm. and wrapped in heavy waxed paper before being placed in jars. A sufficient number of cakes was prepared so that a fresh cake could be taken for each analysis, and all samples were analyzed at the time of packing and after storage for 1, 3, 5, 8, 12, and 24 months.

Methods of Analysis

In order to secure a representative sample, a section through the center of the cake of the hard soaps was taken in each case, and the soft soaps were thoroughly mixed and a portion was removed for analysis.

Water—Water was determined by distilling 15 to 20 grams of the sample with 50 cc. of dry xylene (about 10 grams of lump rosin being added to prevent foaming) and the distillate was collected in a distilling tube and measured, according to the method described by Dean and Stark.[3]

Fatty Acids—For the determination of fatty anhydrides, nicotine, and insoluble material, a weighed sample of approximately 20 grams was dissolved in hot water and transferred to a separatory funnel and an excess of hydrochloric acid was added. After the solution was cool the fatty acids were extracted with ether, the ether was evaporated in a weighed beaker and the residual fatty acids were weighed. The residue in the separatory funnel was dissolved in alcohol and transferred to a weighed beaker. The alcohol was

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[1] Presented as a part of the Symposium on Insecticides and Fungicides before the Division of Agricultural and Food Chemistry at the 75th Meeting of the American Chemical Society, St. Louis, Mo., April 16 to 19, 1928.

[2] Ind. Eng. Chem., **16**, 819 (1924).

[3] J. Ind. Eng. Chem., **12**, 486 (1920).

Table I—Formulas Used in Making Soap-Nicotine Preparations[a]

Nature of Soap	Linseed Oil	Stearic Acid	Oleic Red Oil	Cottonseed Oil	Menhaden Fish Oil	Potassium Hydroxide	Sodium Hydroxide	Nicotine Solution (40%)	Water
	Grams	Grams	Grams	Grams	Grams	Grams	Grams	Cc.	Cc.
Soda-fish oil:									
A—Neutral, hard	..	..	..	..	3400	...	447	400	1600
B—Alkaline, hard	..	..	..	..	3400	...	500	400	1600
C—Superfatted, hard	..	..	..	..	3400	...	425	350	1600
I—Neutral, hard	..	..	..	..	3400	...	471	700	1600
Potash-fish oil:									
G—Neutral, soft	..	..	..	..	3400	660	...	375	2000
H—Alkaline, soft	..	..	..	..	3400	700	...	350	2000
Soda-cottonseed oil:									
K—Neutral, hard	..	..	..	3400	..	...	475	350	2200
Potash-cottonseed oil:									
M—Neutral, soft	..	..	..	3400	..	666	..	375[b]	2000[b]
Soda-oleic red oil:									
N—Neutral, hard	..	..	3400	..	..	...	485	350	1600[c]
O—Neutral, soft	..	..	3400	..	..	...	485	350	1600
Potash-oleic red oil:									
P—Neutral, soft	..	..	3400	..	..	679	...	350	2000
Soda-stearic acid:									
Q—Neutral, hard	..	3400	..	..	..	...	511	350	1600
Potash-stearic acid:									
R—Neutral, soft	..	1700	..	..	..	358	...	225	3000
Soda-linseed oil:									
X—Alkaline, hard	850	..	..	..	..	...	125	100	400

[a] The saponification number of the oil used in the preparation of samples A, B, C, and H was 184.0; that of the oil used in G and I, 194.2, and those of the cottonseed oil, red oil, and stearic acid were 195.89, 199.8, and 210.5, respectively.

[b] It was necessary to add additional water to this sample to bring it to the desired consistency; additional nicotine solution was also added so that the finished product contained about 2.5 per cent of nicotine.

[c] In order to produce a hard soap it was necessary to evaporate a part of the water from this sample.

evaporated and the residue was dried at 105° C., weighed and reported as "ether-insoluble residue."

NICOTINE—The extracted aqueous solution was made alkaline and steam-distilled and the nicotine was determined by precipitation with silicotungstic acid according to the method of the A. O. A. C.[4]

NITROGEN—Nitrogen was determined by the Kjeldahl-Gunning-Arnold method, the digestion being continued long enough to convert all the nitrogen of the nicotine into ammonia. From the percentage of nitrogen obtained the nicotine equivalent was calculated.

ALKALI—Alkali was determined by ashing approximately 5 grams of the soap in a platinum dish, dissolving the ash in water and titrating with a standard acid solution.

The results of analyses are given in Table II.

Results

An examination of the results shows that at the expiration of 12 months:

(1) All the hard soaps had lost nicotine, although in only two cases was the loss in excess of 0.25 per cent.

Note—Sample (X), the linseed oil soap, was not prepared until after the investigation had been under way for some time and the results showed that the drying or non-drying quality of the oil used had an influence on the loss of nicotine. It was stored for only 8 months, with an intermediate analysis at the expiration of 5 months.

(2) The loss of nicotine from the soft soaps, with one exception, was practically negligible.

(3) Excess of alkali or of fat in the soap had no apparent influence on the rate of loss of nicotine.

(4) The average loss of nicotine from hard soaps prepared from drying or semi-drying oils was greater than that from soaps prepared from the non-drying oils.

The samples were analyzed after an additional 12-month period of storage under the same conditions, and the results indicate that the same general conclusions apply as for the first 12-month period.

The physical appearance of the hard soaps after storage was also of interest. Those prepared from red oil and stearic acid showed no change, but, with two or three exceptions, the samples prepared from fish oil and cottonseed oil had developed a discolored layer, ranging from a light brown to black, which extended into the cake for from 2 to 6 mm. This layer contained the black resinous material noted by McDonnell and Nealon[2] in the hard soda fish-oil soaps after storage. In one case in which no discoloration occurred it was noted on opening the jar that there was an inrush of air, indicating that the jar had been hermetically sealed and that the oxygen had been used up. Also in two other cases the cakes showed no discoloration and the nicotine content was the same as when packed. These facts pointed to some connection between the nicotine loss and oxidation.

Note—It was assumed that the small amount of oxygen in the jars that were hermetically sealed was not sufficient to cause any appreciable change and that where loss of nicotine and marked discoloration occurred the jars were not air-tight.

Effect of Contact with Air on Deterioration

In order to verify the theory that the deterioration of the soaps was caused by contact with the air, the soaps from the jars in which there had been the least deterioration after 12 months' storage were trimmed of all the discolored layer and packed in the following ways: (1) unwrapped and placed in glass jars, care being taken to see that they were tightly sealed; (2) wrapped in tin foil, then heavily coated with paraffin by dipping to give complete protection from the air; (3) wrapped in heavy waxed paper, but not completely air-tight, and stored in a dark closet; (4) the trimmings from these repacked soaps stored in a glass jar but not sealed.

In view of the observation that the soaps prepared from drying oils deteriorated more rapidly than those made from non-drying oils, it was decided to study also the effect of storage under the conditions just described on a soap prepared from linseed oil and containing nicotine. (Sample X, Tables II and III)

In order to determine the influence of contact with the air on the potash (soft) soaps containing nicotine, portions of samples G and H were stored in glass jars and covered only with filter paper to exclude the dust. These samples were stirred occasionally in order to insure more thorough contact with the air, and water was added from time to time to replace that lost by evaporation. They were exposed in this manner for 17 months.

All these samples were analyzed at the end of 12 months except the linseed oil soap, which was stored for only 8 months. The results of this experiment are given in Table III. As the manner of storage caused a marked drying of the samples in some cases, all results in this table are reported on a water-free basis.

In order to illustrate more clearly the effect of air on the two classes of soaps, graphs embodying the data under the subheadings (2), (3*a*), and (3*b*) in Table III were prepared.

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[4] Assocn. Official Agr. Chem., Methods, p. 66 (1925).

Table II—Analyses of Soap-Nicotine Preparations Stored in Glass Jars

TIME OF STORAGE	NICOTINE (Detd.)	NICOTINE (Calcd. from nitrogen)	WATER	FATTY ANHYDRIDES	ALKALI	ETHER-INSOLUBLE RESIDUE
Months	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent* (Na_2O)	*Per cent*
SAMPLE A						
When made	3.18	3.3	19.2	63.2	9.6	None
1	3.14	...	..	63.4	...	Trace
3	3.01	...	..	62.1	...	Trace
5	3.02	...	18.3	63.0	...	Trace
8	2.93	...	..	62.9	...	Trace
12	2.95	...	18.9	62.6	...	Trace
24	2.75	3.1	19.3	62.2	...	1.8
SAMPLE B						
When made	2.53	2.7	24.8	58.9	9.7	None
1	2.53	...	..	59.4	...	Trace
3	2.50	...	..	58.9	...	Trace
5	2.46	...	23.9	59.3	...	Trace
8	2.45	...	..	59.3	...	Trace
12	2.37	...	25.0	58.8	...	Trace
24	1.99	2.5	24.0	57.4	...	2.4
SAMPLE C						
When made	2.66	2.7	22.0	62.4	8.7	None
1	2.63	...	..	62.4	...	Trace
3	2.50	...	..	61.6	...	Trace
5	2.59	...	22.4	62.8	...	Trace
8	2.61	...	..	62.7	...	Trace
12	2.52	...	22.2	62.7	...	Trace
24	2.06	2.1	22.1	60.8	...	2.6
SAMPLE D						
When made	3.83	3.8	66.2	24.4	3.7	None
1	3.84	...	..	24.0	...	Trace
3	3.83	...	..	..	...	Trace
5	3.82	...	66.2	24.4	...	Trace
8	3.79	...	..	24.4	...	Trace
12	3.74	...	66.2	24.5	...	Trace
24	3.65	3.8	65.7	24.2	...	0.2
SAMPLE E						
When made	3.47	3.5	62.4	27.2	4.4	None
1	3.49	...	..	27.2	...	Trace
3	3.47	...	..	27.2	...	Trace
5	3.58	...	62.5	27.6	...	Trace
8	3.52	...	..	27.6	...	Trace
12	3.50	...	62.0	27.6	...	Trace
24	3.54	3.8	61.9	28.4	...	Trace
SAMPLE F						
When made	3.08	3.2	65.9	25.4	3.5	None
1	3.09	...	..	25.5	...	Trace
3	3.08	...	..	25.4	...	Trace
5	3.05	...	65.7	25.6	...	Trace
8	3.10	...	..	25.4	...	Trace
12	3.08	...	66.1	25.4	...	Trace
24	3.08	3.2	66.1	25.4	...	Trace
SAMPLE G						
When made	2.76	2.9	27.8	56.2	(K_2O) 9.1	None
1	2.75	...	..	56.1	...	Trace
3	2.65	...	..	56.3	...	Trace
5	2.73	...	26.7	56.2	...	Trace
8	2.73	...	..	56.3	...	Trace
12	2.73	...	27.0	56.3	...	Trace
24	2.65	3.0	24.7	56.9	...	Trace
SAMPLE H						
When made	2.39	2.4	19.2	59.5	11.0	None
1	2.41	...	..	59.7	...	Trace
3	2.44	...	..	59.6	...	Trace
5	2.42	...	19.5	59.6	...	Trace
8	2.43	...	..	59.9	...	Trace
12	2.43	...	19.8	59.8	...	Trace
24	2.40	2.5	20.0	60.0	...	Trace
SAMPLE I						
When made	5.79	5.7	19.0	61.7	(Na_2O) 7.8	Trace
1	5.48	...	..	60.9	...	0.3
3	5.35	...	..	60.8	...	0.5
5	5.51	...	19.0	61.8	...	...
8	5.35	...	..	61.8	...	...
12	4.96	...	17.6	60.6	...	3.3
24	4.64	5.7	18.4	59.2	...	3.7
SAMPLE J						
When made	5.84	6.1	63.9	24.4	2.6	Trace
1	5.84	...	..	24.5	...	Trace
3	5.82	...	..	24.3	...	Trace
5	5.81	...	64.4	23.7	...	Trace
8	5.83	...	..	24.4	...	Trace
12	5.82	...	64.4	24.4	...	Trace
24	5.84	6.2	64.7	24.4	...	Trace
SAMPLE K						
When made	2.52	2.6	22.5	62.0	7.0	None
1	2.40	...	..	61.4	...	Trace
3	2.27	...	..	..	...	Trace
5	2.02	...	21.8	61.6	...	Trace
8	1.88	...	..	61.6	...	Trace
12	1.59	...	19.6	62.5	...	Trace
24	1.33	2.5	21.4	60.8	...	1.75
SAMPLE L						
When made	2.97	3.0	74.3	19.1	2.2	None
1	2.87	...	..	18.6	...	Trace
3	2.85	...	..	..	...	Trace
5	2.85	...	74.1	18.7	...	Trace
8	2.78	...	..	18.4	...	Trace
12	2.73	...	73.5	18.6	...	Trace
24	2.72	3.1	73.6	18.9	...	Trace
SAMPLE M						
When made	2.32	2.5	71.7	20.9	(K_2O) 3.6	None
1	2.30	...	..	20.7	...	Trace
3	2.28	...	..	20.7	...	Trace
5	2.22	...	70.5	20.2	...	Trace
8	2.20	...	..	20.6	...	Trace
12	2.18	...	70.6	20.6	...	Trace
24	1.99	2.5	71.3	20.6	...	Trace
SAMPLE N						
When made	2.94	3.1	17.9	70.4	(Na_2O) 10.9	None
1	..	...	..	..	...	...
3	2.93	...	..	72.2	...	Trace
5	2.93	...	17.2	71.6	...	Trace
8	2.93	...	..	71.4	...	Trace
12	2.83	...	17.6	71.8	...	Trace
24	2.64	3.1	17.0	71.7	...	Trace
SAMPLE O						
When made	2.49	2.7	31.6	58.2	9.0	None
1	..	...	..	..	...	...
3	2.51	...	..	59.1	...	Trace
5	2.52	...	31.3	59.3	...	Trace
8	2.49	...	..	58.6	...	Trace
12	2.47	...	31.8	58.8	...	Trace
24	2.44	2.7	30.7	59.7	...	Trace
SAMPLE P						
When made	2.45	2.6	35.8	52.3	(K_2O) 9.0	None
1	2.48	...	..	52.7	...	Trace
3	2.46	...	..	53.8	...	Trace
5	2.50	...	34.5	53.4	...	Trace
8	2.47	...	..	53.0	...	Trace
12	2.43	...	34.9	53.2	...	Trace
24	2.14	2.6	35.1	52.7	...	Trace
SAMPLE Q						
When made	2.33	2.4	31.5	59.5	(Na_2O) 9.6	None
1	2.28	...	..	..	...	...
3	2.37	...	..	60.9	...	Trace
5	2.41	...	32.5	60.9	...	Trace
8	2.47	...	..	58.5	...	Trace
12	2.34	...	32.2	57.7	...	Trace
24	2.27	2.3	32.6	59.6	...	Trace
SAMPLE R						
When made	1.95	2.1	55.4	31.0	(K_2O) 6.5	None
1	1.94	...	..	..	...	Trace
3	1.97	...	..	36.4	...	Trace
5	1.97	...	54.7	37.0	...	Trace
8	1.94	...	..	37.1	...	Trace
12	1.95	...	55.3	36.7	...	Trace
24	2.05	2.1	54.9	36.2	...	Trace
SAMPLE X						
When made	3.84	3.9	17.8	63.7	...	None
1	..	...	..	..	...	...
3	..	...	..	..	...	...
5	3.46	3.9	18.4	62.8	...	Trace
8	3.13	4.0	18.6	61.8	...	0.9

Figure 1 represents the average of the data for the drying oil soaps, and Figure 2 that for the non-drying oil soaps. The nicotine originally present is plotted as 100, and the average percentage remaining at the end of a year is calculated to percentage of that originally present and plotted, thus indicating the rate of loss.

At the end of the 12-month storage period there was no discoloration or evidence of physical change in any of the samples packed in tin foil and paraffined, nor in those unwrapped and packed in sealed glass jars, with the exception of sample (I), which was high in nicotine. Neither was there any change in the physical appearance of the soaps made from oleic red oil or stearic acid, other than loss of moisture, regardless of how they were packed. The fish-oil, cottonseed-oil and linseed-oil soaps stored in paper wrappings (not air-tight), however, showed marked discoloration which extended to a depth of from 2 to 6 mm.

An examination of the chemical results sheds much light on the deterioration of nicotine soaps and indicates how the loss of nicotine can be prevented. In the samples packed so as to exclude the air entirely, there was practically no loss of nicotine, except a slight deterioration in the samples packed unwrapped in sealed glass jars, in which cases the soaps were exposed to the small amount of air contained in the jars.

The soaps wrapped in waxed paper (not completely protected from the air) showed considerable loss of nicotine. The fish-oil (a drying oil) soaps showed much surface discoloration, a loss in fatty acids as well as in nicotine and a large insoluble residue. The nicotine equivalent of the total nitrogen, however, was practically the same as the actual nicotine originally present. The soaps prepared from cottonseed oil (a semi-drying oil) reacted very similarly, but did not show so great a loss in fatty acids nor so large an insoluble residue. Here again the nicotine calculated from the nitrogen content of the sample was as high as the nicotine originally present. In the soap prepared from linseed oil (a drying oil) there was also a loss and fixation of the nicotine, but apparently little change in the fatty acids and very little insoluble residue was formed. The fixation product in this case was mostly soluble in the ether and was weighed along with the fatty acids.

Table III—Analyses of Soaps after Storage of One Year Packed in Different Ways

(Results calculated to dry basis)

	Nicotine			
Sample	Detd.	Calcd. from nitrogen	Fatty Anhydrides	Insoluble Material
	Per cent	*Per cent*	*Per cent*	*Per cent*
A(0)	3.94	4.08	78.1	Trace
A(1)	4.01	4.05	78.8	0.3
A(2)	3.95	4.15	79.1	Trace
A(3*a*)	1.24	4.95	48.2	29.5
A(3*b*)	2.61	4.07	78.8	0.5
A(4)	0.45	3.83	51.7	25.5
B(0)	3.37	3.58	78.4	Trace
B(1)	3.15	3.46	77.9	0.7
B(2)	3.30	3.49	79.2	0.3
B(3*a*)	1.24	3.64	62.7	13.6
B(3*b*)	2.67	3.46	78.9	0.3
B(4)	0.62	3.42	59.5	12.8
C(0)	3.41	3.46	80.0	Trace
C(1)	3.27	3.42	80.3	0.5
C(2)	3.32	3.59	79.5	0.4
C(3*a*)	1.32	3.79	62.4	19.3
C(3*b*)	2.23	3.34	79.9	0.4
C(4)	0.67	3.31	59.2	17.9
I(0)	7.14	7.00	76.1	Trace
I(1*a*)	4.38	6.70	58.4	13.5
I(1*b*)	6.19	..	77.4	0.6
I(2)	6.67	6.93	76.0	0.8
I(3*a*)	2.20	6.50	55.3	16.2
I(3*b*)	4.80	6.02	77.3	0.7
I(4)	1.06	7.51	50.7	24.8
K(0)	3.25	3.41	80.0	Trace
K(1)	3.05	3.33	78.2	Trace
K(2)	3.17	3.31	79.7	Trace
K(3*a*)	1.17	3.52	72.6	3.6
K(3*b*)	2.28	2.79	78.7	Trace
K(4)	0.22	3.40	74.1	6.9
N(0)	3.58	3.84	85.8	Trace
N(1)	3.25	3.85	86.3	Trace
N(2)	3.53	3.86	86.2	Trace
N(3*a*)	1.72	2.33	87.6	Trace
N(3*b*)	3.09	3.15	84.6	Trace
N(4)	3.15	3.14	86.2	Trace
Q(0)	3.40	3.46	86.9	Trace
Q(1)	3.23	3.64	85.3	Trace
Q(2)	3.19	3.74	85.5	Trace
Q(3*a*)	0.90	1.24	87.8	Trace
Q(3*b*)	1.35	1.51	87.9	Trace
Q(4)	3.04	3.28	85.6	Trace
X(0)	4.67	4.91	77.5	None
X(1)	3.84	4.90	75.8	1.1
X(2)[c]	4.51	4.93	75.6	0.3
X(3)[c]	2.76	4.65	75.9	0.9
X(4)[c]	2.75	4.60	75.0	0.9
G	3.82	4.05	77.8	None
G[b]	2.32	3.48	71.3	3.2
H	2.69	2.68	67.1	None
H[b]	2.19	2.78	72.5	2.4

(0) Analysis at time of preparation.
(1) Stored unwrapped in sealed glass jars.
(2) Stored wrapped in tin foil and dipped in paraffin.
(3) Stored wrapped in waxed paper (not air-tight) in dark closet.
(4) Trimmings from soap, stored in glass jars without rubbers (not air-tight).
(*a*) Outside layer of soap.
(*b*) Inside portion of cake.
(*c*) Stored for 8 months.
(*d*) Stored for 17 months.

The soaps prepared from oleic red oil and stearic acid (non-drying oils) packed in this way behaved differently. There was a loss of nicotine, although not so great as with the drying oil soaps, but no reaction between the nicotine and the fatty acids occurred. The loss appeared to be due simply to a volatilization of the nicotine.

The soft soaps G and H exposed to the air lost nicotine much less rapidly than the hard soaps to which the air had access.

It is of interest to note that it was the fatty acids of the drying or semi-drying oils with which the nicotine reacted to form the insoluble (soluble in the case of the linseed-oil soap) resinous material and that there was no such reaction with the non-drying oils. Moreover, where loss of nicotine occurred, the nicotine, calculated from the nitrogen determination, in the surface layers of the soaps made from the drying oils is greater after storage than that contained in the center of the cake and greater than that originally present, while in the case of soaps made from the non-drying oils it is less in all parts of the cake but the greater decrease has occurred at the surface. This is explained on the basis that, while there is an actual loss of nicotine in both cases, it volatilizes from non-drying oil soaps, but in the drying oil soaps it is fixed through reaction with the fatty acids and oxygen of the air.

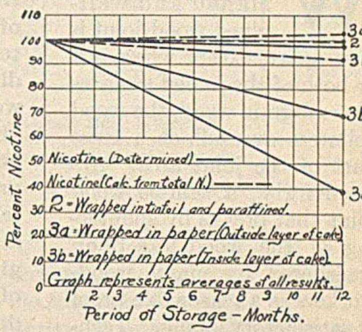

Figure 1—Soaps from Drying Oils

No extended investigation was made to determine the exact composition of the resinous material. However, the work done showed that it was of indefinite composition. It contained nitrogen in quantities ranging in different samples from 0.8 to 3 per cent, equivalent to from 4.5 to 17 per cent of nicotine, but only traces of nicotine could be obtained by adding sodium hydroxide to the residue and distilling with steam.

Summary

Soap-nicotine preparations ordinarily found on the market decrease in nicotine content on storage.

Hard soda soaps lose nicotine more rapidly on exposure to the air than potash soaps. However, soft soda soaps and potash (soft) soaps lose it at about the same rate.

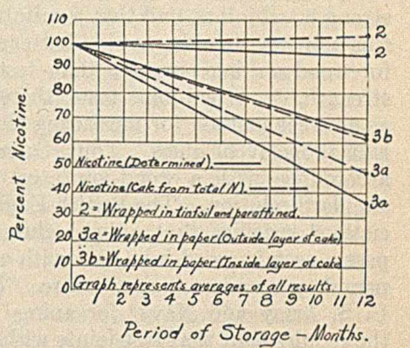

Figure 2—Soaps from Non-Drying Oils

Excess of alkali or fat in the soaps has no appreciable influence on the rate of loss of nicotine.

The loss of nicotine from soap-nicotine preparations made with drying oils (fish oils, cottonseed oil, linseed oil) and packed so that air is not excluded is due mainly to oxidation, the nicotine with part of the fatty acids of the soap being converted into an insoluble condensation product of indefinite composition.

The loss of nicotine from soap-nicotine preparations made with non-drying oils (oleic red oil, stearic acid) and stored without air being excluded is due to volatilization of nicotine, no insoluble condensation product being formed.

Both hard and soft soaps, whether made from drying or non-drying oils, when packed so that they were completely protected from the air, suffered no loss in nicotine content during two years of storage.

Significance of Mechanical Wood-Joint Tests for the Selection of Woodworking Glues[1]

T. R. Truax, F. L. Browne, and Don Brouse

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

The testing of glued wood joints is well adapted to the laboratory study of such problems as the usefulness of new adhesives or new treatments of old ones, the technic of gluing operations, the gluing characteristics of different woods, and the causes of weak joints in specific woodworking operations. Wood-joint tests are not suitable for the grading of animal glues for woodworking, because in practice more direct evidence of the physical properties of the glue is afforded by the viscosity and jelly-strength tests. Strong joints may be made with any animal glue suitable for woodworking, but different gluing conditions must be used according to the grade of the glue. If wood-joint tests are made with glues of different grades under a uniform set of gluing conditions, the grade of glue that will give the best results will be the glue best adapted to the particular gluing conditions and fair deductions regarding the intrinsic "strength" of the glues cannot be drawn. Wood-joint tests are used to some extent for selecting casein and vegetable glues, because no better grading system has been worked out and because such glues yield strong joints under a comparatively wide range of gluing conditions. An unfavorable joint test indicates that the glue is not reliable under the particular gluing conditions tried; it does not prove the glue to be lacking intrinsically in "strength" or "adhesiveness."

WHEN a well-designed and well-glued wood joint is torn apart, except where one or both of the joined surfaces are end-grain wood, the wood splinters over all or a large part of the joint area. Accordingly, a sample wood joint that breaks by splintering of the wood has been considered by many woodworkers as a reasonable proof of satisfactory gluing. Technologists, however, have revealed that wood failure alone is not a satisfactory criterion of good gluing and have therefore designed numerous special types of wood joints suitable for testing in machines that indicate the load under which failure takes place.

It has been generally assumed that woodworking glues possess an intrinsic property known as "strength" or "adhesiveness," which is significant of their value for making strong wood joints, and that a suitable technic for measuring this property should provide a better standard of grading glues for woodworking purposes than tests of viscosity and jelly strength.[1,*] Wood-joint tests, therefore, suggest themselves as a direct method for measuring this supposedly characteristic property of glues. Thus, Sauer[2] would grade glues in accordance with a wood-joint test and the viscosity of a standard solution. The British Engineering Standards Association[3] specifies that animal glues for airplane propellers pass a certain wood-joint test with a breaking stress of 1100 pounds per square inch or more. The specifications of the U. S. Army and Navy[4] for animal glue formerly included the requirement that test joints withstand an average load of 2400 pounds per square inch before breaking with no specimen breaking below 2200 pounds per square inch. However, this joint test has been abandoned and the present specifications[5] are based chiefly upon a comparison with a standard reference glue with respect to viscosity and jelly strength. Proposed specifications of the Federal Specifications Board do not include joint tests for animal glue.

The attempt to grade glues on the basis of wood-joint tests presents a dilemma. If, on the one hand, the test specimens are well designed and depend upon side-grain gluing, well-made joints fail very largely by splintering of the wood even though a very strong wood and a comparatively low-grade animal glue are chosen. Under such circumstances the strength of the wood rather than that of the glue seems to be measured. If, on the other hand, the test specimens are poorly designed, and especially if they depend upon end-grain gluing, the failure is almost certain to take place entirely in the glue line, but the stress producing failure may be materially less than that required to break good joints in side-grain gluing. Furthermore, the wood-worker objects to an end-grain joint as it is unreliable.

Rudeloff,[6] using a test specimen of red beech with end-grain gluing and carefully applying a load in tension uniformly over the joint area, obtained 1630 pounds per square inch for his strongest joint and considered values exceeding about 1000 pounds per square inch representative of strong joints; variations of individual tests from the average ranged from 16 to 123 per cent. Hopp[7] and Gill[8] avoided the dilemma presented by wood-joint tests by breaking specimens of the dried glue jelly in tension, but the preparation of the specimens was a long and tedious task. Bateman and Towne[9] showed that the strength of such glue specimens varies enormously with the relative humidity of the air. Other workers[10] have found it more convenient to impregnate such materials as filter paper with glue and measure the increase in strength, a procedure open to much criticism.

McBain and his co-workers[11] overcome both experimental difficulty and mechanical objection by preparing thin films of the adhesives for measurement of their strengths in tension. However, the results of such direct observations of the mechanical properties of glues present the following facts, which are contrary to the theory that glues possess an inherent "strength" indicative of the strength of the wood joints that can be made with them:

(1) Animal glues of the wide range in grades employed for woodworking do not differ observably in the strength so measured, though they may vary in a property called by McBain and Lee "deformability."

(2) A high-grade animal glue remains practically unchanged in strength after a solution of it has been kept at 140° F. (60° C.) for a month (a treatment that degrades it enormously).

(3) Although animal glue of the woodworking grades is much stronger than wood joints made from it, there are glues which when tested alone by the method of thin films in tension give lower strength values than wood joints made from them.[12]

Influence of Gluing Technic on Strength of Wood Joints

Previous workers have not fully recognized that the strength of a wood joint depends upon the care in making it and have assumed that an arbitrary set of gluing conditions can be adopted in accordance with which the test joints may be prepared, regardless of the nature of the glue to be tested

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[1] Received May 28, 1928.

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

Table I—Influence of Gluing Conditions on Strength and Type of Failure of Side-Grain Glued Sugar Maple Test Joints Made with Animal Glue of High Grade and Low Grade

Glue	Gluing Conditions							Results of Wood-Joint Tests				Character of Joint
	Designation	Temp. of room[a]	Preheating of wood		Glue spread[b]	Time of assembly[c]	Pressure applied	Load required to break		Wood failure[e]		
			Temp.	Time				Averaged[d]	Minimum	Averaged[d]	Minimum	
		° F.	° F.	Min.		Min.	Lbs./sq. in.[f]	Lbs./sq. in.	Lbs./sq. in.	Per cent	Per cent	
A	I	82	82	120	Medium	2 (open)	200	3950	3190	55	10	Good
	II	80	80	120	Medium	5 (open)	200	2500	1823	27	0	Chilled
	III	120	120	20	Medium	13 (open)	200	1550	212	13	0	Dried
	IV	87	87	120	Light	9 (open)	100	2750	1138	34	0	Chilled
	V	85	120	20	Heavy	1/2 (closed)	400	2350	1417	5	0	Starved
B	II	80	80	120	Medium	5 (open)	200	3100	2667	84	35	Good
	I	82	82	120	Medium	2 (open)	200	2950	2065	75	5	Good
	III	120	120	20	Medium	13 (open)	200	1700	918	4	0	Dried
	VI	83	83	120	Heavy	13 (open)	50	3200	2333	15	0	Chilled
	VII	83	120	20	Heavy	2 (closed)	400	2250	1317	5	0	Starved

[a] The 120° F. temperature is maintained in a special chamber in the gluing laboratory.

[b] "Light" means that the glue was applied to the wood in a comparatively thin layer, "heavy," in a comparatively thick layer.

[c] Time elapsing between application of the glue to the wood and application of pressure to the joint. "Open" assembly means that the two surfaces to be joined were not brought together until end of assembly time, "closed" that they were brought together at beginning of assembly time.

[d] Four pairs of maple blocks were glued and 10 test specimens taken from each joint.

[e] Each broken test specimen was examined visually and an estimate made of the proportion of the total area of the joint in which the failure took place by splintering of the wood rather than in the glue line itself.

[f] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

or the use for which it is intended. The fallacies of such a procedure are that some glues give strong joints only when gluing conditions prevail that differ materially from those necessary to make strong joints with other glues, and that the wood-worker cannot arrange the same gluing conditions in all his operations. For example, in gluing plywood panels a relatively long assembly time elapses between spreading the glue on the wood of the first panel and applying pressure to the bundle of panels in the press. In edge-gluing lumber cores, however, pressure is usually applied to the joint within less than a minute after spreading the glue. The wood-worker using animal glue must buy a very different grade for the two operations if he is to obtain joints strong enough to withstand the maximum stresses that the wood itself can sustain.

The several factors—kind of glue, grade of glue, temperature of room, temperature of wood, temperature of glue, quantity of glue spread, time of assembly, and pressure applied—may be termed collectively the "gluing conditions." These factors govern the strength of wood joints and have been described elsewhere.[13] It will therefore suffice to illustrate with typical results the joint-strength values and types of failure obtained with common wood-working glues under different gluing conditions. Two animal glues, one of high grade and one of comparatively low grade, were chosen because most of the published discussions of glue-joint tests have been upon such glues. Animal glues, moreover, are more sensitive than casein or vegetable (starch) glues to changes in the gluing conditions, and there is a recognized system of grading them independently of the making of wood joints.

Glue A was purchased to match the "standard animal glue" used during the World War as the basis for comparison by the U. S. Government inspectors in certifying animal glues for airplane propeller manufacture. The viscosity of glue A as determined by the standard test procedure of the National Association of Glue Manufacturers[1] was 108 millipoises and its jelly strength 303 grams. Glue B was made by the same manufacturer that made glue A and had a viscosity of 65 millipoises and a jelly strength of 190 grams. It represents a moderately low grade of woodworking glue. To prepare them for use, the dry glues were soaked in cold water until thoroughly softened, melted at 140° F. (60° C.), and spread at that temperature on the wood with a mechanical glue spreader. The proportion by weight of water to dry glue was for glue A, 2.25 to 1, and for glue B, 1.95 to 1. These ratios gave glue mixtures of approximately equal viscosity at 140° F. (60° C.).

The wood used in side-grain gluing was sugar maple (*Acer saccharum*). Details of the gluing conditions are given in Table I, together with the results of the tests.

Photographs of representative fractured test specimens are shown in Figure 1. Good, chilled, dried, and starved types of glued joints are illustrated, all four of which have been observed in commercial woodworking operations.

Good joints are characterized by high average strength and by the occurrence of the fracture, at least in part, in the wood rather than in the glue line. Each test specimen characterized in Table I as "good" failed in the wood at least in part, indicating that there is little or no advantage in strength to be gained by using a "stronger" glue. In good joints the difference between the average and the minimum breaking loads observed in the specimens tested is usually less than it is in the chilled, dried, or starved joints.

Chilled joints are obtained when the glue congeals, but does not dry, during the time of assembly to such an extent that the pressure applied proves insufficient to establish adequate contact between glue and wood and to cause the glue to flow into a uniform film. Chilled joints usually have a thick layer of glue, which may either shatter or pull away cleanly from one surface when the joint fails. They are more likely to be obtained in practice with a high-grade than with a low-grade glue. A cold glue room and cold wood, a long time of assembly, and a low pressure favor chilled joints. Of the faulty gluing conditions, that causing chilled joints is most easily overcome because the pressure may be increased, the wood preheated, the time of assembly shortened, or glue may be placed on both surfaces to be joined instead of one only. Only hot glues are subject to chilled joints.

Dried joints are obtained when the glue loses enough moisture during the time of assembly through evaporation or through absorption by the wood to harden appreciably. The fractured test specimens exhibit characteristic glossy areas where contact between glue film and wood was not established. A warm glue room, warm wood, and a long time of assembly cause dried joints. All common woodworking glues are subject to dried joints.

Starved joints are caused by the glue penetrating excessively into the wood or by excessive "squeeze out" of the glue when pressure is applied and, contrary to a common belief, they are favored by a too generous rather than a too stingy spread of glue. The broken pieces of a starved joint show little or no glue between the joined surfaces and microscopic[14] observation of a cross section through the joint reveals deep penetration of the glue into the wood. Warm wood, a heavy spread of glue, a short time of assembly, and a high pressure produce starved joints. They are more likely to be obtained

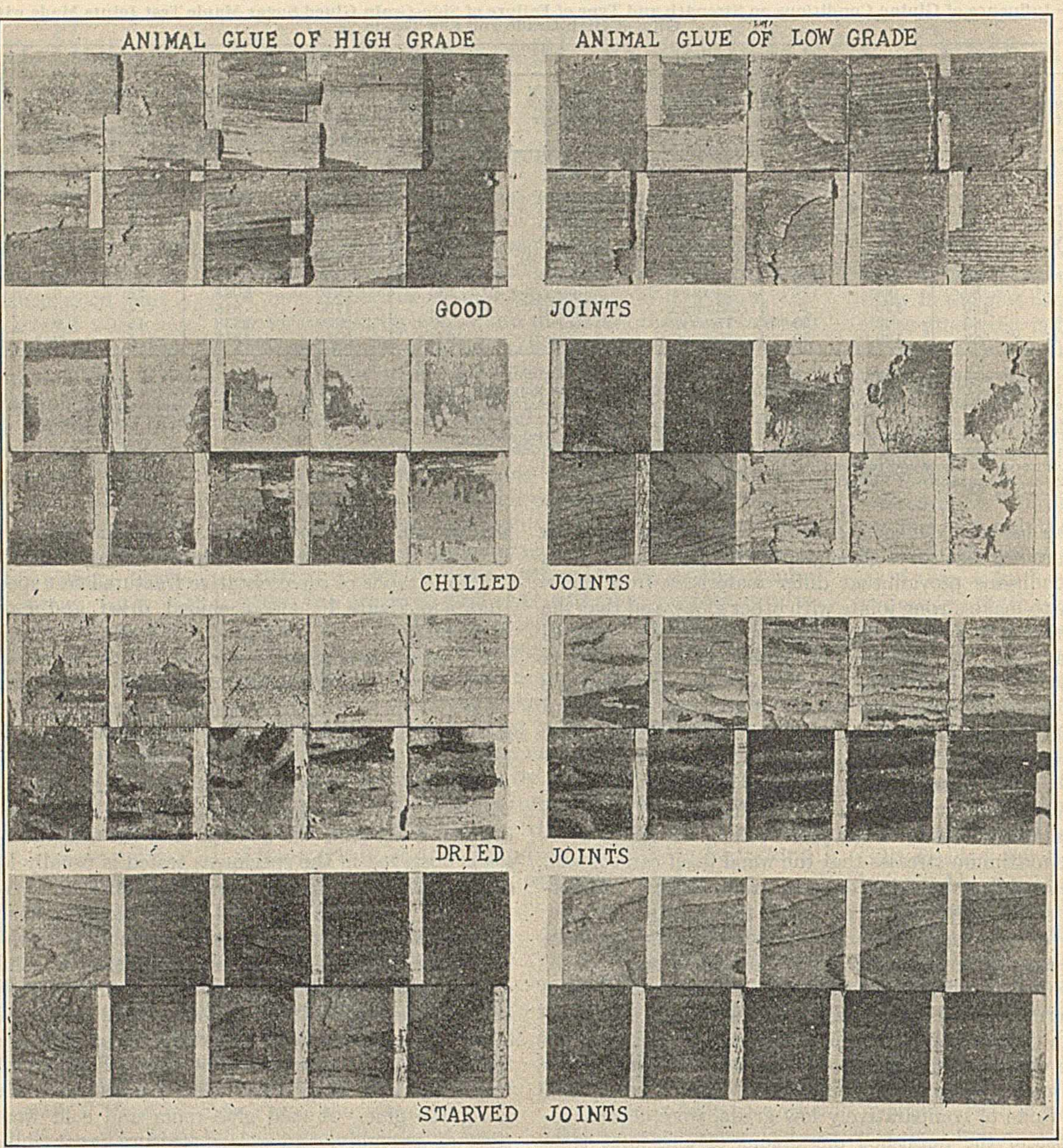


Figure 1—Appearance of Fracture in Broken Test Specimens of Four Types of Wood Joints Made with High-Grade and with Low-Grade Animal Glue

Each group is made up of the two halves of five specimens cut from a single wood joint; the same is true in Figure 2

with a low- than with a high-grade glue. Hot glues are more subject to starved joints than glues that are used cold because the latter usually are less mobile.

It may be noticed in Table I that somewhat different gluing conditions were chosen for glue A than for glue B. This was necessary because the range of gluing conditions in which joints of any of the four types are obtained varies with the grade of glue. The wood-worker is concerned with knowing which grade of animal glue can be trusted to give good joints under the gluing conditions attainable in his particular operations. With the woodworking glues in common use, faulty joints are far more likely to result from maladjustment of glue grade to gluing conditions than from inadequate adhesive power inherent in the glue itself.

Since several of the factors entering into the gluing conditions are interdependent and compensatory, the woodworker has a certain latitude in adjusting them to meet the requirements of various operations without the necessity of changing to a glue of different grade. Changing the water ratio for a given glue has somewhat the same effect as changing the grade. Table II shows a few of the many possible gluing conditions that give good joints with sugar maple using glue A.

Table II—Gluing Conditions that Give Good Joints with Glue A on Sugar Maple

GLUING CONDITIONS						RESULTS OF JOINT TESTS		
						LOAD REQUIRED TO BREAK		
Glue-water ratio	Room temp.	Wood temp.	Glue spread	Time of assembly	Pressure applied	Av.	Min.	Wood failure[a]
	° F.	° F.		Min.	Lbs./sq. in.	Lbs./sq. in.[b]	Lbs./sq. in.	Per cent
1:2	75	75	Medium	1/2	200	3600	3133	37
1:2 1/4	70	70	Medium	1/2	200	4000	3585	72
1:2 1/4	80	80	Medium	3	200	3950	3567	80
1:2 1/4	80	80	Medium	5	200	3750	3478	61
1:2 1/4	90	90	Medium	12	200	3000	2725	73
1:2 1/4	90	90	Medium	18	200	3750	3570	87

[a] Each result based upon ten test specimens cut from one pair of maple blocks glued together.

[b] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

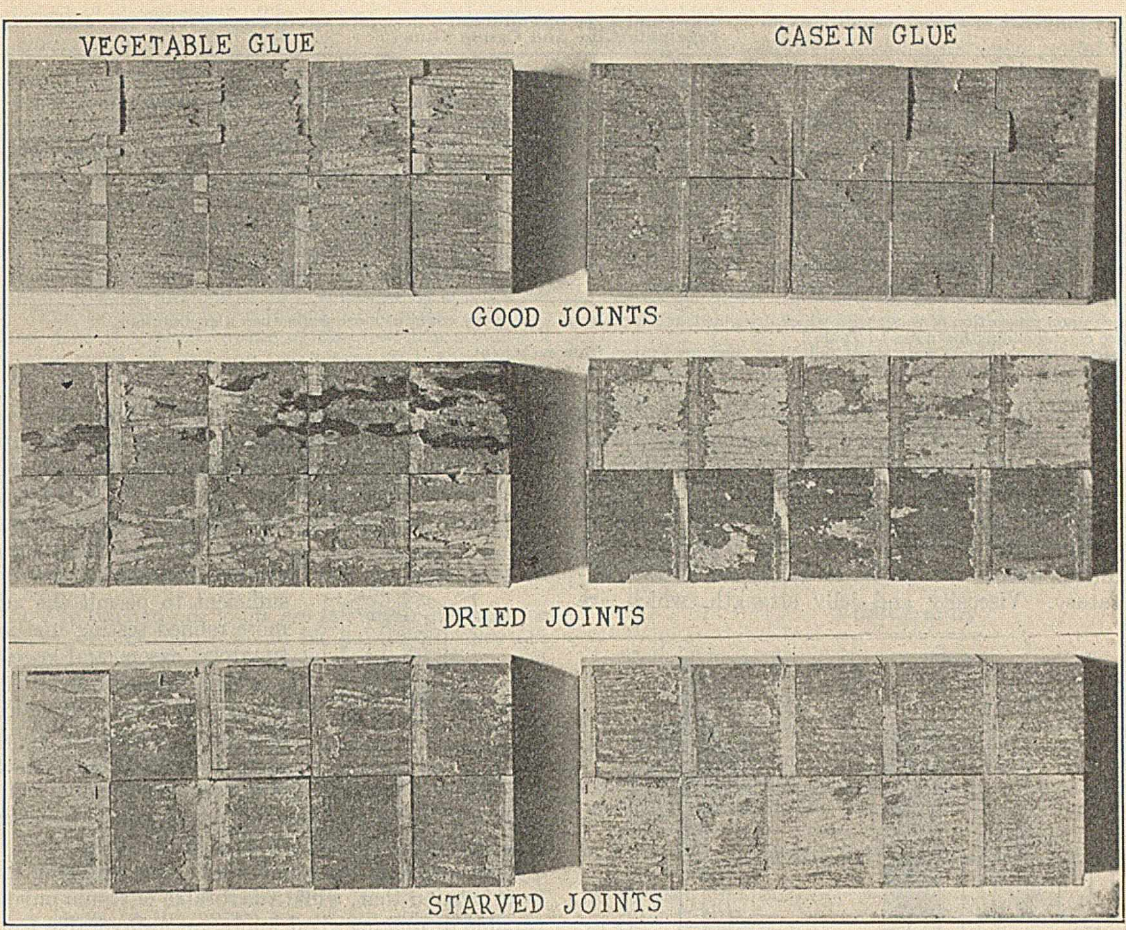


Figure 2—Appearance of Fracture in Broken Test Specimens of Three Types of Wood Joints Made with Vegetable and Casein Glues

Glue Grade and Joint Strength

Proposals to determine the intrinsic strength or adhesiveness of animal glues by means of wood-joint tests usually set forth a standardized routine of gluing conditions to be followed with all of the glues tested, except that some of them permit adjusting the proportion of water so that the glue mixture will have about the same viscosity at the temperature of application. Table I shows that such procedure is fundamentally unsound unless the chosen routine of gluing is definitely related to the particular manufacturing conditions for which a glue is being selected, for no one set of gluing conditions will produce joints that are representative of best practice with glues of every grade.
Thus we find:

Under Gluing Conditions Designated in Table I	Glue A		Glue B	
	Av. joint strength	Wood failure	Av. joint strength	Wood failure
	Lbs./sq. in.[a]	*Per cent*	*Lbs./sq. in.*	*Per cent*
I	3950	55	2950	75
II	2500	27	3100	84

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

Under one set of conditions glue A seems "stronger," under the other, glue B. Neither glue appears to best advantage when applied in accordance with the best practice for the other. With glue A chilled joints resulted under conditions II, which gave the best results with glue B. With glue B the joints made under conditions I, though classed as good, bordered on the starved condition.

If the two glues are compared when each one is used under its most favorable conditions, the chemist, noting the higher average load at failure, is likely to conclude that glue A is "stronger." The craftsman, looking at the fractured test specimens and observing the greater amount of wood failure, would favor glue B. The differences appearing in the table for these particular tests are due mostly to variation in the strength of the maple blocks, because the wood failure in both cases is high enough to indicate that the strength of the wood rather than that of the glue joint governed the load at which failure took place. In support of this interpretation the results of other tests may be cited. Eight pairs of maple blocks were glued with glue A under eight different good gluing conditions; ten test specimens from each joint—eighty specimens in all—gave an average load at failure of 3300 pounds per square inch with 62 per cent wood failure and a minimum load of 2035 pounds per square inch. Another series of eight joints was made with a glue of still lower grade than glue B, the vicosity of which was 42 millipoises and the jelly strength 150 grams; the eighty test specimens gave an average load at failure of 3500 pounds per square inch with 47 per cent wood failure and a minimum load of 1927 pounds per square inch.

What Wood-Joint Tests Tell

From these considerations it is clear that wood-joint tests in side-grain gluing are not suitable for the routine grading and evaluation of animal glues for woodworking. When used under suitable gluing conditions, all the grades of glue used in woodworking give joints whose load at failure depends

Table III—Influence of Gluing Conditions on Strength and Type of Failure of Side-Grain Glued Sugar Maple Test Joints Made with Vegetable Glue and Casein Glue

Glue	Gluing Conditions					Results of Wood-Joint Tests				Character of Joint
	Temp. of room	Consistency of glue[a]	Glue spread[b]	Time of assembly[c]	Pressure applied	Load required to break: Averaged[d]	Load required to break: Minimum	Wood failure[e]: Average	Wood failure[e]: Minimum	
	° F.			Min.	Lbs./sq. in.[f]	Lbs./sq. in.	Lbs./sq. in.	Per cent	Per cent	
Vegetable	80	Medium	Medium	15 (closed)	200	3200	2900	99	95	Good
	80	Medium	Medium	35 (open)	200	2300	600	6	0	Dried
	80	Thin	Heavy	1/2 (closed)	400	2300	1300	24	0	Starved
Casein	80	Medium	Medium	12 (closed)	250	3200	2800	88	50	Good
	80	Medium	Medium	15 (open)	200	2750	1850	21	10	Dried
	80	Thin	Heavy	1 (closed)	400	2450	1350	60	5	Starved

[a] Depends upon proportion of water with which dry glue is mixed; a thin consistency contains more water than a medium one.
[b,c,e,f] See corresponding footnotes to Table I.
[d] Four pairs of maple blocks were glued and 5 test specimens taken from each joint.

chiefly upon the strength of the wood joined. By testing each glue under a range of different gluing conditions wide enough to establish the zone of conditions within which it will give good joints, it would be possible to group animal glues in classes corresponding roughly to the grading on the basis of jelly strength and viscosity as now employed. But such an arduous task is one for the research, not for the control, laboratory. Viscosity and jelly strength, which are quickly and fairly easily measured with precision, give essentially the same information. Viscosity tells the wood-worker how much water to add to get the right amount of the glue on the wood at the least cost. Jelly strength, in so far as it is proportional to the chilling point, indicates how long it will take to reach the right consistency for pressing under the conditions prevailing and how long it will remain in that favorable condition. The two properties together serve admirably for checking successive shipments of glue for uniformity and for comparing competing brands to insure economy in purchasing.

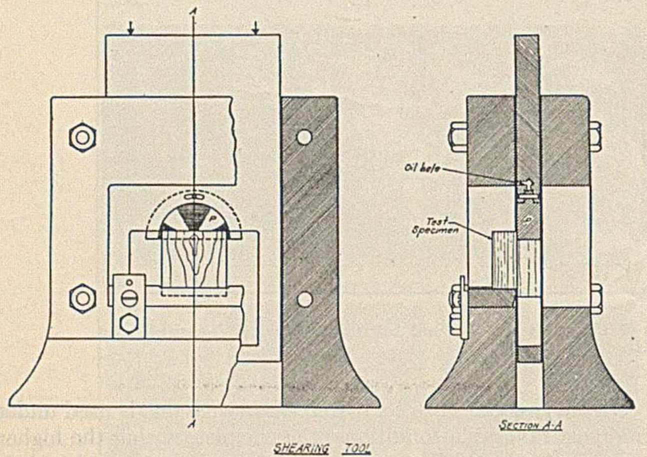
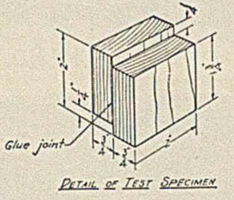


Figure 3—Shearing Tool and Test Specimen Used for Forest Products Laboratory's Glued Wood-Joint Test

On the other hand, the wood-joint test is essential in the glue-research laboratory for studying such problems as the practical usefulness of newly proposed adhesives, the influence of new treatments upon or additions to established glues, the gluing characteristics of different woods, the technic of gluing operations, and for examining glued wood products for their reliability or for the location of the causes of manufacturing difficulties. Direct measurements of the strength of solid specimens of glues may not, in the present state of knowledge, be substituted for the wood-joint test because it has not yet been shown that the "strength" of a glue so measured bears any essential relation to the strength of wood joints made with it, nor do they appear to have a close relation to the viscosity or jelly strength of the glues themselves.[11]

Wood-joint tests were adopted by the U. S. Army and Navy[15] as the foundation of specifications for casein glues. Most attempts to test vegetable glues also rely upon wood-joint tests. Some representative results with these glues are given in Table III and Figure 2. At present wood-joint tests seem necessary for these types of glues, because knowledge of their significant physical and chemical characteristics is not yet sufficient to permit the adoption of more refined testing methods. Fortunately, casein and vegetable glues are much less sensitive to changes in gluing conditions than animal glues and good joints are obtained with them through a fairly wide range in conditions. There is no danger of obtaining chilled joints with cold glues and starved joints are comparatively rare. Dried joints, however, are often encountered.



When making test wood joints with any glue it is well to bear in mind that, while a favorable outcome proves the glue capable of making good joints, an unfavorable test does not prove the contrary. Before the glue can be rejected as inherently weak, it must be tried out under conditions representative of the range under which it might be practicably employed.

Procedure of Forest Products Laboratory in Making Wood-Joint Tests

Two types of wood-joint tests are made at the Forest Products Laboratory. The test of plywood specimens, designed especially to determine the water resistance of glues,

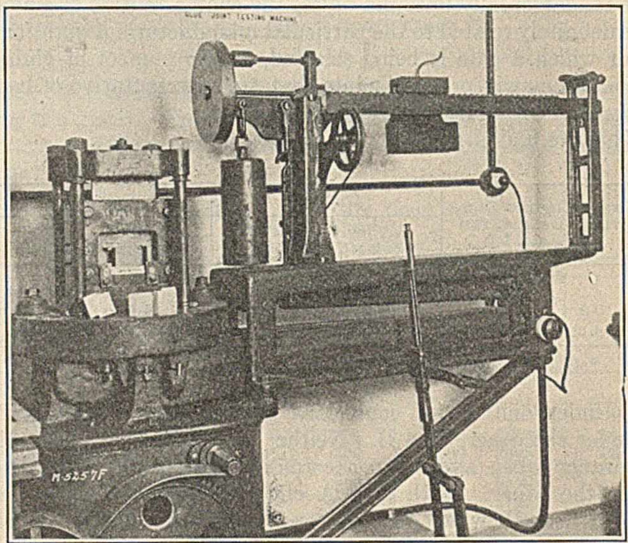


Figure 4—Glue-Joint Testing Machine

has been described elsewhere.[16] The test of lumber joints in side-grain gluing is made as follows:

Commercial 1-inch sugar maple (*Acer saccharum*) lumber is used and wood of average density or higher, straight grained, and free from defects is selected from it. This wood is seasoned thoroughly and stored in a room kept at 30 per cent relative humidity and 80° F. (27° C.) until needed. The moisture content is then about 7 per cent of the oven-dry weight of the wood. Just before gluing, pieces $^{3}/_{4}$ by 5 by 12 inches are cut and planed to uniform thickness and smooth, true joint surfaces. The temperature of the gluing laboratory is subject to control within the range of conditions likely to be encountered in practice, and a steam-heated chamber is provided for preheating the wood when so desired. The two pieces to be joined are weighed together on a balance, glue is applied to one of them with a single-roll mechanical glue spreader, and the two pieces with the applied glue reweighed to obtain the weight of glue spread. As a rule about $1^{1}/_{4}$ ounces of wet glue are applied per square foot of joint area. The second piece of wood is put in contact with the glue line at once or at the close of the time of assembly according as open or closed assembly is decided upon. At the end of the allotted time the joint is put in position in a screw press under caul boards, a hydraulic pressure gage inserted, and the proper pressure applied. Usually the pressure is 100 or 200 pounds per square inch. If it falls off immediately after application by reason of "squeeze out" of glue, the pressure is readjusted at once.

As a matter of convenience joints are left under pressure for 16 to 24 hours. A few hours would be sufficient. They are then conditioned before test for 7 days in a room at 30 per cent humidity at 80° F. (27° C.) and provided with good circulation of air. From each joint ten test specimens of the dimensions shown in Figure 3 are cut and torn apart in shear in the machine (Figure 4) and shearing tool (Figure 3) illustrated. The speed of the machine is such that the shearing blade advances at a rate of 0.0157 inch per minute. Attention is called to the self-adjusting bearing in the upper jaw of the shearing tool, the purpose of which is to distribute the load uniformly over the upper and lower shoulders of the test specimen, even though they may not be truly parallel to each other. The part *P* is a semicylindrical-shaped rocker having a flange that fits in a groove of corresponding shape in the upper jaw of the shearing blade. It is free to rotate around the axis of the semicylinder within limits set by means of a pin inserted in the flange of the rocker and sliding in a groove in the shearing blade. There is also an oil hole for lubricating the bearing.

For each specimen tested, notation is made of the breaking load and the estimated percentage of the glue-line area in which the wood splinters. Two or more duplicate joints are usually prepared, each one giving ten specimens for test. The average and the minimum breaking load and the average percentage of wood failure are generally taken as the final record of the test.

Conclusions

1—The strength and character of failure of test wood joints made with animal glue are greatly influenced by the gluing conditions under which the joints are prepared.

2—The conditions that produce good joints vary with the grade of the animal glue and no one set of gluing conditions gives good joints with all grades of glue.

3—Animal glues of all grades commonly used for woodworking, when applied under conditions suitable for each glue, produce wood joints whose load at failure depends chiefly upon the strength of the wood rather than upon the grade of the glue.

4—It has not yet been shown that animal glues differ among themselves in an intrinsic property of "strength" or "adhesiveness," which is as significant of their value for woodworking purposes as the viscosity and jelly-strength tests now constituting the principal bases of grade.

5—Wood-joint tests are used in the inspection of casein and vegetable glues because a more refined technic for evaluating them has not yet been developed. Although a favorable wood-joint test proves that the glue is capable of making strong joints, an unfavorable test may not prove the contrary.

6—Wood-joint tests are well adapted to the research laboratory dealing with problems involving the technic of gluing and to the engineer in checking glue-room procedure. The tests should be made in side-grain gluing and the nature of the failure as well as the load at which it takes place should be considered.

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12—Browne and Brouse, *Ibid.*, **21**, 80 (1929).
13—Truax, *Timberman*, December, 1922; Jones, *Proc. Am. Soc. Testing Materials*, **23**, Pt. II, 583 (1923); Truax, *Furniture Manuf. Artisan*, May, 1924.
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15—U. S. Army, Air Service, Specification 98-14,020 C (1925); U. S. Navy, Bureau of Aeronautics, Specification 52 G 8 (1924); see also Report No. 66 of the National Advisory Committee for Aeronautics, 1920.
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New Fumigant for Stored Products

Ethylene oxide is a fumigant not hitherto used for exterminating insects, but recently discovered by the United States Department of Agriculture to be highly toxic to certain species. Those commonly infesting stored food products, clothing, and furniture can be easily killed by the vapors of ethylene oxide in concentrations that can be used without danger from fire and that are not dangerous to human beings. Clothes moths, carpet beetles, rice weevils, saw-toothed grain beetles, Indian meal moths, red-legged ham beetles, and flour beetles all succumbed to this new fumigant when it was used experimentally for a period of 20 hours in the proportion of 1 pound of ethylene oxide to 1000 cubic feet of space.

For commercial fumigation work the Department of Agriculture, however, recommended that the fumigant be used at double this quantity per 1000 cubic feet of space. Comparative tests indicated that the vapors of ethylene oxide are somewhat more toxic to stored-product insects than are those of carbon disulfide and about thirty times as toxic as those of carbon tetrachloride.

Owing to its low boiling point, ethylene oxide is effective at comparatively low temperatures, ranging from 60° to 75° F. It has excellent powers of penetration. Insects buried in overstuffed furniture, sealed in packages of cereals, and buried in jars of grain were killed with ease. No deleterious effect was noticeable when the commercial dosage of the fumigant was used for 24 hours on commodities, foodstuffs of various types, clothing, furniture, and metals. Such foodstuffs as nut meats and dried fruits were unaffected, and no foreign taste or odor was discernable after removal from the fumigation chamber. No liquid foods were treated.

Preliminary tests in a vacuum fumigation tank show that ethylene oxide can be successfully used for this type of fumigation.

Seeds for planting purposes, however, should not be fumigated with ethylene oxide, since the vapors seriously affect the germination. Wheat was used for the germination experiments.

Nature of Adhesion between Glue and Wood[1]

A Criticism of the Hypothesis that the Strength of Glued Wood Joints Is Due Chiefly to Mechanical Adhesion

F. L. Browne and Don Brouse

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

The common woodworking glues adhere to wood in part by mechanically anchoring in the cavities of the wood. Glues may adhere specifically as well; that is, they may cling to the wood independent of any mechanical grip upon the wood structure. Evidence obtained principally from microscopical examination of the glue lines of strong and weak wood joints and from the study of the gluing characteristics of different woods has been advanced to show that specific adhesion is essential for satisfactory wood-gluing. A hypothesis, based upon a comparison of the strength of wood joints in shear and tension with the strength of films of "strong" and "weak" glues in tension, has also been advanced by other investigators to indicate that glued wood joints depend for their strength chiefly upon mechanical adhesion.

This paper presents data showing that much stronger wood joints can be made with both "strong" and "weak" glues than were thought representative by the advocates of mechanical adhesion hypothesis, provided that the joints are made by the gluing procedure used by the adherents of the specific-adhesion theory. The theory that specific adhesion is essential for satisfactory wood-gluing is confirmed.

THE assumption has prevailed for a long time that glue sticks to wood because it gains access while fluid to the cavities in the wood structure and then solidifies, the strength of the joint being due to the resultant intertwining of the two strong solids. Apparently the theory escaped critical examination until recently, even though it has been largely responsible for much poor gluing in the woodworking industries and for many wrong conclusions drawn by technologists from data involving tests of the strength of wood joints. For the premise leads logically to the "heat, hurry, and squeeze" method of using animal glue, in accordance with which the glue is applied hot to warm wood in a warm room, and the joint assembled and placed under substantial pressure as quickly as possible. Splendid penetration and interlocking of glue and wood are thereby secured—together with weak joints. During a decade of study of gluing practice in the wood-working industries the starved joint,[2] produced as just described, has been found to be the most common type of unsatisfactory wood joint made with animal glue. It seems reasonable to suppose that in the past practice has been seriously influenced by inadequate theory and that the establishment of sound theory for the adhesion between glue and wood will exert a desirable influence on gluing practice.

Mechanical and Specific Adhesion Theories

In recent years notable contributions have been made to the understanding of the nature of adhesion by describing clearly and naming two distinct kinds of adhesion and by ingeniously studying joints between surfaces of different "smooth" and "porous" materials made with a variety of adhesives, as well as inventing technic for measuring the strength in tension of films of the adhesives themselves. However, since some of these contributions have been interpreted as giving support to a theory that is hostile to good wood-gluing practice, it seems desirable to examine such evidence critically. Such an examination discloses that the wood joints assumed representative were probably typical starved joints, for when similar joints are made under more favorable gluing conditions much higher strengths are obtained and characteristics are observed that the upholders of the mechanical hypothesis attribute to joints depending upon specific adhesion.

One advocate of the mechanical-adhesion hypothesis concluded that:

> Adhesive joints may be placed into two categories, namely, the specific type of true adhesion and the mechanical type of mere embedding. In some joints with porous materials both factors may be operative.[3]
>
> Strong joints may be made without adhesiveness and it will be shown that glued wooden joints appear to belong to this purely mechanical class.[3]
>
> The most important and rather surprising example of a purely mechanical joint is wood joined with gelatin or glue, where apparently even adsorption does not take place.[4]
>
> The second class of joints has a purely mechanical explanation in that the adhesive is embedded in the pores and surface irregularities of the materials joined. Here the film of adhesive acts as a solidified casting holding the materials together. Glued wooden joints appear to be a conspicuous example of this class.[5]

On the other hand, advocates of the specific-adhesion theory[6] pointed out that specific adhesion between glue and wood is a necessary prerequisite of mechanical adhesion, at least with glues that contain large amounts of a volatile solvent whose evaporation causes the glue to shrink. Such shrinkage of the glue jelly on drying would loosen the "solidified casting holding the materials together" were specific adhesion lacking. They presented photomicrographs of sections through glued wood joints proving that the common woodworking glues cling firmly during drying to the walls of those cavities of wood cells into which the glue penetrates while fluid; shrinkage of the glue jelly takes place by the menisci at glue-air interfaces in wood cavities into which the glue penetrates, changing from convex to deeply concave, and by a decrease in the thickness of the glue layer, drawing the joined surfaces closer together. They showed further that studies of the technic of making strong joints with different woods and glues and of the penetration of glue into the wood cavities reveal facts difficult to reconcile with the theory that the adhesion has "a purely mechanical explanation."

This evidence of specific adhesion was set aside by the believers in mechanical adhesion with the statement that such evidence

> overlooked the fact that the interstices and mechanical embedding to which we have referred are on an ultra-microscopic

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[1] Received May 28, 1928.

[2] Truax, Browne, and Brouse, Ind. Eng. Chem., 21, 74 (1929).

[3] McBain and Hopkins, Second Report of (British) Adhesives Research Committee, London, 1926.

[4] McBain and Hopkins, *J. Phys. Chem.*, 29, 188 (1925).

[5] *Ibid.*, 30, 114 (1926).

[6] Browne and Truax, Colloid Symposium Monograph, vol. IV, p. 258 (1926).

scale and therefore (not) subject to direct microscopic test; for example, we stated that gelatin passes freely through smooth continuous sheets of viscose.[7]

It was not unreasonable for the specific-adhesion advocates to assume that "pores and surface irregularities" of walnut meant the vessels that give walnut its characteristic appearance and the smaller cavities of the wood fibers easily revealed by the microscope. If mechanical adhesion is defined in terms of ultra-microscopic interstices, the conception cannot be very useful until it is first proved that the walls of the wood elements are porous in a supermolecular and submicroscopic sense and that the metals taken as typical of "smooth" surfaces are not. Though gelatin may pass freely through viscose, it has been shown[8] that the walls of the wood elements are impervious to woodworking glues even though water-soluble alkalies present in some of them apparently pass through the wood substance fairly easily and may stain the wood far beyond the limits to which the glue itself penetrates.[5,9] It may be doubted that the surfaces of wood cell walls afford an opportunity for an ultra-microscopic mechanical embedding of glues toward which they act as semipermeable membranes. For these reasons it will be necessary, for the present at least, to classify the surfaces studied as "smooth" or "porous" according to the ordinary sense perceptions of those qualities.

In a later paper the same advocates changed the adverb qualifying mechanical adhesion for wood joints from "purely" to "mainly:"

> This mechanical joining must always occur with porous bodies whether specific adhesion is present or entirely lacking. They [the mechanical advocates] found that gelatin is not adsorbed by wood from aqueous solution, and concluded that glued wood joints are mainly of the mechanical type. However, they explicitly stated that many joints will be the resultant of both factors, mechanical and specific. Indeed it may now be taken for granted that at least a small amount of specific action occurs in every case where the adhesive wets the surface.[10]

The experiment just described on the adsorption of gelatin by wood may be interpreted[6] as indicating that wood probably does adsorb gelatin. In the experiment adsorption must have occurred if the wood took up more than 24 per cent of water as hygroscopic moisture. The investigators did not think it would absorb so much, because they found that filter paper takes up only 10 per cent from saturated air. However, wood comes to equilibrium at 24 per cent moisture content when the relative humidity is only about 90 per cent at 70° F. (21° C.) and the fiber saturation point is considerably above 24 per cent.

The hypothesis of the predominance of mechanical adhesion over specific for wood joints is based upon comparisons of the strength of wood joints with the strength of films of the adhesives tested separately. Starting originally with the idea that

> for both classes of joint the tensile strength of the film itself imposes an upper limit on the strength of joint obtainable, since the film in both cases must transmit the strain,[5]

supporters of the mechanical hypothesis found subsequently that

> there is no general relation between the strength of joints involving smooth surfaces and the tensile strength of various adhesives such as glue and sodium silicate. For example, gelatin may be twenty times stronger than sodium silicate, but the latter may give as strong a joint with smooth surfaces of metal. On the other hand, for any single adhesive the strength of film does appear to be parallel with the strength of the specific joint resulting.[10]

But they still hold that, for mechanical adhesion,

> with a given porous material there should be a distinct agreement between joint strength and the strength of the film of adhesive itself provided always that the adhesive is not stronger than the porous body.[10]

Nevertheless, after reviewing their own data, they write:

> Qualitatively all the results * * * agree with the mechanical explanation of joints between porous materials. It must be admitted, however, that * * * it is not so easy to obtain a decisive disproof of the specific explanation as contrasted with the mechanical explanation for a given case. At first sight it would appear that a mechanical joint should always be weaker than the adhesive in contrast to the specific type of joint. * * * Actually, however, our experiments have shown that thin films between surfaces are much stronger than the same adhesive in bulk, and this must therefore be a possibility even with porous joints. Indeed, the data * * * for sodium silicates show that the adhesive may be distinctly weaker than the wooden joints made from it.
>
> The most conclusive argument in favor of the mechanical explanation as distinguished from specific adhesion for glued wooden joints is obtained by comparing such widely different adhesives as sodium silicate with gelatin glue. As was pointed out, there is no relation between tensile strength of these unrelated adhesives and the strength of the specific joints which they give between smooth surfaces. On the other hand, with wood the sodium silicates give joints which are as strong as those given by gelatin glue which has been weakened to the same tensile strength. This seems a clear indication in favor of the mechanical explanation as the chief factor in the formation of glued wooden joints.[10]

The evidence offered in support of these conclusions may be summarized as follows:

Glue	Strength		
	Glue film in tension	Walnut wood joints in side-grain gluing tested in:	
		Shear	Tension
	Lbs./sq. in.[a]	Lbs./sq. in.	Lbs./sq. in.
Animal glue, high grade	12,000	1500	825
Glue mixed with an equal part of dextrose	Less than 1000	600	420
Sodium silicate	600	700	...

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

Experimental

Since the joint strengths indicated for "good" walnut joints made with animal glue are lower than joint strengths obtained at the Forest Products Laboratory, it seemed desirable to determine whether the low values can be due to the nature of the test specimen employed or whether they must be attributed to poor gluing technic. If poor gluing technic is responsible, a repetition of the joint tests with the "weak" glues under more suitable gluing conditions might give very different results. Such tests show that both sodium silicate and glue-dextrose mixtures are capable of joining wood surfaces so strongly that the failure takes place very largely in the wood when the joints are torn apart either in tension or in shear.

GLUE USED—The animal glue used in the Forest Products Laboratory experiments was of a moderately high grade for a woodworking glue (viscosity 108 millipoises, jelly strength 303 grams by the standard methods of the National Association of Glue Manufacturers[11]). The film strength of its mixture with an equal weight of pure dextrose was found to be 1950 pounds per square inch when in equilibrium with air of 65 per cent relative humidity at 80° F. (27° C.). Since this value is higher than that reported by the mechanical advocates, a mixture of 1 part of glue with 1.5 parts of dex-

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[7] McBain and Lee, IND. ENG. CHEM., **19**, 1005 (1927).

[8] Truax and Gerry, *Furniture Manfr. Artisan*, April, 1922.

[9] Browne, *Veneers*, April and May, 1928.

[10] McBain and Lee, *J. Soc. Chem. Ind.*, **46**, 321 (1927); see also *J. Phys. Chem.*, **32**, 1178 (1928).

[11] IND. ENG. CHEM., **16**, 310 (1924).

trose was also prepared. It had a film strength of 1100 pounds per square inch. The sodium silicate had a density of 1.415 grams per cubic centimeter and a SiO_2–Na_2O ratio of 3.25. At 30 per cent relative humidity and 80° F. (27° C.) the film strength was found to be 1900 pounds per square inch, several times the value reported by the upholders of mechanical-adhesion hypothesis.

One advocate of the mechanical hypothesis states that the strength of a film of glue may be seriously influenced by the nature and amount of "lubricant" used on the ferrotype plate on which the glue film is cast. The differences in the figures given here and those reported may be due to this cause.

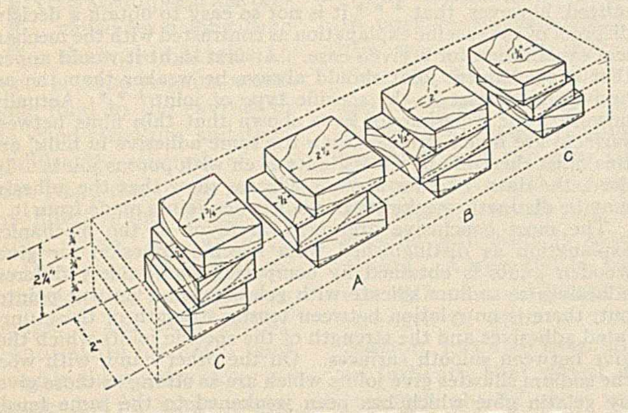

Figure 1—Method of Cutting a Glued Block into Three Types of Specimen for Test in Shear

Specimen *A* is the R. A. E. type, *B* the old type F. P. L. specimen, and the two specimens *C* the new type F. P. L. specimen

Manner of Making Joints—Joints for tests in shear were made with black walnut, *Juglans nigra*, and for test in tension with black walnut and the following woods, which are comparatively strong in tension at right angles to the grain: red gum, *Liquidambar styraciflua;* white ash (commercial), *Fraxinus sp.;* beech, *Fagus grandifolia;* pecan, hickory, *Hicoria pecan*; yellow birch, *Betula lutea;* persimmon, *Diospyros virginiana*. The lumber was seasoned by storage for many months in a room kept at 30 per cent relative humidity and 80° F. (27° C.).

For the tests in shear three pieces of wood, each approximately 7/8 by 2 1/2 by 12 inches, were glued together to make a block 2 5/8 by 2 1/2 by 12 inches containing two "glue lines" designated "glue line *A*" and "glue line *B*." Nine of these blocks were prepared with each kind of glue and, after reconditioning, they were cut into test specimens as indicated in Figure 1. One test specimen from each block was of the form used by the mechanical adhesion advocates[3] and known as the R.A.E. (Royal Aircraft Establishment) compression-shear specimen. A second specimen from each block was patterned after a type of specimen used by the Forest Products Laboratory several years ago;[12] it was inserted in the shearing tool[2] in such a way as to tear off first the outside piece held in place by glue line *A* and then turned about to tear off the piece held by glue line *B*. Two remaining specimens from each block were essentially similar in form to the present standard specimen of the Forest Products Laboratory, permitting the operator to test first glue line *B* and then glue line *A*.

The joints for tests in tension were made by edge gluing two pieces 7/8 by 1 7/8 by 6 inches and then cutting them into test specimens as indicated in Figure 2. From each joint were obtained six test specimens 1/4 by 7/8 by 3 1/4 inches and nine specimens 1/8 by 7/8 by 3 1/4 inches. These specimens were broken in tension in a cement tester fitted with special jaws.[13]

Gluing Procedure—The gluing was done in a room at about 80° F. (27° C.) and the wood was at the same temperature. The surfaces to be joined were smoothed on a jointer just before gluing. The animal glue, whether with or without added dextrose, was prepared with 2 1/4 parts by weight of water to 1 part of dry animal glue. The glue, after soaking in the cold water for about an hour, was melted in a thermostatically controlled glue pot at 140° F. (60° C.). The glue was applied within an hour after melting. Sodium silicate was applied at room temperature and without any addition of water. For the blocks tested in shear, glue was applied to only one of the two surfaces joined; it was applied to both surfaces of the joints to be tested in tension. "Open assembly"[2] was used so that the consistency of the glue on the wood could be observed readily; when the layer of glue congealed sufficiently to retain the imprint of the finger the joints were assembled and placed under pressure. The pressure applied in gluing the joints for test in shear was 200 pounds per square inch. No pressure gage suitable for use with the clamps holding the joints for test in tension being available, the correct pressure was judged by the amount and nature of the "squeeze out." Joints were left under pressure overnight. Those for test in shear were seasoned for 1 week in a room at 60 per cent relative humidity and at 80° F. (27° C.) before cutting the specimens and testing them, those for test in tension were seasoned for 2 days at 30 per cent relative humidity and at 80° F.

Results—The results of the tests in shear are given in Table I and of the tests in tension in Table II. The average joint strength found for each of the four glues is higher than the representative value given by the mechanical-adhesion advocates for good joints in walnut with high-grade animal glue and two or three times as high as their representative values for glue-dextrose and sodium silicate. For glue-dextrose and sodium silicate the minimum joint strengths are much higher than their representative values. Even with these very "weak" glues the joints withstand as much load as the wood itself can reasonably be expected to sustain, and most of the test specimens fail very largely, many of them entirely, in the wood rather than in the glue line.

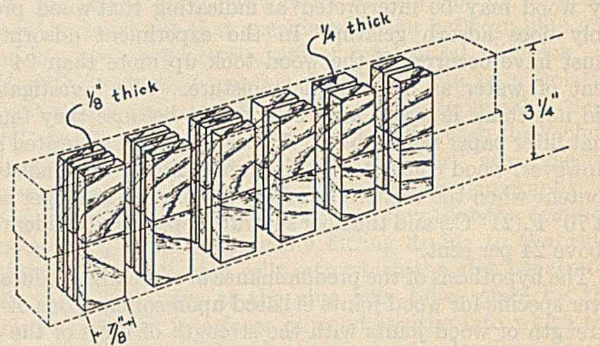

Figure 2—Method of Cutting a Glued Block into Specimens for Test in Tension

Nine specimens 1/8-inch thick and six specimens 1/4-inch thick were obtained from each block

Comparison of Results with Those of Previous Workers

The striking difference between the Forest Products Laboratory results and those obtained by the expounders of mechanical adhesion is undoubtedly due chiefly to fundamental differences in gluing technic. When critically examined,

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[12] Allen and Truax, National Advisory Committee for Aeronautics, Report 66 (1920); see also Bogue, "Chemistry and Technology of Gelatin and Glue," p. 530, New York, 1922.

[13] Browne and Hrubesky, Ind. Eng. Chem., 19, 215 (1927).

Table I—Tests in Shear of Walnut Joints Made with Various Kinds of Glue

GLUE	R. A. E. TYPE TEST SPECIMEN[a]						F. P. L. TEST SPECIMEN, OLD TYPE[b]						F. P. L. TEST SPECIMEN, NEW TYPE[c]					
	LOAD AT FAILURE			WOOD FAILURE			LOAD AT FAILURE			WOOD FAILURE			LOAD AT FAILURE			WOOD FAILURE		
	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
	Lbs. per sq. in.[d]			*Per cent*			*Lbs. per sq. in.*			*Per cent*			*Lbs. per sq. in.*			*Per cent*		
Animal glue	1829	1503	1650	100	85	98	2389	1561	2050	100	25	88	3105	2008	2650	100	5	86
Glue-dextrose mixed 1:1	1758	1402	1550	100	100	100	2380	1310	1850	100	10	73	2832	1735	2250	100	5	63
Glue-dextrose mixed 1:1.5	2025	1495	1750	100	35	86	2180	1169	1750	100	5	65	2677	948	1800	100	0	48
Sodium silicate	1781	1206	1550	100	35	93	1998	1062	1600	100	5	55	2673	1310	1900	95	0	40

[a] There were nine R. A. E. specimens with each glue. Failure usually took place by crushing of the wood in compression parallel to the grain in the projecting central piece of the specimen. A few specimens appeared to fail by cleavage of the central piece as the two side pieces spread apart under the load. Other specimens appeared to fail in shear at or near one of the glue lines.

[b] There were nine F. P. L. specimens, old type, with each glue. Each average value is therefore based upon 18 measurements, since each specimen had two glue lines tested separately.

[c] There were 18 F. P. L. specimens, new type, with each glue. Each average value is therefore based upon 36 measurements.

[d] 14.22 lbs. per sq. in. = 1 kg. per sq. cm. The speed of the testing machine was such that the shearing blade advanced at a rate of 0.0157 inch per minute. It usually took about 3 minutes to apply a load of 10,000 pounds to a test specimen. Our rate of loading was probably slightly slower than that reported by McBain and Lee.

Table II—Tests in Tension of Side-Grain Wood Joints Made with Various Glues

GLUE	WOOD	LOAD AT FAILURE						WOOD FAILURE		
		1/4-IN. SPECIMEN			1/8-IN. SPECIMEN					
		Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
		Lbs. per sq. in.[a]			*Lbs. per sq. in.*			*Per cent*		
Animal	Gum	1136	800	1000	1625	980	1200	100	100	100
	Walnut	1560	1120	1400	1750	1310	1600	100	30	94
	Ash	1617	1300	1550	1668	1175	1500	100	100	100
	Beech	1765	1570	1650	1666	1470	1550	100	100	100
	Hickory	1863	1617	1750	1917	1567	1750	100	100	100
	Birch	2072	1790	1900	2512	1870	2050	100	100	100
	Persimmon	2300	1910	2150	2303	1617	2050	100	100	100
	Av.			1650			1650			99
Animal-dextrose mixed 1:1	Gum	1224	940	1050	1130	634	950	100	0	36
	Walnut	1430	1200	1300	1590	1250	1350	100	10	93
	Ash	1600	1412	1500	1715	1126	1300	100	50	83
	Beech	1643	1323	1500	2140	1658	1900	100	100	100
	Hickory	1765	1001	1550	2108	1176	1600	100	100	100
	Birch	2130	1715	2000	2108	735	1650	100	5	74
	Persimmon	1857	1528	1700	2010	1520	1850	100	10	94
	Av.			1500			1500			83
Animal-dextrose mixed 1:1.5	Gum	1224	990	1150	1765	1030	1250	100	10	87
	Ash	1715	1225	1500	1862	1373	1500	100	0	42
	Beech	1862	930	1350	1812	1520	1600	100	20	77
	Hickory	1960	1225	1500	1900	997	1500	100	0	65
	Birch	2090	1566	1850	2110	871	1300	100	5	73
	Persimmon	1960	1250	1750	2060	882	1650	100	0	87
	Av.			1500			1450			72
Sodium silicate	Gum	1078	760	900	1568	784	1050	100	0	87
	Walnut	1050	850	950	1360	870	1100	100	5	72
	Ash	1295	965	1150	1604	963	1350	100	0	70
	Beech	1642	710	1100	1496	1070	1350	100	10	88
	Hickory	1436	683	1100	1476	963	1350	100	0	66
	Birch	1570	1030	1300	1627	859	1300	100	0	35
	Persimmon	1790	1176	1450	1912	833	1600	100	5	69
	Av.			1150			1300			70

[a] 14.22 lbs. per sq. in. = 1 kg. per sq. cm. One glued joint was made with each wood and glue from which were cut six 1/4-inch test specimens and nine 1/8-inch test specimens.

results of the latter indicate that the gluing conditions that they adopted produced "starved" joints.[2] They applied the glue to both surfaces to be joined and then

> immediately the joint was set up it was placed in a pressure device, the total pressure applied to each joint being 28 pounds, or about 7 pounds per square inch. The joints were kept under this pressure until thoroughly dry.[3]

the glue was mixed in the proportion of 20 grams of glue to 50 cc. of water in the earlier experiments,[3] but in later work 10 and 20 per cent glue solutions were applied on the theory that

> the more viscous the solution of adhesive applied, the thicker the layer and the less the penetration and the weaker the joint.[10]

Such procedure would certainly produce starved joints if commercially practicable joining pressures were used, and the results indicate that the very low pressure of 7 pounds per square inch gave starved joints even with high-grade animal glue. The Forest Products Laboratory tests indicate that the addition of dextrose retards the setting of animal glue and calls for a longer assembly period. A cold glue like sodium silicate also needs a longer assembly period. It is therefore easy to understand why the exponents of the mechanical-adhesion hypothesis found their glue-dextrose and sodium silicate joints still weaker than their joints with unadulterated glue.

Table I shows that, although walnut joints made with the "weak" glues are strong enough to fail very largely in the wood itself, nevertheless joint strengths are slightly higher with unadulterated animal glue than with glue-dextrose or sodium silicate. Table II exhibits the same tendency, but indicates further that the "weak" glues may give higher joint strengths in strong wood than "strong" glue with weaker wood.

It seemed desirable, therefore, to repeat the tests in shear with the four glues and dense sugar maple, *Acer saccharum*. Table III records the results. Again all the glues make joints that break very largely in the wood; the joint strength obtained with "weak" glue in maple is higher than that obtained with unadulterated animal glue in walnut.

Comparison of Joint Strengths with Film Strengths

In the light of the notably different results obtained at the Forest Products Laboratory, in making wood joints with the "weak" glues used by the expounders of the mechanical-adhesion hypothesis, the deductions drawn by them from comparison of joint strengths with film strengths must be reëxamined. They find that the following trends are characteristic of specific adhesion between smooth surfaces:

(1) Such joints often exceed by several fold the tensile strength of the adhesive itself.[14]

(2) The strength of such joints is parallel to the mechanical constants of the materials joined.* * * Joint strengths rise with tensile strength and elasticity (of the materials joined).[15]

(3) There is no general relation between the strength of joints involving smooth surfaces and tensile strength of various adhesives such as glue and sodium silicate. For example, gelatin may be twenty times stronger than sodium silicate, but the latter may give as strong a joint with smooth surfaces of metal. On the other hand, for any single adhesive (such as animal glue of different grades or with added dextrose) the strength of film does appear to be parallel with the strength of the specific joint resulting.[9]

(4) The thinner the layer of adhesive, the stronger the joint. The effect of thickness is not appreciable with very thick films but is rapidly increasing when the thinnest possible films are studied.[14]

Table III—Tests in Shear of Maple Joints Made with Various Kinds of Glue

GLUE	NUMBER OF:		LOAD AT FAILURE			WOOD FAILURE		
	Joint	Specimens[a]	Max.	Min.	Av.	Max.	Min.	Av.
			Lbs. per sq. in.[b]			*Per cent*		
Animal	4	40	4810	3190	3950	100	10	55
Glue-dextrose 1:1	4	20	3802	2808	3350	100	10	70
Glue-dextrose 1:1.5	7	35	3950	2470	3150	95	5	23
Sodium silicate	4	40	4015	2290	3000	100	5	68

[a] New type of F. P. L. test specimen.

[b] 14.22 lbs. per sq. in. = 1 kg. per sq. cm.

Illustration of the first and third of these trends is afforded by the wood-joint data of Tables I, II, and III; the strength of wood joints is often more than twice the strength of the adhesive itself, "weak" sodium silicate has a joint strength of the same magnitude as "strong" animal glue, yet wood joints made with glue-dextrose are consistently, though very slightly, lower in strength than joints made with unadulterated animal glue. The second trend of specific adhesion, connecting joint strength with the strength of the material joined, also finds illustration in these data, but wood is so different in structure and chemical composition from the metals and crystalline compounds chosen by the investigators of mechanical adhesion to represent joints depending upon specific adhesion, that no importance should be attached to the agreement in this respect. The fourth trend cannot be demonstrated in wood joints, because the surface of wood is by nature rough enough to bring the thickness of the glue film into the region in which the effect of thickness is not appreciable.

When wood joints are made with the "weak" glues used by the interpreters of mechanical-adhesion hypothesis under gluing conditions favoring the production of good joints, and when the characteristics of the joints are compared with those of typical joints between "smooth" surfaces after the manner adopted by them, no differences are found that indicate a fundamental difference in the nature of the adhesion. On the contrary, there are striking similarities suggesting that the same kind of adhesion is probably operative. Nevertheless, no conclusions should be drawn about the nature of adhesion solely from evidence involving joint tests, especially when it is remembered that glue-dextrose mixtures and sodium silicate have not been studied so carefully as unadulterated animal glue and the gluing conditions under which they give best results are not so well known. The technic of testing the strength of films of glue is also in an early stage of development and the results reported so far may not be truly representative. Fortunately, considerations of a different kind, which are open to less serious criticism, have already been presented[6] to show that customary woodworking glues adhere specifically to wood surfaces. Strong wood joints could probably be made with ordinary glues if the wood presented only smooth, non-porous surfaces, but the fact that wood is porous makes it easier to glue it well, because it provides a larger area of interface between glue and wood for the action of specific adhesion and because it brings mechanical adhesion into play as well.

Mechanical adhesion to wood without concomitant specific adhesion is theoretically possible, of course, and practical examples of it can probably be found. There is reason to believe that the usual linseed-oil house paints cling to wood chiefly, if not entirely, by mechanical adhesion. The ease with which the bond between such coatings and the wood can be broken in blistering and peeling and the characteristic ultimate failure of the coatings by crumbling or flaking off the dense summerwood of the conifers while it remains clinging to the neighboring springwood suggest that the nature of the adhesion between paint and wood may be fundamentally different from the adhesion between glue and wood.

Conclusions

1—Wood joints materially stronger than those reported by the advocates of the mechanical-adhesion hypothesis can be made with (1) animal glue, (2) animal glue containing dextrose, and (3) sodium silicate, provided that more favorable gluing procedure be chosen for making the joints.

2—Wood joints obtained with these three glues under good gluing conditions display two striking properties that have been previously described as characteristic of specific adhesion—namely:

(*a*) The wood joints may be several times as strong as the glues from which they are made, (*b*) the strength of the glued joint is decreased, although slightly, by adulterating the glue with a material that weakens the film of the glue tested separately.

3—Wood joints obtained with the three glues satisfy all criteria of joints depending largely upon specific adhesion with respect to which they have been examined.

4—Wood joints made with the woodworking glues in common use depend for their strength very largely upon specific adhesion, although the porous nature of wood brings mechanical adhesion into play also.

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[14] McBain and Lee, *J. Phys. Chem.*, **31**, 1675 (1927).

[15] McBain and Lee, *Proc. Roy. Soc.* (*London*), **113**, 606 (1927).

New American Fabric Used in Parachutes

A new silk fabric, known as "Mock Leno," developed by the Bureau of Standards in coöperation with silk manufacturers, has been adopted by the Navy Department for use in parachutes, three hundred and twenty-six parachutes having been manufactured from it during the past year. Heretofore Japanese imported fabrics have been used exclusively for this purpose.

"Mock Leno" appears to possess all the desirable characteristics of the Japanese Habutai, except that its permeability is slightly higher. Its resistance to tear is considerably higher than Habutai, which makes the new product highly desirable for use in parachute construction.

The Silk Association of America is continuing its coöperation with the Bureau of Standards in an effort to develop a plain-woven domestic silk which will have all the advantages of the Japanese Habutai, with the added advantages of greater strength and resistance to tear. A number of samples of plain-woven silk have been manufactured by members of the Silk Association of America and are now undergoing tests at the Bureau of Standards. The Bureau of Aeronautics is extremely optimistic that the results of these tests will be highly beneficial. Considerable credit is due the Silk Association of America for the splendid spirit of coöperation which it has evidenced. Since the bureau instigated the investigation of domestic-woven parachute silk the price on parachutes has decreased considerably.

A Study of Water-Miscible Mineral-Oil Preparations[1]

Textile Oils, Leather Oils, Metal Cutting Oils, Etc.

Ralph Hart

The Hart Products Co., 1440 Broadway, New York, N. Y.

It is shown that the manufacture of clear water-miscible or "soluble" mineral oils is primarily a problem in miscibility, and that free oleic acid is essential to a uniform product. Miscibility curves for several emulsifiers, mineral oil, and oleic acid are given, by means of which uniform and non-uniform mixtures were traced. Free oleic acid decreases the stability of the emulsion, and may even prevent it altogether.

A number of terms have been defined which simplify investigation of soluble oils, and make for greater convenience in comparing them.

It is shown that the kind and quantity of mineral oil have practically no effect on the quantity of oleic acid that the mixture will tolerate and still give a good emulsion. This factor, on the other hand, varies with the kind of emulsifier, and even with the same type of emulsifier provided it is subject to adjustments.

It is further shown that alcohol has the following effects: (a) acts as a liquefier for the soap; (b) at first decreases and then, as more alcohol is added, increases the quantity of free oleic acid required for a homogeneous product; and (c) exerts no direct effect on the emulsion.

The addition of alkali to a soluble oil containing acid-sulfonated oil as the emulsifier yields the following results: (a) in the absence of alcohol, it at first decreases and then increases the quantity of free oleic acid required for a homogeneous product; (b) in the presence of sufficient alcohol, the more alkali the less oleic acid required to clear; and (c) the more neutralized the sulfonated oil the better it functions as emulsifier, the completely neutralized oil being the best in this respect.

Procedures are developed for testing the raw materials used in soluble oils. These tests may also be employed for examining kindred products.

Finally, methods are outlined for testing the stability of soluble oils, which may also be of service in stabilizing such oils during manufacture.

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THE many water-miscible or "soluble" mineral oils on the market are clear, uniform, oily liquids that give spontaneous stable emulsions with water, and which in the form of such emulsions are extensively used in a number of industries. Thus, in the manufacture of wool, soluble oil is used as a lubricant to facilitate the carding and spinning processes and as a means of preserving the staple of the interlocking fibers. As cotton softener or sizing oil, it is used to overcome the harshness of sizing mixtures, intended for increasing the tensile strength of the yarn before being woven. It is likewise recommended to facilitate removal of cotton hosiery from forms and to impart a desirable feel to the finished article. It is often recommended for cotton hosiery dyed sulfur black, since the film of oil supposed to surround the yarn is assumed to prevent "bronzing," or reddening of the color by protecting it from oxidation.

In the leather industry emulsifying oils are used in stuffing many kinds of leather, also to facilitate vegetable drum tannage and to aid in the drying of finished leathers. Spray oils for insecticidal purposes, while not identical with the products under discussion, involve similar principles in their manufacture.

Probably the greatest use for soluble oil emulsions is as cooling and lubricating agents in drilling, boring, and heavy-cutting of metals. These emulsions make very efficient cooling mixtures, owing to the high specific heat of water, and help to give a better and smoother finish to the work.

The principal ingredient in soluble oils is mineral oil, usually a low-viscosity spindle oil. The emulsifier may be (*a*) saponified rosin, oleic acid, or other fatty acids, with more or less alcohol; or (*b*) a sulfonated animal or vegetable oil such as castor, corn, cod, neat's-foot, etc., with or without alcohol. Another type of emulsifier of comparatively recent origin is a sulfonated mineral oil obtained as a by-product from the alcohol wash in refining mineral oil for medicinal purposes by the oleum process.

Klemgard[2] gives the following formula for a soluble oil:

	Parts by weight
Paraffin oil, 28° to 30° Bé	250
Rosin	22
Oleic acid	22
Caustic soda	3
Water	10
Alcohol	7

He claims that "the purpose of the alcohol is to keep the oil clear and bright and to aid in producing a perfect emulsion when the oil is mixed with water. The finished oil should contain from 20 to 30 per cent of the soda soap. The mineral oil generally used in this type of product has a viscosity of from 100 to 180 at 100° F. In some cases this type of oil has a tendency to evaporate off a portion of the alcohol, which permits separation of the oil and water."

Bingham[3] enumerates the purposes of soluble cutting oils, gives several formulas that have proved successful in practice and expresses a preference for one made with soap as the emulsifier, as it may be made without expensive apparatus and requires much less technical skill to fabricate. Heyden and Typke[4] describe the properties which cutting oils and their emulsions should possess from the user's point of view, and specify that the oil should contain not over 5 per cent water. Bumcke[5] compares the quality of sulfonated fish oils by determining their carrying capacity for mineral oil—i. e., the maximum quantity of mineral oil with which the sulfonated oil will give a homogeneous mixture—and concludes that it was not a mere coincidence that the best oil had the greatest carrying capacity.

In the manufacture of soluble oil the aim is to produce a clear, bright, uniform liquid that will give a spontaneous emulsion with water equal to or better than a specified permanency, and which, furthermore, will not cloud, separate, or in other ways be detrimentally affected on storing under

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[1] Received June 1, 1928.

[2] "Lubricating Greases," p. 162, Chemical Catalog Co., 1927.

[3] Bur. Standards, *Tech. Paper* **204** (1922).

[4] *Chem.-Ztg.*, **48**, 571 (1924).

[5] *J. Am. Leather Chem. Assocn.*, **22**, 621 (1927).

reasonable conditions. To attain these results simultaneously requires a very careful adjustment of the ingredients, even where the formula has been carefully standardized.

Little of a fundamental nature seems to have been published on this subject, and it is the writer's experience that the manufacture of soluble oils, as well as laboratory experiments dealing with the development of new formulas, has heretofore been based mostly on past experience or upon empirically acquired information. In this investigation the factors influencing the homogeneity and emulsifying properties of soluble oils were studied in detail, and the results reduced to general principles. These principles were then utilized to develop simple procedures for manufacturing, as well as for testing and experimenting with, oils of this kind. The findings may also be employed as methods for controlling the quality of the raw materials, and of kindred products, used in the preparation of soluble oils.

Materials Used

Two types of soluble oils were investigated, depending upon the emulsifier. In one case the emulsifier was the sodium soap of oleic acid; in the other, sulfonated (or, more properly, sulfated) castor oil, also known as Turkey red oil. The same mineral oil was used in both cases. The mineral oil had a specific gravity of 0.847 and a viscosity of 82 seconds Saybolt at 100° F. (37.8° C.). The sulfonated castor oil was a high-concentrated commercial oil, containing 25.8 per cent moisture and 4.8 per cent organically combined SO_3; it had an alkalinity of 38 mg. KOH per gram and an acidity of 44 mg. KOH per gram.[6] The oleic acid used was the ordinary commercial thin red oil with a low chilling point. The alkali used for neutralization was a solution of 30° Bé. caustic soda. Throughout the work, where temperature was of importance, the experiments were performed at about 30° C.

Effect of Oleic Acid on Uniformity

Most of the soluble oils on the market contain more or less oleic acid. In Table I are listed a few commercial products with the per cent emulsifier and the quantity of free oleic acid they contained. It will be observed that the free oleic acid varied from 14 per cent in sample 1 to zero in sample 4.

Table I—Free Oleic Acid in Commercial Soluble Oils

Sample	Use	Nature of Emulsifier	Emulsifier	Free Oleic Acid
			Per cent	*Per cent*
1	Hosiery softener	Sulfonated castor oil	30	14
2[a]	Cutting oil	Rosin soap	10	7
3[a]	Cutting oil	Sulfonated corn oil	15	6
4	Wool oil	Sulfonated corn oil	40	0

[a] Contained also some alcohol.

Oleic acid has long been known as a demulsifier, particularly for breaking petroleum emulsions. It has even been considered as a demulsifying[7] reagent in connection with an emulsion test for mineral oils. The question then arises—why introduce a demulsifying ingredient in a product in which the emulsion is of paramount importance? Experience with soluble oils, however, has shown that in order to obtain a homogeneous product free oleic acid is necessary, especially with certain types of oil. A study of various formulas for soluble oils, as well as some preliminary experiments, soon disclosed the fact that the manufacture of clear, uniform products was primarily a problem in miscibility, and that the function of the oleic acid, which is the most miscible with all the constituents in soluble oil, was to make mutually soluble the other partly miscible ingredients. It is obvious that the more immiscible the other ingredients in a given soluble oil, the more oleic acid will be required to bring about mutual solubility and vice versa.

Miscibility of Soap, Mineral Oil, and Oleic Acid—A series of tests was therefore undertaken to determine the relation existing in clear, soluble oils between the emulsifier, the free oleic acid, and the mineral oil. The soap emulsifier was first investigated. It was found at the outset that neutral hydrated soap was very little soluble in mineral oil, even in the presence of a large excess of oleic acid. On the other hand, by adding a small quantity of alcohol to the soap or to the mixture, a uniform product was easily obtained, provided sufficient free oleic acid was added. In the following experiments the emulsifier consisted of a practically neutral alcohol-water soap solution having the following composition: oleic acid 30 grams, 30° Bé. caustic soda 15 cc., and alcohol 30 cc.

In making this soap oleic acid was added to a warm mixture of alcohol and caustic, giving a clear, thin liquid. Successive portions of mineral oil were then added, the mixture warmed to about 30° C. and the quantity determined of free oleic acid just sufficient to turn the muddy mixture clear and uniform. The results are plotted in Figure 1.

Clear and Cloudy Mixtures with Soap as Emulsifier—The effect of more mineral oil or oleic acid on the uniformity of a given soluble oil can readily be seen from Figure 1. It is evident that only mixtures above the curve will be homogeneous. Hence, upon adding more mineral oil to clear mixture—represented on the curve, say, by point *a*—the oil will turn cloudy; since the new mixture will now be represented by point *b*, which is in the heterogeneous field (shaded in figure). In order to make the latter mixture clear again, it is only necessary to add more oleic acid, which will bring the mixture up to point *c* on the curve or beyond—i. e., in the homogeneous field. It is to be noted, however, that a large excess of oleic acid will ultimately cloud the oil, but that it may be cleared again with more alcohol. This reaction is probably due to a secondary effect of the excess fatty acid on the alcohol soap—the alcohol being miscible both with the soap and the oleic acid, would be expected to act as a corrective.

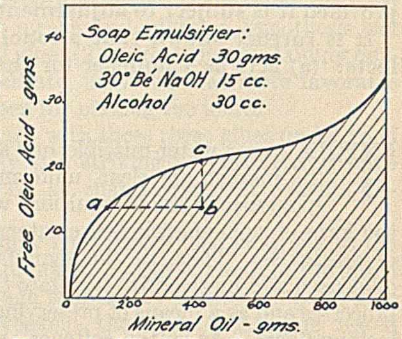

Figure 1—Miscibility Curve for Soap, Mineral Oil, and Oleic Acid

Miscibility of Sulfonated Castor Oil, Mineral Oil, and Oleic Acid—As already stated, sulfonated castor oil or other sulfonated oils or a combination of sulfonated oil and soap may be used as the emulsifier. Such preparations contain free oleic acid also which serves the same purpose as above—namely, to produce a uniform, homogeneous product. The effect of the different ingredients on the uniformity of soluble oils containing sulfonated oil is similar to the case just discussed, and will now be considered in detail for a product containing sulfonated castor oil as the emulsifier. Those familiar with such oils will have noticed that the proper amount of oleic acid added to all the other ingredients will change the cloudy mixture to a clear, uniform oil, but that excess of the fatty acid will cause it to cloud again. If more mineral oil is added, the product, contrary to expectations, becomes clear again, but excess mineral oil will cloud it once more. At this stage the transparency may be restored by adding, as above, more oleic acid. This brings the process back to the beginning of the cycle, which may be repeated.

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[6] Hart, J. Ind. Eng. Chem., **9**, 950 (1917); *J. Am. Leather Chem. Assocn.*, **16**, 525 (1921).

[7] *Proc. Am. Soc. Testing Materials*, **23**, 343 (1923).

CLEAR AND CLOUDY MIXTURES WITH SULFONATED OIL AS EMULSIFIER—Though puzzling at first these effects may readily be traced by referring to Figure 2, which gives the miscibility curves for mixtures of sulfonated castor oil, mineral oil, and oleic acid. A ternary system of this kind is best represented on a triangular diagram. The system composed of sulfonated castor oil, mineral oil, and oleic acid represents: (*a*) two pairs of partly miscible components—sulfonated oil and mineral oil, and sulfonated oil and oleic acid; and (*b*) one pair miscible in all proportions—mineral oil and oleic acid. A system of this type gives two curves,[8] represented in Figure 2 by *LM* and *RS*. To obtain curve *LM*, successive portions of mineral oil were added to a given quantity of the sulfonated oil and enough oleic acid was introduced to render the mixture homogeneous and bright. The data are given in Table II. To obtain curve *RS*, successive portions of mineral oil were added to a given quantity of the sulfonated oil, the cloudy mixtures at first cleared with oleic acid and then excess added until they turned cloudy again. Data for this curve are given in Table III.

The curves were not completed for mixtures containing low percentages of the sulfonated oil, since such mixtures could not be made clear. This may be due to a disturbance of the homogeneous equilibrium existing between the oleic acid and mineral oil, on the one hand, and the miscible and non-miscible parts of the sulfonated oil (which bear a constant ratio to each other), on the other. For it must be noted that the sulfonated oil, though for the sake of convenience assumed to be a single component, is actually a clear, uniform mixture of a number of miscible and partly miscible components such as water, soap, sulfonated fat, neutral fat, fatty anhydrides, etc. A similar phenomenon may be observed in the case of sulfonated corn oil or similar sulfonated oil—i. e., they are miscible, without the aid of oleic acid, with a certain quantity of mineral oil but not with excess. (See sample 4, Table I.)

Table II—Relation between Sulfonated Castor Oil, Mineral Oil, and Oleic Acid to Clear

MIXTURE	SULFONATED CASTOR OIL		MINERAL OIL		OLEIC ACID	
	Grams	*Per cent*	*Grams*	*Per cent*	*Grams*	*Per cent*
1	100	92.4	8.2	7.6	0.0	0.0
2	100	88.5	10.0	8.9	2.9	2.6
3	100	76.1	20.1	15.3	11.4	8.6
4	100	68.7	30.2	20.7	15.4	10.6
5	100	62.9	40.2	25.3	18.7	11.8
6	100	58.1	50.3	29.2	21.8	12.7
7	100	54.2	60.4	32.8	24.0	13.0
8	100	45.4	99.7	45.3	30.3	13.5
9	20	42.8	20.3	43.5	6.4	13.7
10	20	28.5	40.9	58.4	9.2	13.1
11	20	17.2	81.2	70.1	14.8	12.7
12	20	10.7	141.9	76.1	24.7	13.2
13	20	9.5	161.8	77.0	28.3	13.5

Table III—Relation between Sulfonated Castor Oil, Mineral Oil, and Oleic Acid to Cloud

MIXTURE	SULFONATED CASTOR OIL		MINERAL OIL		OLEIC ACID	
	Grams	*Per cent*	*Grams*	*Per cent*	*Grams*	*Per cent*
1	50	62.5	0	0.0	30	37.5
2	50	54.4	10	10.9	32	34.7
3	50	48.1	20	19.2	34	32.7
4	50	42.4	30	25.4	38	32.2
5	50	22.0	100	44.0	77	34.0
6	50	16.5	150	49.5	103	34.0
7	50	13.0	200	52.0	134	35.0
8	50	6.5	400	52.5	314	41.0
9	50	4.6	600	55.8	426	39.6

It is evident that the mixtures in Figure 2 represented by the area between the curves and the respective sides of the triangle (shaded in the diagram) are heterogeneous systems, but that outside of that field the mixtures will be clear. If a cloudy mixture of a certain composition is represented by point *a* it will become uniform and bright if enough oleic acid is added to bring its percentage composition to point *b*, or where the constant relative composition line, *BD*, intersects the curve *LM*. If more oleic acid is added, the mixture will stay clear until the composition is represented by point *c*, which is the intersection of the same line with curve *RS*, at which point a slight excess oleic acid will turn the mixture cloudy. If mineral oil is added to the mixture at *d*, the percentage composition will travel along *AE* until it strikes the curve *RS* at *e*, when more mineral oil will turn the mixture clear. The mixture will stay clear until the other curve is crossed at *f*, at which point the mixture will turn cloudy.

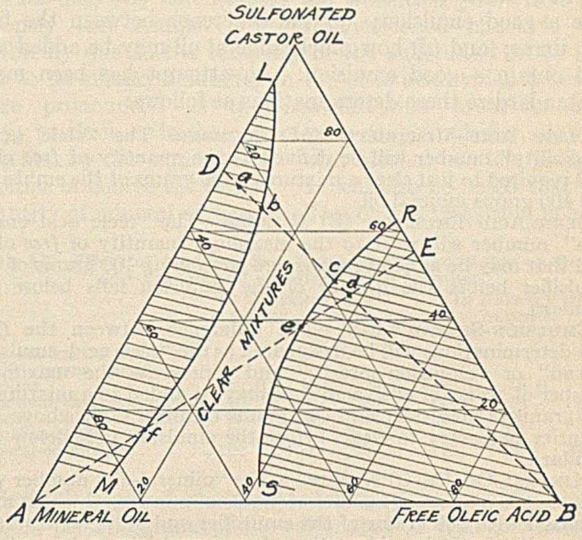

Figure 2—Miscibility Curves of Sulfonated Castor Oil, Mineral Oil, and Oleic Acid

Influence of Oleic Acid on Emulsion

As anticipated, increasing the quantity of free oleic acid in a given soluble oil caused a decrease in the permanency of the emulsion, and with considerable excess, prevented emulsification altogether. To determine this effect quantitatively, 50 grams of oleic acid and 200 grams of mineral oil were just neutralized with 25 cc. of 30° Bé. caustic soda to which had been added twice the volume of alcohol. The mixture was then just clarified with oleic acid (mixture No. 1 in Table IV), and a 5 per cent emulsion in 25 cc. of water made. Definite quantities of oleic acid were then added to the clear mixture, similar emulsions made after each addition, and the quality of all the emulsions compared after 24 hours' standing. The results are given in Table IV.

Table IV—Effect of Free Oleic Acid on Emulsion

MIXTURE	FREE OLEIC ACID	FREE OLEIC ACID PER 100 GRAMS SAPONIFIED OLEIC ACID	EMULSION
	Grams	*Grams*	
1	21	42	Good
2	26	56	Good
3	30	60	Good
4	34	68	Fair
5	38	76	Poor
6	42	84	Poor
7	46	92	None

It will be noticed that as long as the free oleic acid per 100 grams of the saponified oil was less than 68 grams the emulsions were satisfactory, but when above that the emulsions gradually decreased in stability until the free oleic acid content reached 88 grams, when the oil refused to emulsify altogether. The emulsions were graded as follows: "good" when the emulsion showed no separation at all or at most a fine white line on the edge of the surface; "fair" when the separation consisted of a thin creamy layer on top; "poor" when the upper layer was considerable; and "none" where there was a distinct water separation. It was also noticed that excess mineral oil caused a separation of clear oil, the

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[8] Findlay, "The Phase Rule," p. 216, Longmans, Green & Co., New York, 1927.

rest of the liquid remaining well emulsified, whereas excess oleic acid produced a creamy, emulsified separation over a clear water layer.

For the purpose of this paper, a 5 per cent emulsion as good as or better than that described as "fair" will be referred to as standard emulsion.

Definitions

In working with soluble oils it is important to determine: (*a*) how much oleic acid is required to produce a clear mixture; (*b*) how much oleic acid the mixture will tolerate and still give a good emulsion; (*c*) the difference between the first two items; and (*d*) how much mineral oil may be added and still obtain a good emulsion. An attempt has been made to standardize these determinations as follows:

OLEIC ACID–MISCIBILITY (M) NUMBER—The "oleic acid–miscibility" number will be defined as the quantity of *free* oleic acid required to just clear a mixture of 100 grams of the emulsifier and 400 grams mineral oil.

OLEIC ACID–EMULSION (E) NUMBER—The "oleic acid–emulsion" number will refer to the maximum quantity of *free* oleic acid that may be added to a mixture containing 100 grams of the emulsifier before the quality of the emulsion falls below the standard.

EMULSION-SPREAD (E-S)—The difference between the first two determinations will be designated as the "oleic acid–emulsion spread" or "emulsion-spread," and represents the maximum number of grams of oleic acid that may be added to a mixture of 100 grams of emulsifier and 400 grams of mineral oil, above the quantity necessary to clear, before the emulsion falls below the standard.

MINERAL-OIL (M-O) NUMBER—The "mineral-oil" number will indicate the maximum number of grams of mineral oil which may be mixed with 100 grams of the emulsifier and still give a standard emulsion. It is evident that the mineral-oil number will be equal to 400 when the emulsion spread is zero, above 400 when the emulsion spread is positive, and below when negative.

Effect of Mineral Oil

ON OLEIC ACID–EMULSION NUMBER—The experiments reported in Table V indicate that this factor is practically a constant for different kinds and quantities of mineral oil. In the last two experiments different oils were used. P1 oil had a specific gravity of 0.839 and a viscosity of 67 seconds Saybolt at 100° F. (37.8° C.); No. 500 oil was a heavy superrefined white medicinal mineral oil with a specific gravity of 0.897 and a viscosity of 293 Saybolt at 100° F.

Table V—Effect of Mineral Oil on Oleic Acid–Emulsion Number

MIXTURE	MINERAL OIL–SOAP	OLEIC ACID–EMULSION NUMBER
1	2:1	68
2	4:1	68
3	8:1	68
4	12:1	70
5	8:1 (P1 oil)	72
6	8:1 (No. 500 oil)	70

Effect of Emulsifier

ON OLEIC ACID–MISCIBILITY AND OLEIC ACID–EMULSION NUMBERS—Experiments recorded in Table VI indicate that not only do these numbers vary for different emulsifiers but that they may also vary for the same type emulsifier, provided the latter is subject to adjustments.

Table VI—Effect of Emulsifier on Oleic Acid–Miscibility and Oleic Acid–Emulsion Numbers

MIXTURE	EMULSIFIER	FREE SULFONATED ACIDS PER 100 GRAMS EMULSIFIER	OLEIC ACID–MISCIBILITY NUMBER	OLEIC ACID–EMULSION NUMBER
		Grams		
1	Soap	..	44	68
2	Sulfonated oil	0.0	82	80
3	Sulfonated oil	8.0	60	64
4	Sulfonated oil	22.0	84	40

Effect of Alcohol

ON CONSISTENCY OF SOAP—Practically all soluble oils on the market made with pure soap as the emulsifier and many oils with sulfonated oil as the base contain alcohol. The impression seems to be current that alcohol helps directly with the emulsification of the mineral oil—i. e., that it functions in a similar way as the emulsifier. The present investigation, however, indicates that the purpose of the alcohol is primarily to liquefy the soap or other emulsifier and consequently to make it more soluble—probably in the oleic acid. In fact, as far as the emulsion is concerned, it seems to exert an indirect negative effect. The progressive liquefying and solvent action of the alcohol can best be illustrated qualitatively by adding oleic acid to a caustic soda solution containing different amounts of alcohol. As the oleic acid is added to a solution with little alcohol, the mixture becomes white, thick, and pasty, ultimately liquefying and brightening, but only with a large excess oleic acid. On the other hand, a mixture containing alcohol remains liquid throughout the process and may require much less free oleic acid to make it bright.

These reactions in the presence of mineral oil are further illustrated in Table VII. To a mixture of mineral oil and 30° Bé. caustic soda, different quantities of alcohol (from 0.0 to 82 per cent by volume based on the lye) were added; oleic acid was next introduced, at first to complete neutralization, then in some excess, and finally in sufficient excess to clear the mixtures where possible. The appearance of the various mixtures and their corresponding oleic acid–miscibility numbers are given in this table. It will be observed that in the absence of alcohol the product could not be made bright with a reasonable excess oleic acid though it ultimately liquefied, but with 25 per cent alcohol and over the mixtures readily cleared with excess oleic acid and were easily liquefied.

Table VII—Effect of Alcohol and Oleic Acid on Soap Solution

ALCOHOL	OLEIC ACID TO NEUTRALIZE		OLEIC ACID TO CLEAR		OLEIC ACID–MISCIBILITY NUMBER
	Consistency	Appearance	Consistency	Appearance	
%[a]					
0	Pasty	Cloudy	Liquid	Cloudy	...
25	Less pasty	Cloudy	Liquid	Bright	113
40	Liquid	Clear	Liquid	Bright	107
60	Liquid	Cloudy	Liquid	Bright	44
65	Liquid	Cloudy	Liquid	Bright	44
77	Liquid	Cloudy	Liquid	Bright	53
82	Liquid	Cloudy	Liquid	Bright	93

[a] Per cent by volume of lye.

ON OLEIC ACID–MISCIBILITY NUMBER—It will be seen in Table VII that the oleic acid–miscibility number of the mixtures decreased with the increase in the per cent alcohol, until the latter reached 60 to 65 per cent, at which point the oleic acid–miscibility number was at its minimum; from there on, increasing the per cent alcohol caused an increase in the acid-miscibility number. It is therefore obvious that up to a certain point, which we shall call the "alcohol-soap liquefaction" point, alcohol increases the mutual solubility of the ingredients in the mixture, and that beyond that point it decreases the solubility. The reason for the last-mentioned effect will be evident when it is considered that alcohol and mineral oil are only sparingly miscible with each other, and consequently require a certain quantity of free oleic acid to make them mutually soluble. On the other hand, decreasing the amount of alcohol below this optimum causes the liquid soap to become pasty or jelly-like, as a result of which the soap dissolves with more and more difficulty, indicated by the increase in the oleic acid–miscibility numbers or the greater quantity of oleic acid required to affect uniformity.

It was found that the soap must be liquefied before a satisfactory product could be made. It is evident from Table VII that there are two methods of achieving this—namely, by adding either oleic acid or alcohol. The liquefying action of oleic acid on soap has been pointed out by the writer elsewhere.[9] It is absolutely ruled out in soluble oils, except where an economical formula is of no consequence, since its effect is to decrease the emulsion-spread by increasing the oleic acid–miscibility number. Alcohol is the only alternative, and hence its use in soluble oils. As shown above, however, there is a limit to the quantity of alcohol that may be added for efficient results, for beyond the soap-liquefaction transition point increasing the alcohol causes an increase in the oleic acid–miscibility number, thereby counteracting in part its beneficial effect.

Liquefaction Point—The alcohol-soap liquefaction point for oleic acid soap saponified with 30° Bé. caustic soda, as shown in Table VII, occurred in the presence of 60 to 65 per cent alcohol by volume based on the lye. At this point, corresponding to the lowest oleic acid–miscibility number, the transition was very marked—a slight increase in the quantity of alcohol being sufficient to transform the jelly-like consistency into a thin liquid. It was also noticed that the quantity of the mineral oil had no effect on the transition point, as will be evident from Figure 3, which gives the oleic acid–miscibility numbers for soap mixtures containing different amounts of alcohol and mineral oil. In all cases the mixtures containing 60–65 per cent alcohol of the lye had the smallest acid-miscibility numbers. It is needless to mention that the best emulsion number was obtained for a mixture with an alcohol content corresponding to the alcohol-soap liquefaction point.

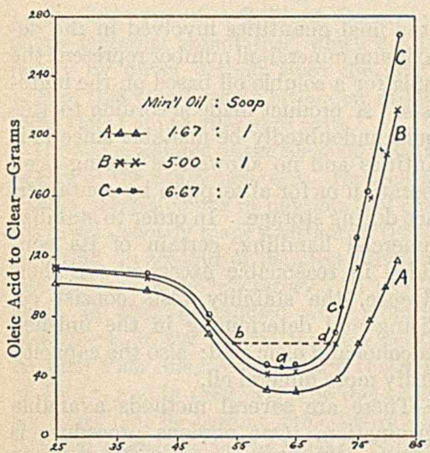

Figure 3—Effect of Alcohol on Miscibility

On Oleic Acid–Emulsion Number—Alcohol seems to exert practically no effect on the oleic acid–emulsion number, as reference to Table VIII shows. In these experiments 200 grams of mineral oil and 50 grams of neutralized sulfonated oil were mixed with different amounts of alcohol and the maximum oleic acid to give standard emulsions determined, from which the oleic acid–emulsion numbers were calculated. It will be observed that the oleic acid–emulsion numbers varied only from 80 to 84 for an alcohol range of 2.0 to 20 cc. per 50 grams sulfonated oil.

Table VIII—Effect of Alcohol on Oleic Acid-Emulsion Numbers

Alcohol, cc.	0.0	2.0	6.0	10.0	14.0	20.0
Oleic acid-emulsion number....		80	84	84	80	84

Effect of Alkali

On Oleic Acid–Miscibility and Oleic Acid–Emulsion Numbers—Alkali added to soluble oils containing sulfonated oil changes both the oleic acid–emulsion and the oleic acid–miscibility numbers. In Table VI it will be noticed that the oleic acid–emulsion number of the sulfonated oil mixture improved with the increase in alkali, reaching a maximum when the free sulfonated fatty acids were completely neutralized. The effect of alkali on the oleic acid–miscibility numbers is shown by curve *A*, Figure 4, in which different amounts of 30° Bé. caustic soda were added to a mixture of 8 parts mineral oil to 4 parts sulfonated castor oil, and then cleared with oleic acid. This series was repeated with the standard ratio of 4 parts mineral oil to 1 of emulsifier *B*. It will be observed that the oleic acid–miscibility numbers decreased with the increase in alkali, until a minimum was reached with 6 cc. caustic per 100 grams of the sulfonated oil (corresponding to 10 grams of free sulfonated fatty acids); beyond that point more alkali caused the oleic acid–miscibility number to increase, gradually attaining a maximum when the oil was completely neutralized. This behavior indicates that up to this transition point the more neutralized the oil the more soluble in the mixture (probably in the mineral oil), but that beyond the transition point it is apparently less soluble. The last-mentioned effect is undoubtedly due to the tendency of the sulfonated oil to jell, and to its smaller solubility in the oleic acid which becomes more pronounced as the neutralization proceeds. The soapy product, as in the case of pure soap emulsifier, may be liquefied by the same means—viz., alcohol or oleic acid, in practice of course the former. It will also be noted that the quantity of mineral oil had no effect on the transition point.

Table IX—Effect of Alkali or Free Sulfonated Fatty Acids on Emulsion-Spread and on Mineral-Oil Number

	In Presence of 6 Grams Alcohol			In Absence of Alcohol		
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Free sulfonated acids per 100 grams emulsifier, grams	22.0	8.0	0.0	22.0	8.0	0.0
Oleic acid-emulsion number	40	64	80	40	64	80
Oleic acid-miscibility number	96	68	64	84	60	82
Emulsion-spread	−56	−4	+16	−44	+4	−2
Mineral-oil number	100	400	600	140	440	340

Series *B*, Figure 4, was repeated in the presence of 6 grams of alcohol per 100 grams of the sulfonated oil (the alcohol-soap liquefaction quantity for this mixture) and the results are represented by curve *C*. In this case as the neutralization advanced there was a constant decrease in the oleic acid–miscibility number, reaching a minimum at complete neutralization. In other words, alcohol by overcoming the jellying effect of the soap had entirely obliterated the transition points in curves *A* and *B*. The effect of alkali on the oleic acid–miscibility and oleic acid–emulsion numbers is further illustrated by data given in Table IX.

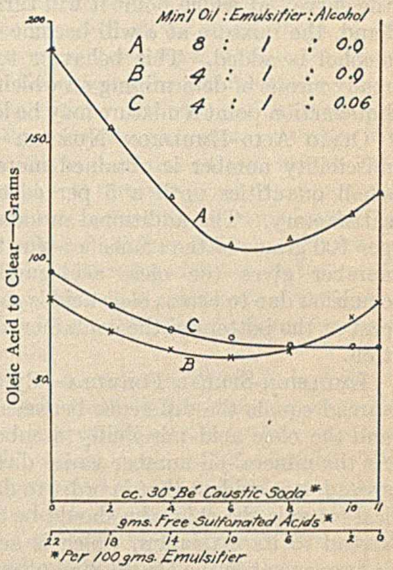

Figure 4—Effect of Free Sulfonated Acids on Miscibility

On Mineral-Oil Number—The effect of alkali on the mineral-oil number is similar to its effect on the emulsion-spread. In the presence of the "alcohol-soap liquefaction" quantity of alcohol, the emulsion-spread increases with the increase in the alkali content, being a maximum when the sulfonated oil is completely neutralized. (Table IX) The mineral-oil number consequently increases in a similar manner.

In the absence of alcohol, however, the emulsion-spread may not vary directly with the alkali, owing to the peculiar effect of the alkali on the oleic acid–miscibility number, whereby the latter at first is decreased and then increased as alkali is added. This, as well as the consequent effect on the emulsion-spread and the mineral-oil number, is also shown in Table IX, in which it will be noticed that the mineral-oil

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[9] Hart, J. Ind. Eng. Chem., 10, 598 (1918).

number increases from 140 to 440 and then drops to 340, as the amount of alkali is increased. Consideration of the mineral-oil numbers, Nos. 3 and 6, Table IX, will make it clear why certain soluble oils on the market, in which sulfonated castor oil is the emulsifier and which contain a comparatively small percentage of mineral oil, do not require alcohol, whereas the latter is always present in mixtures containing large percentages of mineral oil.

Tests for Raw Materials

These consist in determining the factors defined above—namely, (*a*) the oleic acid-miscibility number, (*b*) the oleic acid-emulsion number, (*c*) the emulsion-spread, and (*d*) the mineral-oil number.

OLEIC ACID-MISCIBILITY NUMBER—Fifty grams of the emulsifier are just neutralized with 30° Bé. caustic soda, alcohol added until the soap is thoroughly liquefied, 200 grams of mineral oil added, and oleic acid gradually introduced until the mixture becomes clear and uniform, the temperature being as low as that to which the finished product is likely to be exposed. The quantity of oleic acid required to clear the oil multiplied by 2 gives the oleic acid-miscibility number.

In case of soap emulsifier it is more feasible, owing to the pasting tendency of the neutralized soap and the danger of causing lumps, to add the oleic acid to the mixture of alkali and alcohol completing the liquefaction of the soap with the rest of the alcohol later. With sulfonated oil this precaution is not necessary.

To determine whether the proper amount of alcohol has been added to give the lowest oleic acid-miscibility number—i. e., to correspond to the optimum at *a*, curve *C*, Figure 3, the test should be repeated using in one case more alcohol and in the other less. If the proper amount had been used, the mixture with less alcohol will correspond to point *b*, Figure 3, and with more alcohol, to point *c*; in both cases evidently requiring more oleic acid to clear. Furthermore, the mixture at *b* will absorb more alcohol without clouding until the amount added corresponds to point *d* (the intersection of a horizontal line through *b* with the other arm of the curve), at which point it will turn cloudy. On the other hand, the mixture at *e* will become cloudy as soon as more alcohol is added. This behavior toward alcohol affords a ready means of determining on which side of the alcohol-soap liquefaction point a mixture may be located.

OLEIC ACID-EMULSION NUMBER—After the oleic acid-miscibility number is obtained more oleic acid is added in small quantities until a 5 per cent emulsion is no longer satisfactory. The additional amount of oleic acid required per 100 grams of the emulsifier plus the oleic acid-miscibility number gives the oleic acid-emulsion number. A poor emulsion due to excess oleic acid is soon indicated by a bluish cast at the bottom of the container, denoting a water separation.

EMULSION-SPREAD FORMULA—By definition the emulsion-spread equals the difference between the oleic acid-emulsion and the oleic acid-miscibility numbers, or (E-S) = (E-M). As the mineral-oil number varies directly with the emulsion-spread, it is evident that in order to develop the most economical formula the chief aim should be to increase the emulsion-spread to its maximum, which is accomplished by the best improvement in the emulsifying properties of the emulsifier—i. e., by increasing E—and by making all the other ingredients as soluble as possible in the mineral oil—i. e., by decreasing M.

MINERAL-OIL NUMBER—After the oleic acid-emulsion number is determined enough mineral oil is added to render the mixture faintly opalescent. The total amount of mineral oil in the final mixture, per 100 grams of emulsifier, represents the mineral-oil number. Some allowance should be made for overstepping the end point.

This test may be more precisely carried out as follows: The oleic acid-emulsion test is repeated but with less oleic acid than required; mineral oil is then added until the mixture turns cloudy, the latter cleared with more oleic acid, and the emulsion test made. One gram of oleic acid is now added to the mixture, more mineral oil introduced until it turns cloudy again, more oleic acid added to clear, and the emulsion test repeated. This is continued until the emulsion test is no longer satisfactory.

Tests for Stability of Product

It is obvious that the final quantities involved in the determination for the maximum mineral-oil number represent the most economical formula for a soluble oil based on the ingredients used in the tests. A product made according to this formula, however, would undoubtedly be unstable since it is based on critical quantities and no allowances having been made for loss by evaporation or for absorption by container, very likely to take place during storage. In order to stabilize the product for commercial handling, certain of its constituents must be added in reasonable excess above their critical quantities. Hence, the stability tests consist essentially of standardizing and determining in the finished product the excess of alcohol and oleic acid; also the capacity of the product to emulsify more mineral oil.

EXCESS ALCOHOL.—There are several methods available for making this determination. One obvious procedure is to run a volatilization test and notice the point where the oil turns cloudy. Another more convenient method is the following: A sample of the oil to be tested is heated until free from volatile ingredients and, while still warm, is added to the unheated oil; the amount of the heated oil required to produce cloudiness is a measure of the stability of the oil toward volatilization. The rationale of this method, which is equivalent to an exposure test, is evident.

EXCESS OLEIC ACID—In considering this test it should be remembered that solubility factors are affected by temperature changes. Hence, if a soluble oil just cleared with oleic acid is cooled to a lower temperature, it will probably turn cloudy, owing to insufficient oleic acid. This test, therefore, may consist in simply chilling the oil to a definite temperature, and noting whether or not the product remains clear and bright. Another method consists in determining the quantity of either mineral oil or alcohol that may be added to the soluble oil before it turns cloudy; for a mixture containing excess oleic acid above the quantity necessary to clear will evidently absorb more or less mineral oil, or alcohol, before clouding.

AVAILABLE MINERAL-OIL CAPACITY—This test which is an indication of the presence of more than sufficient emulsifiers to carry the mineral oil in the mixture, consists in determining the quantity of mineral oil that may still be added to the product, clearing with oleic acid if necessary, before the quality of the emulsion falls below the standard.

Acknowledgment

The writer wishes to express his appreciation and thanks to F. W. Breth, of W. H. Daugherty & Son Refining Co., for samples of medicinal oils; to Samuel Lehrer for encouragement during this work; and particularly to Morris B. Hart for drawing the graphs and other assistance in preparing this paper.

High-speed cinematographic apparatus has been constructed to photograph explosions of various kinds of dynamite to assist in determining their probable safety in coal mines.

AMERICAN CONTEMPORARIES

Russell Henry Chittenden

ONE of the recollections of my youth is the reading of the clear-cut medico-legal evidence given in a celebrated New Haven case by a young man named Chittenden. I was partly reared at Guilford, Conn., upon the ancestral lands of my maternal grandfather, which has been in the Chittenden family by direct descent since the first immigration in 1639. It is of this young man Chittenden, of his influence and personality, that I am privileged to write.

He was graduated at the Sheffield Scientific School at the age of nineteen. He then pursued a special course in physiological chemistry, was shortly made assistant in the subject, and on account of manifest fitness was given charge of the laboratory. In 1880 and again in 1882 he studied with Kühne in Heidelberg, in the interim teaching at Yale. In 1880 Yale conferred upon him the degree of Ph.D., and in 1882, when he was twenty-six years old, he became professor of physiological chemistry in the Sheffield Scientific School. This position he held for forty years, but prior to this he had been a student for three years and an instructor for seven, so that fifty years of his life was intimately identified with that of the university. In 1898 he became director of the Sheffield Scientific School and guided its destinies for twenty-four years.

Russell Henry Chittenden

Now what did he accomplish? He built up the first true school of scientific endeavor concerned with premedical education in this country; that is to say, he formed a group consisting of the master himself surrounded with pupils who in their turn became masters. And later as director of the Sheffield Scientific School he added to the resources of the institution great laboratories of mechanical and electrical engineering, the fine dormitories of the Vanderbilt quadrangle, and many other buildings, while his own department carried on in an ancient residence once the home of Mr. Sheffield, which had been converted into a laboratory. This old-fashioned house had few modern conveniences, which, however, counted as little in comparison with the high development of the mental processes of the human beings associated together for a great purpose. In the laboratory Chittenden worked hard and demanded the same of others. One of his students, who suffered from physiological laziness in college, has said he never worked so hard for any man and nevertheless was awarded scant praise for his endeavor. Another, the well-known pediatrician, the late Dr. John Howland, said that he received a greater stimulus from his course under Chittenden than was obtainable in the medical schools of that day. Chittenden diverted Harvey Cushing from the contemplated study of architecture into medicine. He inspired Theodore Janeway, E. P. Joslin, Samuel W. Lambert, Richard P. Strong, Joseph A. Blake, John A. Hartwell, Lewis A. Conner, L. B. Mendel, A. N. Richards, Gideon Wells, and many others, and gave them the power to become great teachers of mankind. He would persuade a pupil to spend an extra year with him after graduation and work in physiological chemistry. One heard it said in those days that such a one was "wasting a year with Chittenden," but it is a long time since anyone has thought such crass crudities, for the men who thus "wasted" became the leaders in their profession. Chittenden and his school provided teachers in physiological chemistry in thirty-one institutions.

In his laboratory Chittenden worked unceasingly winter and summer for many years until failing health brought doctors' orders that he must seek recreation. Like Charles Darwin in a similar predicament, he at first did not know where to find pleasure outside of his own work. Fortunately, however, he discovered that he was fond of fishing, and the waters of Maine and Florida have brought him health and happiness. They also gave the world a masterpiece, his "Physiological Economy in Nutrition," which showed that health and strength could be maintained upon a low protein dietary. He has recorded the laboratory findings upon himself during a period of a year and a half. Christmas passed with no alteration of his regimen. Only once, on the occasion of the annual dinner of the American Physiological Society, did the daily protein intake show a slight increase, a proof—were any needed—of the humanity of his character.

In the winter of 1918 Chittenden and I went to Europe as members of the Interallied Scientific Food Commission under instructions from our Government to reduce the food requisitions upon the United States to a minimum. The Food Committee of the Royal Society had adopted 3000 utilizable calories per day as the requirement of an average man doing an average day's work, and at the Paris meeting of the Interallied Commission their representatives were inflexible in holding to this position. Before one of the meetings, while walking over the Pont Royal which took us to the left bank of the Seine, Chittenden said to me, "Lusk, we are here to aid these suffering peoples to the maximum of our power." A few minutes later he said before the startled commission, "If you will not hear us we might as well go home." This led to the unanimous adoption of a modification of statement that read: "It was agreed that in case this ration could not be provided a reduction of not more than 10 per cent could be borne for some time without injury to health."

Chittenden was a friend of Lord Bryce, whom he had entertained in New Haven, and others in England respected his opinions, though in the nature of things the mission was not popular. He spoke well, clearly, and always forcibly. His weekly letters to Mr. Hoover were models of accurate observations transmitted from England, France, and Italy, and served to enlighten the Food Administration at Washington with regard to events during the difficult winter of 1918. This was at a time when fifteen large British ships were being sunk weekly by submarines and unnumbered others were limping back to port, and when food from the United States was of supreme importance.

Chittenden is short in stature and slender in frame, with piercing dark eyes which nothing escapes, a true born New Englander, shrewd and able. By scientific conviction he is of frugal habits and—except for fishing—he has never sought personal pleasure.

His greatest joy lies in the realization of the help he has given to the many distinguished men who have been his pupils. Through the Chittenden school of biological chemistry and largely through his personal influence the subject which he expounded has attained greater prominence in the United States than in any other country. As Germany honors a Kossel, so this country, did it have a like appreciation of scientific values, would honor a Chittenden.

It is reported that Henry Ford is interested in scientific nutrition. No more appropriate undertaking could be imagined than a Chittenden Laboratory of Nutrition at Yale University. The statement that water can flow no higher than its source is contradicted by the appearance of the great Imperial Government Laboratory at Tokyo in charge of a pupil of Chittenden. There is no reason why an institute of nutrition should not be as extended as the Rockefeller Institute for Medical Research, for this country consumes the equivalent of twelve billion dollars worth of food per annum and exports a large surplus. There is every reason why such an institute should bear the name of Russell Henry Chittenden. Graham Lusk

BOOK REVIEWS

Annual Survey of American Chemistry. Volume III—July 1, 1927, to July 1, 1928. Prepared under the auspices of the Division of Chemistry and Chemical Technology of the National Research Council. Edited by Clarence J. West. 395 pages. The Chemical Catalog Company, Inc., New York, 1928. Price, $3.00.

Fifty-three experts, many of them of considerable distinction, have reviewed the year's contribution to chemical advancement in America. This work has been classified under forty-six chapter headings and it would seem improbable that anything had escaped. But, for instance, one does not find a chapter on electrochemistry, and it is not likely that all the contributions in this field have received adequate notice elsewhere in the book.

It is a very impressive demonstration of the amount and character of work done in our country. Moreover, most of the chapters make very interesting reading and will undoubtedly prove helpful to workers in the several fields. Having demonstrated how well their task can be accomplished, cannot those responsible for the enterprise be induced to make future volumes truly worth while by including reviews of the year's foreign work as well as the domestic? After all, chemistry is not American, nor can there be such a thing as an American Chemistry.

Some of the contributors have done little more than list titles, so that the reader learns that Smith worked on so and so, but nothing of what Smith found or accomplished. Others have been bold enough to offer occasional running criticisms, which, in every case this reviewer noted, have been to the advantage of the text. Again, other contributors have proposed, in more or less specific terms, subjects for research. This does not appeal to this reviewer as worth while, competent workers will find their problems of themselves.

Perhaps a minor criticism is the somewhat lurid use of prepositions in many of the chapters. "Crystallizing out," "crystallizing out of," "flattening out," "scaling off of" are unfortunate expressions frequently encountered.

The book must appeal to every chemist who has an occasional hour to "browse," and he will find it, among other things, a pleasant and profitable task to see how one and the same article has made its different appeals to two or more of the experts responsible for the various chapters.—Frank K. Cameron

Nitroglycerine and Nitroglycerine Explosives. By Phokion Naoum, translated into English by E. M. Symmes. The World Wide Chemical Translation Series, edited by E. Emmet Reid. 469 pages. The Williams & Wilkins Company, Baltimore, 1928. Price, $7.00.

When the original of this text, written by the director of the research laboratories of the Nobel Dynamite Company in Hamburg, appeared in 1924, it was widely reviewed and highly praised. It is fortunate that its translation into English has been undertaken by an American chemist who has had a considerable and intimate contact with the dynamite works of the Hercules Powder Company. The chief adverse criticism of the original text was its omission of any reference to American practice. The translator has met this criticism by introducing observations from his experience in American manufacture, generally in the form of footnotes.

The translation of so large a book on so technial a subject was a considerable undertaking, which Mr. Symmes has, on the whole, performed very well. He has not, however, escaped altogether from the influence of the involved construction of the original text, nor of its descriptive terms, as evidenced in the legend "Powdery Dynamites" for Chapter XIX, when in English the terms "pulverulent" or "granular" are commonly used.

The most serious matter for criticism is the use of the term "permissible" in the title and throughout the text of Chapter XXIII, which deals with nitroglycerin explosives for use in gaseous and dusty coal mines. "Permissible explosive" is a highly specified term adopted by the U. S. Bureau of Mines to designate such explosives as have passed its prescribed tests in its particular form and design of apparatus, the first such list having appeared May 15, 1909. This chapter opens, however, with a historical review of the development of systems of testing explosives for use in gaseous and dusty coal mines, beginning approximately in 1884, and the author points out in great detail that, because of the differences in the conditions surrounding the making of the tests and the varying practices that prevail in different countries, the list of these official explosives for use in coal mines varies with the country issuing the list. As "permissible explosives" are designed to protect life and property by decreasing the dangers attending coal-mining, it is most unfortunate that this confusion has been introduced.

Through the make-up of the book, with other dimensions the same, the thickness of the translation is 6 cm., where that of the original is but 2 cm. In fact, the book is so large as to be cumbersome and, with the large increase in the rate of publication of books, one is led to wonder where, if their sizes increase at such a rate as this, we may find the space in which to store them.

Notwithstanding the above criticisms, this work is the most authoritative and up to date on its subject extant.—Charles E. Munroe

Colloid Symposium Monograph. Volume VI. Papers presented at the Sixth Symposium on Colloid Chemistry, University of Toronto, June, 1928. Edited by Harry Boyer Weiser. 346 pages. The Chemical Catalog Company, Inc., New York, 1928. Price, $6.50.

The Sixth Colloid Symposium became an international meeting with speakers from Canada, England, Germany, and the States. In this volume are published the twenty-five papers presented. About two-thirds of these papers are equally divided between biological topics and various aspects of adsorption and interfacial phenomena. Several papers illustrate industrial problems with colloid features; the remainder treat of gels, coagulation, and miscellaneous topics.

The place of honor is deservedly held by an essay in which Sir William B. Hardy, pioneer in the field of colloid science and guest of honor at the Symposium, offers a fascinating discussion of the intriguing physico-chemical problems presented by living matter. Other biological papers attracting the reviewer's attention are H. A. Abramson's describing the remarkable permeability of various gels to blood cells and other microöbjects undergoing cataphoretic migration; A. Stamm's ingenious use of various colloid and capillary phenomena to reveal the structure of wood; and the coördination of the surface properties and phagocytosis of bacteria by Stuart Mudd, *et al.* Useful technics are described by J. B. Nichols (ultra-centrifuge), E. A. Hauser (micro-vulcanizer), and D. R. Briggs (electrokinetics and surface conductance). An interesting conflict in viewpoint appears in papers by W. D. Harkins and J. W. McBain concerning the cause for discrepancies between Gibbs's adsorption equation and direct measurements. Harkins' argument seems the more convincing to the reviewer. The forms of precipitates receive quite different but effective treatments at the hands of S. E. Sheppard *et al.* and of H. B. Weiser *et al.* It is unfortunate that the movies of the latter could not be reproduced in the book.

On the whole, the collection recalls a statement by the guest of honor that "the colloidal kingdom seems to be an Alsatia wherein difficult states of matter find refuge." A greater diversification of papers than here presented could scarcely be obtained by choosing at random from a complete A. C. S. program. It scarcely could be more difficult to hold a real symposium (in the modern sense) on chemistry in general than on colloids in general. By focusing the attention and unifying the thought, the consideration of only two or three somewhat restricted topics might increase the value of these symposia.—ELMER O. KRAEMER

Calculations in Quantitative Chemical Analysis. BY JOHN A. WILKINSON. 139 pages. McGraw-Hill Book Co., Inc., New York, 1928. Price, $1.75.

This little book "is intended to accompany the course in quantitative analysis which is generally given to sophomores in colleges and universities." It covers systematically and quite thoroughly the mathematical calculations encountered in various types of quantitative analyses. The first chapter takes up the elementary calculations of quantitative yields from chemical reactions. In subsequent chapters the author discusses calculations for the various types of gravimetric and volumetric analyses, the last three chapters being devoted to oxidation-reduction methods.

It is refreshing to note that on page 47 attention is called to a point so often overlooked by analysts—namely, that "one may spend an unnecessarily large amount of time trying to cut down an error in one part of the analysis while in another part of the same determination an unavoidable error enters which is many times the value of the first one." Many of the problems given in the book, however, are not consistent with this statement. For example, on page 18 the WO_3 on a 0.2000-gram sample of steel weighs 0.0050 gram and the tungsten percentage is given in the answer as 1.983. In problem 4 on page 117, with a titration of 20.33 cc. it is useless to weigh the sample and standardize the solution to five significant figures.

The statement on page 64 that "the per cent of any constituent is equal to the weight of the constituent divided by the total weight" is, of course, incorrect, even though baseball batting averages are thus calculated. The book is remarkably free from typographical errors. If the abbreviation for decagram is "dag." and for decameter "dam." should not the abbreviation for hectogram be "hog."? The U. S. Bureau of Standards uses the abbreviations dkg., dkm., and hg. Table II would be more convenient if arranged alphabetically, and a table of volumetric factors might well have been included.

The book is well written and should be valuable to beginners in quantitative analysis. The chapter on Balancing Equations can be recommended even to experienced analysts.—ROGER C. GRIFFIN

The Chemical Engineering Catalog. Thirteenth Annual Edition. 1107 pages. The Chemical Catalog Company, Inc., New York, 1928. Price, $10, except to special classes of technical men, to whom it is loaned gratis, or sold at $3 per copy.

The Thirteenth Annual Edition of the Chemical Engineering Catalog retains all the advantages of previous editions of this indispensable reference work and, at the same time, introduces certain changes in format and arrangement which are highly to be commended.

The subject index, which has necessarily become extremely voluminous, has been split into two separate indexes, one restricted to equipment and supplies and the other devoted to chemical and raw materials. Furthermore, both of these indexes have been very carefully edited so as to reduce the number of headings to those absolutely necessary. This simplification should be much appreciated by those who have occasion to use the catalog constantly for reference purposes. Another improvement is the establishment of a separate trade-name index, which should be extremely useful in determining the name and location of a manufacturer of a product of which the brand or trade name only is known.

The constant effort exerted by the publishers to get manufacturers to regard the catalog as a means of disseminating technical data rather than as an advertising medium seems to be bearing fruit. The amount of exact technical data in the book is considerably amplified. However, there is still room for improvement. For instance, it is hard to understand why all the manufacturers of chemicals do not furnish detailed information similar to that given by the Dow Chemical Company (to mention one of many) on their splendid pair of pages. It seems peculiar that one of the largest chemical manufacturers of the country with a huge variety of products is represented by merely a single page giving a meager list of a few organic chemicals accompanied by no useful information. Detailed technical data accompanied by graphs such as those furnished by the Calorizing Company and the Corning Glass Works (to mention only two conspicuous instances) are most useful and it is hoped that many other concerns will incorporate data of this character in future editions of the catalog.

The supervising committee and the publishing company are both to be congratulated on the constant progress displayed by the catalog, and the chemical process industries are fortunate indeed in having such a standard reference work available.—L. V. REDMAN

A Survey of Nitrocellulose Lacquer. BY BRUCE K. BROWN AND FRANCIS M. CRAWFORD. 368 pages. The Chemical Catalog Company, Inc., New York, 1928. Price, $7.50.

This book comprises an introductory chapter on solvents and plasticizers; a section containing abstracts of United States, Canadian, English, French, German, Dutch, and Japanese patents in the field of cellulose lacquers; a bibliography of the literature on the subject; and patentee and compound indexes to the patent section. Because of these bibliographic features it should prove valuable to the lacquer technologist.

In the introduction solvents and plasticizers are discussed, and there is also a treatment of various faults in lacquer films such as "blush," "orange peel," and gelling. Consideration of the conditions affecting hardness, flexibility and durability, "lifting," shrinking, adhesion, gloss, etc., is not attempted. The authors emphasize the colloidal nature of lacquer dispersions, but use this word too infrequently, employing the less desirable term "solution" in most cases. In connection with their discussion of evaporation rate of solvents, a series of curves illustrative of vapor pressure–temperature relations might have simplified their treatment and clarified the discussion. The use of triaxial diagrams might likewise have simplified the discussion of the compatibilities of lacquer components. Solvent and solution viscosity are dismissed with but slight attention, although these will probably be of considerable importance in the future when higher concentrations of solids in lacquers are realized. On page 12 the authors assail the generalization that "like dissolves like" in connection with their discussion of the solubility of nitrocellulose in various solvents. Their attack on the generalization would be more convincing were it not for the fact that the materials cited in disproof all contain at least one of the functional groups of the nitrocellulose molecule. A particularly unfortunate citation is that of the solubility of nitrocellulose in hydroxy esters, since nitrocellulose is itself a hydroxy ester and from the generalization it would be presumed that hydroxy esters would be good solvents for nitrocellulose.

The major portion of the book consists of a compilation of patent abstracts, and its value is self-evident. The inclusion of more cross references to equivalent patents in other countries might, however, be an improvement. A minor item is the manner of listing United States reissues, which are placed out of chronological order. The authors are to be thanked for their service in thus rendering available the large number of patents on nitrocellulose lacquers in a form convenient for use.

It is to be hoped that the publication of this very valuable book will stimulate interest in the production of similar works in other fields, since such books are of more permanent value than many of the popular treatises, which rapidly become obsolete.—PAUL J. CULHANE

Report of the Fuel Research Board for the Period Ended 31st March, 1928. DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. 70 pages. His Majesty's Stationery Office, London, 1928. Price, 1 s. 3 d., net.

This annual report gives brief résumés of the year's progress on the following investigations: Physical and chemical survey of the national coal resources; methods of sampling and analyzing coal; tests of coal in vertical and horizontal gas retorts and water-gas machines; low-temperature carbonization; study of domestic and metallurgical coke; briquetting; purification of coal; hydrogenation of coal; internal-combustion engines and power alcohol; miscellaneous investigations.—A. C. FIELDNER

Chemical Publications. Their Nature and Use. By Melvin Guy Mellon. 253 pages. McGraw-Hill Book Co., Inc., New York, 1928. Price, $2.50.

If it appears on first glance that this book is an unnecessary undertaking after the publication of Crane and Patterson's "Literature of Chemistry," the reader will soon find by examination of the contents that the new publication is fully justified. "Literature of Chemistry" is a manual and reference work; "Chemical Publications" is a college textbook, based on the course taught by Doctor Mellon at Purdue.

Its logical sequence takes the student from the origin of chemical literature, through the essential source lists, to a chapter on searching procedure. Sources are classified as original and secondary. The first class includes those containing new matter or discussions of known matter (unorganized information); the second comprises compilations of known matter in organized form. Original sources are discussed in separate chapters on periodicals, institutional and government publications, patents, and miscellany (including bulletins of commercial concerns and dissertations). In the secondary sources, separate chapters are given to abstract and review periodicals, bibliographies, and reference works (which include monographs and textbooks). For searching, general instructions are given on the use of libraries and on classification systems, card catalogs, indexes, etc. Suggestions both to makers and users of indexes are a helpful feature. Then specific instructions are given for ten different types of searches. Finally, a section of library problems (14 in number) furnishes material for class work or opportunity for one who studies the book alone to perfect his technic in use of the literature. A thorough study of this book, alone or in class, will lay the necessary foundation for acquiring such technic; practice will do the rest.

The book-making features and typography speak well for the publishers. In future editions it might be well to repeat the footnote references at the end as a convenient bibliography of the subject.—Julian F. Smith

Chemical Calculations. By J. S. Long and H. V. Anderson. 2nd edition. ix + 227 pages. 13.7 × 20.3 cm. McGraw-Hill Book Co., Inc., New York, 1928. Price, $1.75.

Those who have used this book will welcome the new edition. The concepts of atomic structure and electron transfer are used in explaining chemical reactions. Several new chapters have been added, the chief of which are those on atomic structure and oxidation-reduction reactions. Additional problems without answers have been given at the end of each chapter.

The chapter on reversible reactions, mass action, and common ion effect should be given earlier rather than almost at the end of the book. The electrochemical equivalent of an element is defined as its "atomic weight divided by its valence." This erroneous definition also appears in the International Critical Tables and should be corrected to read the "atomic weight divided by the change in valence." Emphasis should be placed on the fact that the chemical equivalent depends on the reaction under consideration, since even in neutralization reactions the same substance may have two or three different chemical equivalents. Distinction should be made between ionic and non-ionic reactions. Since it is not desirable to state that the sulfur atom loses four electrons in uniting with oxygen to form sulfur dioxide, it may be necessary to introduce the idea of sharing of electrons. The atomic weight table should contain the year. In the first edition the table on solubility products gives Hg_2Cl_2, $[Hg_2^{++}] \times [Cl^-]_2 = 2.0 \times 10^{-18}$, while in the second edition (page 220) the table gives HgCl, $[Hg^+]\ [Cl^-] = 2.0 \times 10^{-18}$. It is generally accepted that the mercurous ion is bivalent.

The emphasis on the solution of concrete problems as "a source of satisfaction to a vigorous, growing intellect" will be welcomed by those who are of the opinion that our education in some circles is drifting too much toward the insistence that chemistry be made easy and interesting at the sacrifice of discipline and logical and mathematical thinking.—Stephen Popoff

Practical Bacteriology. An Introduction to Bacteriological Technic. By Fred W. Tanner. xiv + 235 pages. 72 figures. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London, 1928. Price, $2.50.

This laboratory guide for beginners in general bacteriology should prove useful in those institutions where a general course in bacteriology is given and where no special emphasis is desired on a particular branch of the science. It is well written and profusely illustrated. A few of the figures could have been omitted without injuring the high character of the book, but these shortcomings are more than compensated for by the very good illustrations showing glassware, apparatus, microscope, and other equipment.

Careful attention was paid to details in describing the apparatus, sterilization, the microscope, the preparation of media, and the staining and examination of bacteria. Other chapters on the isolation and study of the characteristics of bacteria are equally well done. There is a short chapter on the study of molds. A plan for laboratory work for a class meeting three times a week on alternate days is given in the thirty-four pages of Chapter IX. Special exercises on the isolation and physiology of various types of microörganisms, an appendix containing staining and other formulas, and lists of laboratory guides and textbooks complete the book. The author has avoided the use of pathogens for the most part by the substitution of a harmless saprophyte of similar character. This should give the student a broader conception of microörganic life without detracting from the interest in the subject. Most guides have so stressed the importance of the pathogens, either intentionally or unintentionally, that this departure from the ordinary is very welcome and should prove popular in a good many institutions.—Nathan R. Smith

Finding and Stopping Waste in Modern Boiler Rooms. A Reference Manual to Aid the Owner, Manager, and Operator in Securing and Maintaining Boiler Plant Economy. By the Cochrane Corporation, Philadelphia, Pa. 788 pages. Price, $3.00.

The title and subtitle define the purpose and suggest the scope of the work. The book is divided into five sections: Fuels, Combustion, Heat Absorption, Boiler Efficiency and Testing, and Feed Water Heating and Conditioning. Within themselves, the first, third, and fourth are well organized and carry a continuity of subject. The section on combustion could have been improved, if the classification had been in some such order as: theory, methods of firing, controls, and equipment. Instead, the material on hand firing precedes the controls and equipment, while the other methods of firing follow. In a similar fashion the last section treats of boiler scale and its elimination and then includes embrittlement, corrosion, and de-aeration.

The book is freely illustrated with clear sketches and pictures and contains many tables and graphs. Its thesis is, "Exact knowledge rests upon measurements." Although there is frequent mention of authorities, specific references are almost entirely lacking. This is a handicap for those who desire to search further into the literature, but it lends interest to the statements cited.

Altogether, the work is quite comprehensive and well modernized. It presents a desirable combination of theory and practice for those to whom it is directed.—Lincoln T. Work

Chemie der Zuckerindustrie. Ein Handbuch für Wissenschaft und Praxis. By Oskar Wohryzek. Second corrected and enlarged edition, with 17 illustrations. 696 pages. 6¼ × 9¼ inches. Julius Springer, Berlin, 1928. Price, bound, 36 marks.

The many friends of the first edition of Wohryzek's handbook, which was published in 1914, will welcome the appearance of this new revision.

The subject matter, as in the previous edition, is treated under three main divisions. The first division, upon the Chemistry of the Beet, discusses the chemistry of the beet cell; biochemistry of the beet; composition of the beet; chemistry of beet marc; chemistry of nitrogenous and non-nitrogenous constituents of beet juice; valuation of beets; sugar-beet refuse; and chemical changes during storage of sugar beets. The second division, upon the Chemistry of Raw Sugar Manufacture, treats of the chemistry of diffusion; composition and disposal of exhausted cossettes; composition and properties of raw juice; chemistry of preheating and clarification of juice; chemistry of press cake; clarifying agents; composition and properties of clarified juice; chemical processes during evaporation; composition and properties of sirup; chemical processes during boiling of sirup; fillmass and its manipulation; chemistry of raw sugar, after-products and molasses; course of the nitrogenous and nitrogen-free non-sugars during raw-sugar manufacture; and sources of chemical losses in raw-sugar manufacture. The third division, upon the Chemistry of Raw-Sugar Refining, discusses the storage of raw sugar; affination; clarification; bone black and bone-black filtration;

decolorizing carbons; use of colors and bleaching agents; course of non-sugars in refining; and source of chemical losses during refining. An appendix gives an account of developments which occurred in various branches of the subject while the book was in press, thus bringing the material up to the middle of June, 1928.

Owing to the rejection of obsolete and non-pertinent matter that was included in the first edition, such as that relating to the chemistry of the Hyross Rak, Naudet, Pfeiffer-Bergreen, and other abandoned processes of beet-sugar manufacture, the author has been able to include much new material, such as that upon the vitamins of the sugar beet, decolorizing carbons, etc., in the second edition without increasing the size of the volume. The work shows evidence of careful painstaking revision, although the important work of some American investigators has been overlooked. The title of the book is also somewhat misleading, for nothing is mentioned about the chemistry of cane-sugar manufacture. "The Chemistry of Beet-Sugar Manufacture in Europe" would be a more accurate designation of the volume. The typography of the volume is excellent, the book is provided with a good index, and there are copious footnote references to original publication.

This new edition of Wohryzek's Chemistry of the Sugar Industry is warmly recommended as an indispensable laboratory and factory manual to all beet-sugar technologists. For the field which it covers the book is not only the best but the only volume of its kind.—C. A. Browne

Chemische Laboratorien. Ihre Neuzeitliche Einrichtung und Leitung. By Alfred Behre. 113 pages. 33 illustrations. Akademische Verlagsgesellschaft, M. B. H., Leipzig, 1928. Price, paper, 6 marks; bound, 7 marks.

The author has endeavored to show the progress in the construction and equipment of laboratories during the past ten years. He has treated the subject in a general way so that any industry can adapt the plans to its own particular needs.

He distinguishes four kinds of laboratories: (1) technical or factory, (2) experimental, (3) educational, and (4) research. While these overlap, as a technical high school may have both educational and research laboratories and a factory may have experimental and research laboratories, yet in general the division is possible.

Very good suggestions are made concerning the location of a new building or the adaptation of an old building; with regard to construction of the building itself, of the floors, walls, work tables, the arrangement of plumbing, and a complete list of possible rooms with suggested arrangements.

The laboratories given as examples are all located in Germany. It is unfortunate that new laboratories built in other European countries and in the United States have not been included. The laboratories described are of five types—industrial, applied chemistry, technical high school or university, agricultural research, and municipal. They are hardly comparable with those required by the larger American educational institutions, but are good examples of the types. The suggestions concerning individual rooms are pertinent to every type of laboratory.—Edward Bartow

Das Anthracen und die Anthrachinone mit den zugehörigen vielkernigen Systemen. By J. Houben and W. Fischer. 890 pages. Georg Thieme, Leipzig, 1929. Price, paper, 85 marks; bound, 90 marks.

This work takes the highest place among the few books which cover the very important field of anthracene, anthraquinones, and their polynuclear systems. The author covers the field of anthraquinone from its beginning to its tremendous expansion at the present time. This book should be in every dyestuff chemist's library.

The clear presentation and the thorough treatment and arrangement of the material with full reference to the literature and patents permit the chemist to become thoroughly acquainted with this field in a short time without a tedious research in the literature.

First the book gives the history of anthracene, and clearly presents the nomenclature of anthracene chemistry and the chemical constitution in connection with fluorescence of anthracene derivatives and color of anthraquinone derivatives. The fundamental theories and facts on the color and chemical constitution of anthraquinone derivatives are covered in a clear and well-arranged manner. The classification of the anthracene dyes is made from the standpoint of a scientific system. Special emphasis is laid on the vat dyes, their relationships being shown with beautiful clarity in a diagram. In fact, the book contains numerous diagrams and tables which present the extensive field in the simplest form.

The general chapters are followed by special chapters on anthracene and dianthranyl derivatives, quinones of anthracene and dianthranyl with their derivatives, and condensed ring systems both isocyclic and heterocyclic, finally treating dyes of unknown constitution and the nuclei of condensed anthracenes as well as the radicals of importance in anthracene chemistry.

An index of the patent literature concludes the book. More than thirteen hundred German patents are covered and are considered in the various chapters. The working up and expert classification of this immense number of patents alone would be sufficient to make this book extremely valuable to the chemical industry.—A. O. Jaeger

Schmiermittel und ihre Richtige Verwendung. By Curt Ehlers. 112 pages. Otto Spamer, Leipzig, 1928. Price, paper, 8 marks; bound, 10 marks.

This little book apparently represents Continental, or at least German, opinion and practice in the field of lubricants and lubrication. The emergencies of war, the scarcity of suitable native materials, and the desire to be independent of foreign supplies have prompted in Europe the attempt to use inferior crude petroleums and such substitutes as coal-tar oils for the production of lubricants. The European user must therefore be more on his guard to make sure of the quality of his purchases than is necessary in this country. This condition is reflected in the present book by the tendency to emphasize certain tests little used in this country, such as ash content and tar number. The discussion also reflects the dependence of Europe on American refiners for the bulk of its lubricating oil demands.

The book is clearly written in semi-technical language and only a few bibliographic references are given. There is a fairly accurate but not strictly up-to-date discussion of the various petroleum oils of the world, a short chapter on tests, and another of pointed common sense for purchasers. This is followed by discussion of individual types of machinery, with recommendations as to suitable lubricants for each and analytical data on oils actually so used. The author has apparently been a little too uncritical in his acceptance of the claims made for certain types of lubricating oils. At the end miscellaneous lubricants are discussed and there are a few paragraphs on reclaiming used oils.

American exporters of lubricants may find this book of value as related to the probable demands of their Continental customers.—W. A. Gruse

Die Bestimmung der Dauerfestigkeit der knetbaren, veredelbaren Leichtmetallegierungen. By Richard Wagner. 63 pages. 56 figures. 15.5 × 23.5 cm. Julius Springer, Berlin, 1928. Price, paper, 6 marks.

This short monograph on the fatigue testing of the so-called strong alloys of the light metals, aluminum and magnesium, is a report from the Institut für mechanische Technologie und Material-kunde der technischen Hochschule of Berlin. The investigation included the determination of the elastic limit, yield point, tensile strength, the static endurance (creep) limit, the dynamic endurance limit (with reversed flexural stress), and the repeated impact endurance limit. The tests were carried out with Duralumin (three grades), Lautal, Skleron, and Elektron (a magnesium-base alloy). Several of the so-called short-time methods of determining fatigue strength were tried, but found to be unsatisfactory for giving reliable information as to the endurance limit of the materials tested. This is in agreement with the experience of other investigators. A number of the methods employed are open to criticism, but workers in this field will find the data presented of interest.—Junius D. Edwards

New Books

A. S. T. M. Tentative Standards, 1928. 932 pp. American Society for Testing Materials, Philadelphia, Pa. Price, paper, $7.00; cloth, $8.00.

Elementary Laboratory Experiments in Organic Chemistry. Roger Adams and John R. Johnson. 304 pp. The Macmillan Co., New York. Price, $1.90.

Introductory Qualitative Analysis. Jacob Cornog and Warren C. Vosburgh. 155 pp. The Macmillan Co., New York. Price, $1.60.

Principles and Practice of the Dilution Method of Sewage Disposal. W. E. Adeney. 161 pp. The Macmillan Co., New York. Price, $5.00.

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

Statistical Abstract of the United States, 1928. Fiftieth Number. 841 pp. Cloth, $1.00.

The Italian Chemical Industry. E. Humes. *Trade Information Bulletin* 577. 48 pp. Paper, 10 cents.

Bureau of Mines

A Comparison of the Acidity of Waters from Some Active and Abandoned Coal Mines. R. D. Leitch and W. P. Yant. *Reports of Investigations* 2895. 8 pp.

Asphalt and Related Bitumens in 1927. G. R. Hopkins and A. B. Coons. *Mineral Resources of the United States, 1927.* Part II, pp. 67–80. Paper, 5 cents.

Bauxite and Aluminum in 1927. J. M. Hill. *Mineral Resources of the United States, 1927.* Part I, pp. 7–24. Paper, 5 cents.

Consumption of Explosives in September, 1928. *Consumption of Explosives* 79. 8 pp.

Consumption of Primary or Virgin Tin in the United States, 1927. J. B. Umhau. *Circular* 6084. 2 pp.

Copper in 1926 (General Report). C. E. Julihn and H. M. Meyer. *Mineral Resources of the United States, 1926.* Part I, pp. 559–615. Paper, 10 cents.

Determination of Flakiness of Ores. W. H. Coghill, O. W. Holmes, and A. B. Campbell. *Reports of Investigations* 2899. 7 pp.

Ferrous Oxide from Iron and Magnetite. C. Travis Anderson. *Reports of Investigations* 2898. 7 pp.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1926. Mine Report. C. W. Henderson. *Mineral Resources of the United States, 1926.* Part I, pp. 617–25. Paper, 5 cents.

Methods of Preparing and Cleaning Some Common Heavy Liquids Used in Ore Testing. R. G. O'Meara and J. B. Clemmer. *Reports of Investigations* 2897. 6 pp.

Mine Explosions in the United States during the Fiscal Year Ending June 30, 1928. *Circular* 6085. 4 pp.

National Survey of Fuel Oil Distribution, 1927. E. B. Swanson. Prepared in coöperation with the American Petroleum Institute. 27 pp.

Official Changes in the Active List of Permissible Explosives for October, 1928. *Reports of Investigations* 2900. 2 pp.

Petroleum, Petroleum Products, and Natural Gasoline, September, 1928. *Monthly Petroleum Statement* 43. 11 pp.

Potash in 1927. A. T. Coons. *Mineral Resources of the United States, 1927.* Part II, pp. 43–50. Paper, 5 cents.

Production of Explosives in the United States, Calendar Year 1927. W. W. Adams. *Technical Paper* 435. 49 pp. Paper, 10 cents.

Study of Less Volatile Oils in Salt Creek, Wyoming, Crude. H. M. Smith. *Technical Paper* 428. 28 pp. Paper, 5 cents.

The Production of Magnesia and Silica Crucibles in the Induction Furnace. C. N. Schuette. *Reports of Investigations* 2896. 6 pp.

The Relations between Specific Volume, Voids, and Size Composition in Systems of Broken Solids of Mixed Sizes. C. C. Furnas. *Reports of Investigations* 2894. 10 pp.

Volumetric and A. P. I. Gravity Changes Due to the Solution of Gas in Crude Oils. R. Van A. Mills and R. E. Heithecker. *Reports of Investigations* 2893. 15 pp.

Bureau of Standards

A Study of the Hydrogen-Antimony-Tin Method for the Determination of Oxygen in Cast Irons. Bengt Kjerrman and Louis Jordan. *Research Paper* 25. Reprint from *Bureau of Standards Journal of Research* (November, 1928), pp. 701–20. Paper, 5 cents.

Effect of Temperature Change on the Color of Red and Yellow Lovibond Glasses. D. B. Judd. *Bureau of Standards Journal of Research,* 1 (November, 1928), pp. 859–66.

Metallic Packing for Condenser Tubes (Specification) Approved May 23, 1928, as American Marine Standard E No. 20–1928. *American Marine Standards Committee* 41. 8 pp. 5 cents.

Sensitization of Photographic Emulsions by Colloidal Materials. B. H. Carroll and Donald Hubbard. *Bureau of Standards Journal of Research,* 1 (October, 1928), pp. 565–88.

The International Temperature Scale. George K. Burgess. *Research Paper* 22. Reprint from *Bureau of Standards Journal of Research* (October, 1928), pp. 635–40. Paper, 5 cents.

Thermal Expansion of Magnesium and Some of Its Alloys. Peter Hidnert and W. T. Sweeney. *Research Paper* 29. Reprint from *Bureau of Standards Journal of Research* (November, 1928), pp. 771–92. Paper, 10 cents.

United States Government Master Specification for Powder, Scouring, for Floors. *Circular* 370. 6 pp. Paper, 5 cents.

Same. Trisodium Phosphate, Technical (Phosphate Cleaner). *Circular* 369. 5 pp. Paper, 5 cents.

Coast and Geodetic Survey

Measurement of Salinity of Sea Water. *Special Publication* 147. 20 pp. Paper, 10 cents.

Department of Agriculture

Application of Sodium Fluosilicate by Airplane in Attempt to Control Sugar-Cane Moth Borer. T. E. Holloway, W. E. Haley, and J. W. Ingram. *Circular* 45. 8 pp. Paper, 5 cents.

Carbon Disulfide as an Insecticide. *Farmers' Bulletin* 799, reprinted. 13 pp. Paper, 5 cents.

Dietary Requirements for Fertility and Lactation: A Dietary Sterility Associated with Vitamin Deficiency. Barnett Sure. *Journal of Agricultural Research,* 37 (July 15, 1928), 87–92.

Same. The Vitamin A Content of Wheat Oil. Barnett Sure. *Journal of Agricultural Research,* 37 (July 15, 1928), 93–9.

Fungicide as Term Commonly Used Has Three Definitions. *Separate* 1011 from Agriculture Yearbook 1927. 2 pp. Paper, 5 cents.

Phosphorus Distribution in Grains. J. E. Webster. *Journal of Agricultural Research,* 37 (July 15, 1928), 123–5.

Rapid Growth of Chicks on Rations of Natural Foodstuffs. A. G. Hogan, C. L. Shrewsbury, and H. L. Kempster. *Journal of Agricultural Research,* 37 (July 15, 1928), 115–21.

Regulations for the Enforcement of the Insecticide Act of 1910, 3rd revision. Service and Regulatory Announcements, *Insecticide and Fungicide* 1. (Superseded Department *Circular* 34.) 12 pp. Paper, 5 cents.

Report of the Chief of the Bureau of Chemistry and Soils for Fiscal Year Ended June 30, 1928. 30 pp.

Rubber Possibilities of Many Kinds Exist in United States. O. F. Cook. *Separate* 993 from Agriculture Year Book 1927. 4 pp. Paper, 5 cents.

The Energy Metabolism of Cattle in Relation to the Plane of Nutrition. E. B. Forbes, W. W. Braham, Max Kriss, C. D. Jeffries, R. W. Swift, R. B. French, R. C. Miller, and C. V. Smythe. *Journal of Agricultural Research,* 37 (September 1, 1928), 253–300.

The Influence of the Soil Reaction on the Ionizable Constituents of the Tomato as Determined by Electrodialysis. E. S. Haber. *Journal of Agricultural Research,* 37 (July 15, 1928), 101–14.

Geological Survey

Surface Water Supply of the United States, 1924. Part XI—Pacific Slope Basins in California. N. C. Grover, H. D. McGlashan, and F. F. Henshaw. *Water-Supply Paper* 591. 448 pp. Paper, 50 cents.

The Pumpkin Buttes Coal Field, Wyoming. C. H. Wegemann, R. W. Howell, and C. E. Dobbin. *Bulletin* 806-A. 14 pp. Paper, 10 cents.

Navy Department

Chemical Warfare and Naval Medical Officer. Treatise on Chemical Warfare Defense. Issued by Training Division. E. W. Brown. Navy Training Courses. 30 pp.

President of the United States

Fluorspar. Proclamation authorizing certain increase in duty on fluorspar containing not more than 93 per centum of calcium fluoride, in order to equalize difference in costs of production of said fluorspar in the United States and England. No. 1854. 2 pp. October 17, 1928.

Smithsonian Institution

Notes on the Principles and Process of X-Ray Examination of Paintings. Alan Burroughs. *Publication* 2951 from the Smithsonian Report for 1927, pp. 529–33.

The Coming of the New Coal Age. E. E. Slosson. *Publication* 2935 from the Smithsonian Report for 1927, pp. 243–53.

The Nucleus of the Atom. J. A. Crowther. *Publication* 2932 from the Smithsonian Report for 1927, pp. 209–16.

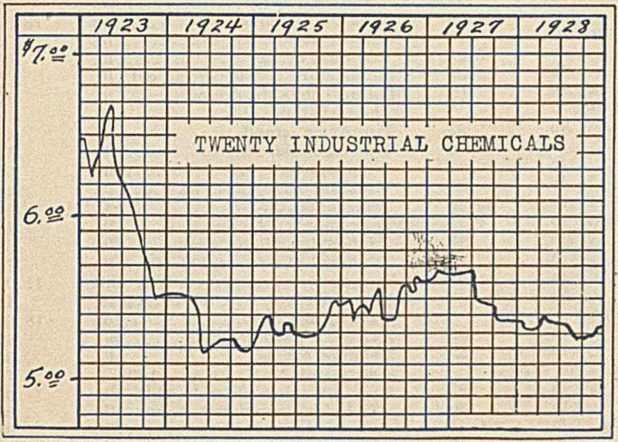
Tariff Commission

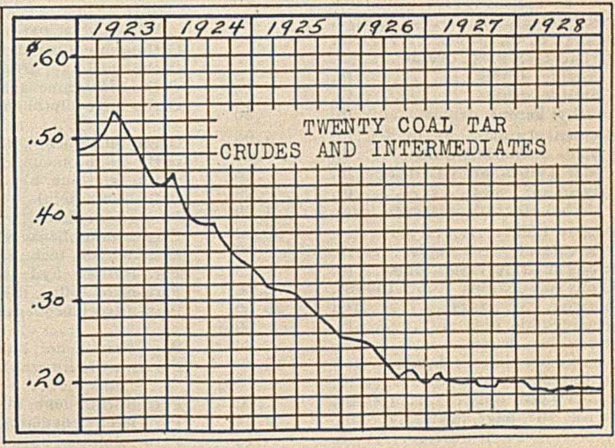
Census of Dyes and of Other Synthetic Organic Chemicals, 1927. *Trade Information Series* 37. 191 pp. Paper, 30 cents.

MARKET REPORT—DECEMBER, 1928

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON DECEMBER 15

Acetanilide, U. S. P., bbls.	lb.	.36
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.15
Acetophenetidine, bbls.	lb.	1.40
Acid, acetic, 28%, c/l. bbls.	100 lbs.	4.13
56%, c/l. bbls.	100 lbs.	7.35
Glacial, c/l. bbls.	100 lbs.	13.68
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.57
Boric, bags	lb.	.06¾
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.21
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.05
Chromic, pure, 98%, drums.	lb.	.21
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.46
Cresylic, pale, drums	gal.	.74
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.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.10
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.	.85
Lactic, 22%, dark, bbls.	lb.	.04¾
66%, light, bbls., wks.	lb.	.26
Mixed, tanks, wks.	N unit	.07¾
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphate, bulk	ton	9.00
Phosphoric, 50%, cbys.	lb.	.08
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.86
Salicylic, tech., bbls.	lb.	.37
Stearic, d. p., bbls., c/l.	lb.	.14½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks.	ton	15.50
60°, tanks, wks.	ton	11.00
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.35
Tartaric, U. S. P., cryst., bbls.	lb.	.38
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.69½
Amyl, 10%, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.18¼
Cologne spirit, bbls.	gal.	2.67
Denatured, No. 5, comp. denat., c/l. drs.	gal.	.48
No. 1, comp. denat., drs.	gal.	.49
Isoamyl, drums	gal.	3.50
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.	.240
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. kegs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.14
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.	5.40
Lump, casks	lb.	.11
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.06
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.31
Phosphate, dibasic, tech., bbls.	lb.	.18
Sulfate, bulk, wks.	100 lbs.	2.40
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	gal.	1.72
Aniline oil, drums	lb.	.15¼
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.90
Antimony, metal	lb.	.09¾
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls.	lb.	.10½
Salt, dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs	lb.	.50
Red, kegs, cases	lb.	.10½
White, c/l. kegs	lb.	.03¾
Asbestine, bulk, c/l.	ton	14.75
Barium carbonate, bbls., bags, wks.	ton	57.00
Chloride, bags, wks.	ton	68.00
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04⅜
Nitrate, casks	lb.	.08¼
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.	.23
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.	1.70
Bismuth, nitrate, 25-lb. jars	lb.	1.80
Oxychloride, boxes	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	2.05
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.	.02½
Bordeaux mixture, bbls.,	lb.	.10½
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.45
Bromobenzene, drums	lb.	.50

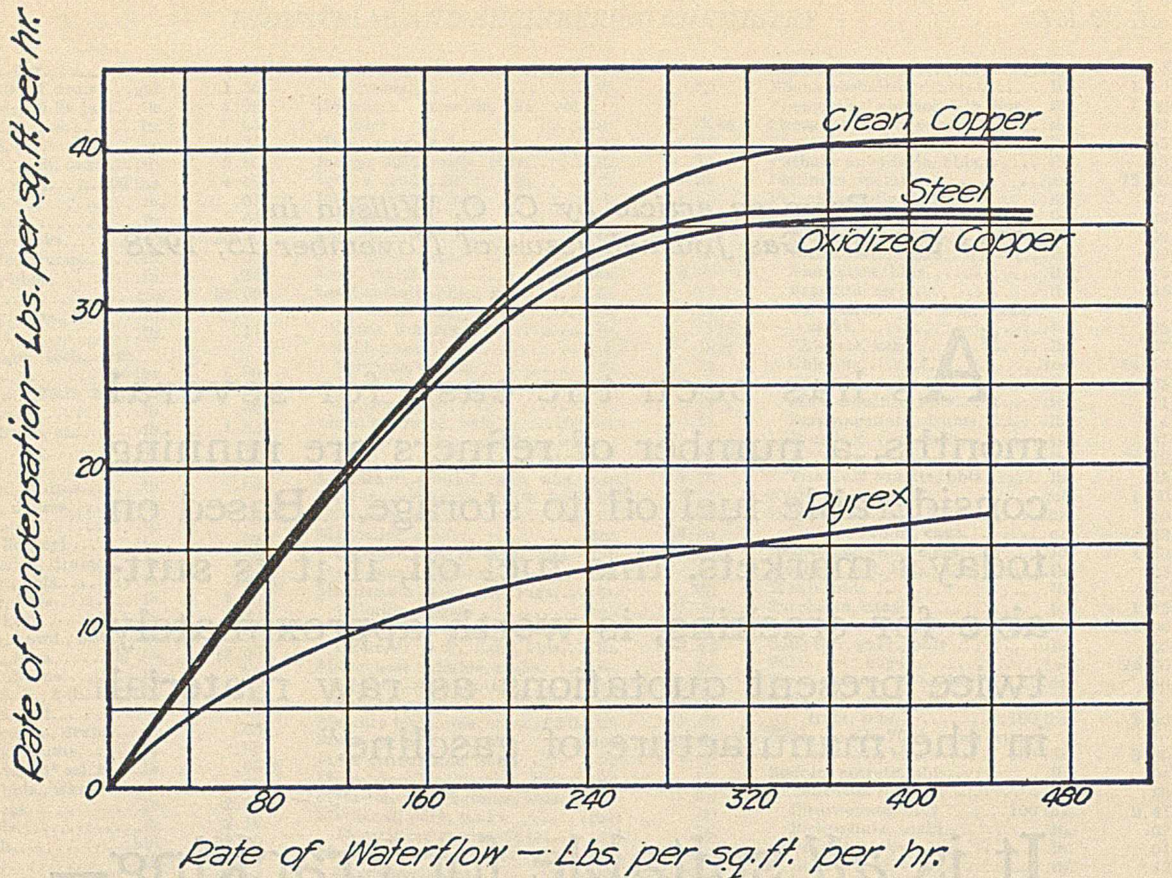




Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.38
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.65
Cadmium sulfide, cs.	lb.	1.35
Caffeine, U. S. P., 5-lb. cans	lb.	2.80
Calcium acetate, bags	100 lbs.	4.50
Arsenate, bbls.	lb.	.07
Carbide, drums	lb.	.05
Chloride, drums, wks.	ton	20.00
Cyanide, 100-lb. drums	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, 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.	.10
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls.	lb.	.14½
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bags	100 lbs.	15.00
Chloral hydrate, drums	lb.	.70
Chloramine, U. S. P., 5-lb. bot.	lb.	1.75
Chlorine, liq., c/l., cyl.	lb.	.03½
Chlorobenzene, mono-, drums	lb.	.08
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.	2.10
Cod-liver oil, bbls.	bbl.	39.50
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lbs.	16.00
Copper carbonate, bbls.	lb.	.17
Chloride, bbls.	lb.	.25
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.20
Sulfate, c/l., bbls.	100 lbs.	5.50
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.27¾
Cyanamide, bulk, N. Y.	Ammon. unit	1.67½
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	2.85
Dibutylphthalate, drums, wks.	lb.	.29½
Diethylaniline, drums	lb.	.55
Diethylene glycol, l. c. l. lots, drums	lb.	.20
Carload lots, drums	lb.	.15
Diethyl phthalate, drums	lb.	.24
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.27
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.35
Dinitrophenol, bbls.	lb.	.31
Diphenylamine, bbls.	lb.	.45
Diphenylguanidine, bbls.	lb.	.40
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.20
Ethyl acetate, 85%, drums	gal.	.87
Bromide, drums	lb.	.70
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene dichloride, tanks	lb.	.07
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.26
Ethyl ether, drums, cars	gal.	1.79
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.09½
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.	.70
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.15
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.	280.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lbs.	6.50
Lead acetate, bbls., white	lb.	.13
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.08½
Red, bbls.	lb.	.09½
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.	.06½
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06
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	122.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, pure, tanks	gal.	.60
Denaturing grade, tanks	gal.	.60
Methyl acetone, drums	gal.	.92
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.	.33
Nickel salt, single, bbls.	lb.	.10
Double, bbls.	lb.	.10½
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.10¼
Oil, castor, No. 1	lb.	.13
China wood, bbls.	lb.	.14½
Coconut, Ceylon, tanks	lb.	.08⅜
Cod, N. F., tanks	gal.	.60
Corn, crude, tanks, mills	lb.	.08¾
Cottonseed, crude, tanks	lb.	.08½
Lard, edible, bbls.	lb.	.16
Linseed, bbls.	lb.	.102
Menhaden, crude, tanks	gal.	.48
Neat's-foot, pure, bbls.	lb.	.15¼
Oleo, No. 1, bbls.	lb.	.11¾
Olive oil, denat., bbls.	gal.	1.25
Foots, bbls.	lb.	.10½
Palm, Lagos, casks	lb.	.08½
Peanut, crude, bbls.	lb.	.12
Perilla, bbls.	lb.	.20
Rapeseed, bbls., English	gal.	.82
Red, bbls.	lb.	.10⅛
Soy bean, crude, bbls.	lb.	.12¼
Sperm, 38°, bbls.	gal.	.84
Whale, bbls., natural, winter	gal.	.78
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.17
Ortho-toluidine, bbls.	lb.	.29
Palladium, metal	oz.	46.80
Para-aminophenol, kegs	lb.	1.15
Para-dichlorobenzene	lb.	.17
Paraldehyde, tech., drums	lb.	.26
Para-formaldehyde, cases	lb.	.40
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, 250-lb. kegs	lb.	.23

Phenol, drums	lb.	.13
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.	72.00
Potash, caustic, drums	lb.	.07⅛
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.09
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅜
Chlorate, kegs	lb.	.07½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.11½
Permanganate, drums	lb.	.14½
Prussiate, red, casks	lb.	.37
Yellow, casks	lb.	.18
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.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.40¼
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.40
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.00
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.41
Bichromate, casks	lb.	.07¼
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.42
Carbonate, sal soda, bbls.	100 lbs.	1.30
Chlorate, kegs	lb.	.06½
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.	2.17½
Nitrite, bbls.	lb.	.08
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisodium	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.12
Silicate, drums, tanks, 40°	100 lbs.	1.20
Silicofluoride, bbls.	lb.	.05¼
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.	.80
Strontium carbonate, bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.08¾
Strychnine alkaloid, 100 oz., powd.	oz.	.46
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.08
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand.	lb.	.49½
Tin bichloride, 50% sol., bbls.	lb.	.14½
Oxide, bbls.	lb.	.50
Titanium oxide, bbls., wks.	lb.	.40
Toluene, tanks	gal.	.40
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.70
Tungsten	WO_3 unit	11.00
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.40
Xylidine, drums	lb.	.38
Zinc, metal, N. Y.	100 lbs.	6.70
Zinc ammonium chloride, bbls.	lb.	.05⅛
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls.	lb.	.07⅜
Stearate, bbls.	lb.	.19
Zinc dust, bbls., kegs c/l.	lb.	.09



PYREX Cooler and Condenser Tubes as indicated by the above chart have approximately one-half the heat transfer value of metal tubes at the more rapid rates of flow

In cooler and condenser tubes

PYREX Tubing offers you these advantages

T.M. Reg. U. S. Pat. Off.

AS *PYREX Condenser Tubes successfully resist corrosion, high temperatures and thermal shock and at the same time have a surprisingly high rate of heat transfer, they are preferable to metal tubes for some liquids.

The measurements for the above curves were made on (1) clean copper tubes, (2) oxidized copper tubes, (3) Shelby steel tubing and (4) PYREX Glass Tubing. These curves show that the surface film resistance is practically the controlling factor in the case of metal condenser tubes and that volume conductivity has only a small effect. For this reason copper having a conductivity coefficient of more than three hundred times that of the glass, only condenses 2.5 times as much steam as PYREX Tubing for the more rapid rates of flow.

Permanence
Chemical resistance
Heat transfer
Transparency
Hardness

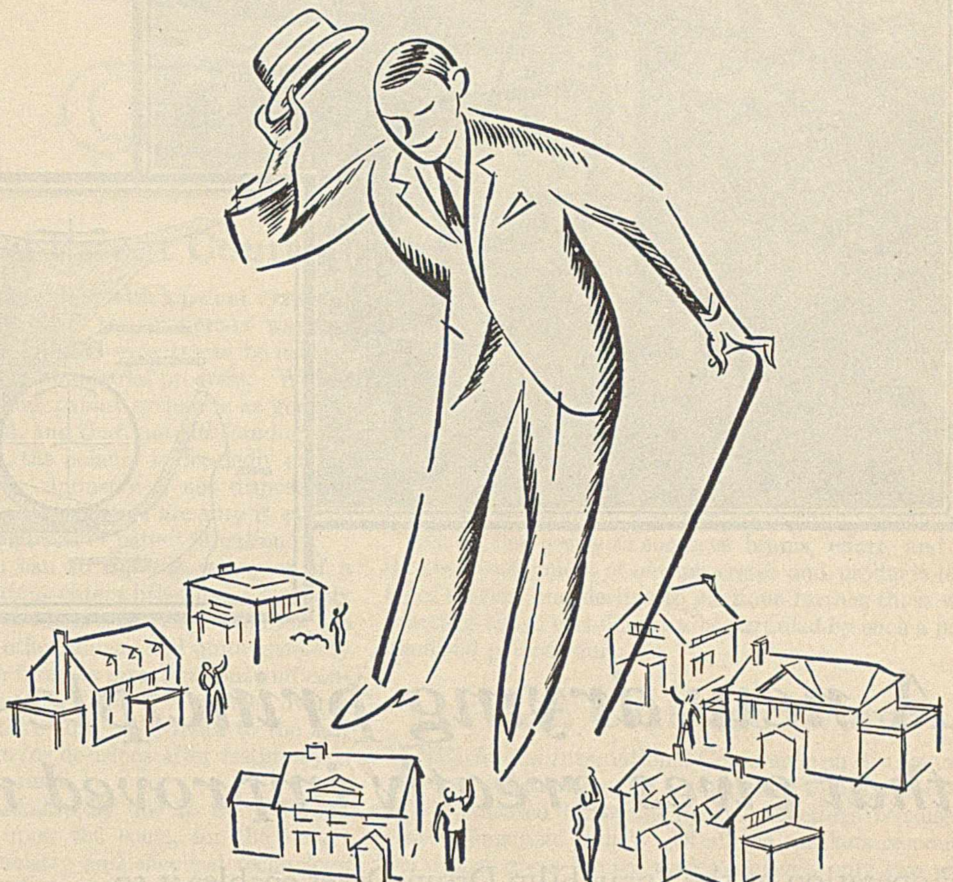
PYREX Condenser Tubes have this unique combination of properties. They are chemically stable — they resist corrosion. They will not break under extremes of temperature encountered in condensation apparatus. Their heat transfer values are surprisingly high. And their transparency permits direct observation of the processes. PYREX Condenser Tubes are permanent.

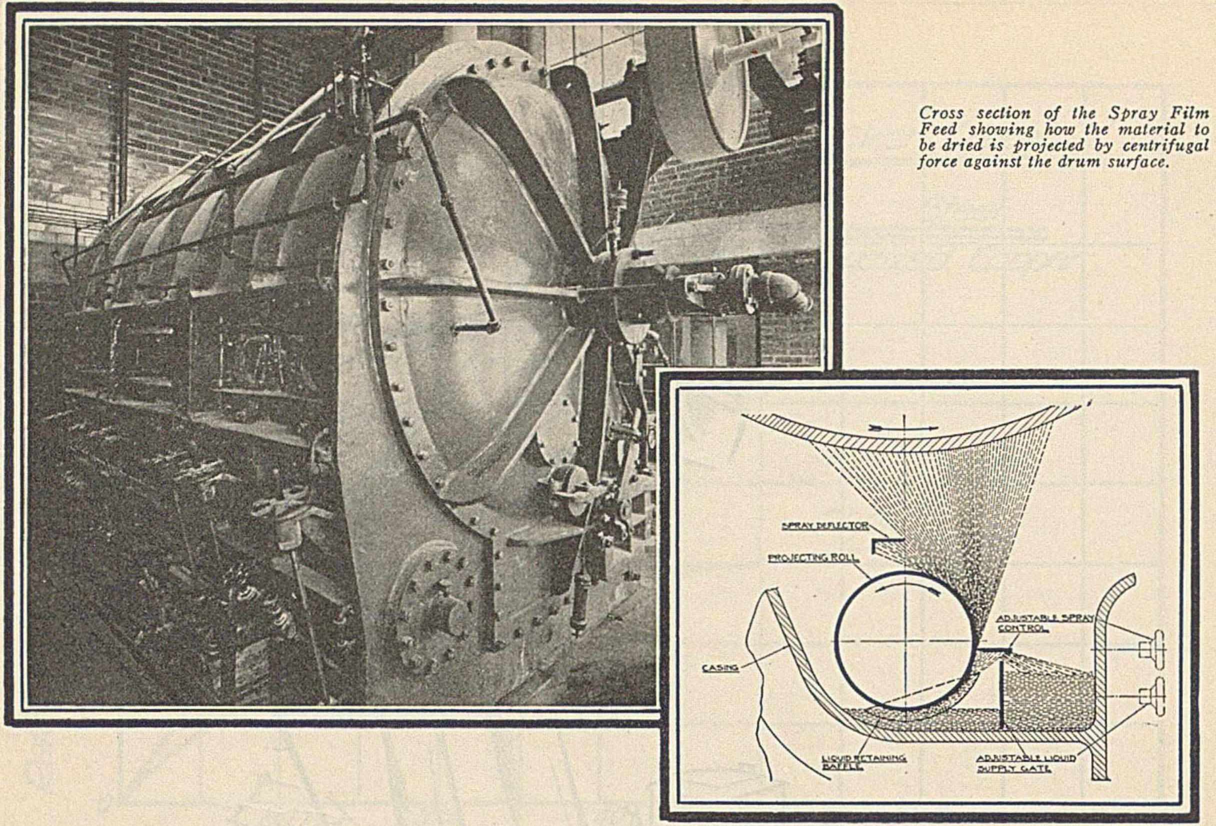
PYREX Cooler and Condenser Tubes are furnished in lengths up to 17′ 0″ in bores up to 3″. Return bends are supplied with sockets for cemented joints or plain rubber connections—the latter particularly for cooling and condensing hydrochloric acid.

Write for the booklet PYREX Industrial Glass Products, which contains full technical information.

CORNING GLASS WORKS
Industrial and Laboratory Division
Corning, New York

*Trade-mark Reg. U. S. Pat Off.





Cross section of the Spray Film Feed showing how the material to be dried is projected by centrifugal force against the drum surface.

A new drying principle—
that gives greatly improved results

THE operation of the Spray Film Drum Dryer enables it to dry certain materials which cannot be dried successfully in any other way. It also gives improved operating results, greater capacity and a much denser finished product for many other materials.

These features are traceable directly to the method of applying the material to the drum. The projecting roll throws the material in small globules against the bottom of the heated drum. Drying begins instantly as the particles impinge on the drum surface and build up the film thickness progressively. This type feed is applicable to both vacuum and atmospheric drum dryers.

The BUFLOVAK Research Laboratory will gladly conduct a test of your product on the Spray Film Dryer installed in our plant.

Complete information upon request.

Features of the Spray Film Dryers

1. A denser, heavier dry product is obtained.
2. Permits use of smaller containers.
3. Uniform moisture content in finished product.
4. Greater capacity.
5. Lower production cost.
6. Material not subjected to heat until actual drying operation begins.
7. No violent agitation of material.
8. Uniform film on drying drum.
9. Film can be regulated to any required thickness.
10. Dryer is thoroughly sanitary and easy to clean.

BUFFALO FOUNDRY & MACHINE CO.
1549 Fillmore Ave., Buffalo, N. Y.

CHICAGO NEW YORK ST. LOUIS SAN FRANCISCO

BUFLOVAK DRYERS & EVAPORATORS