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TABLE OF CONTENTS

EDITORIALS:

| | |
|--|------|
| Useless Work for the Tariff Commission..... | 1084 |
| Expanding Nitrate Plans..... | 1084 |
| The Platinum Situation..... | 1085 |
| The Chemist, the Draft, and Patriotism..... | 1085 |
| An Appeal to the National Association of Retail Druggists..... | 1085 |
| Wonders Will Never Cease..... | 1086 |
| An A. C. S. Pin for Every Member..... | 1086 |

THE SCHOOL OF CHEMICAL ENGINEERING PRACTICE—

| | |
|--------------------------|------|
| A YEAR'S EXPERIENCE..... | 1087 |
|--------------------------|------|

ORIGINAL PAPERS:

| | |
|---|------|
| Comparative Tests of Chemical Glassware. Percy H. Walker and F. W. Smither..... | 1090 |
| Effect of Copper on Crude Rubber. Chas. P. Fox..... | 1092 |
| Copper in Sewage at the New Haven Sewage Experiment Station. F. W. Mohlman..... | 1093 |
| Tannin Content of Pacific Coast Trees. H. K. Benson and Frank M. Jones..... | 1096 |
| Saturated Hydrocarbons in Basking-Shark Liver Oil. Mitsumaru Tsujimoto..... | 1098 |
| Some Data on Sperm Oils Used for Burning Purposes. Abraham G. Blakeley and Edmund A. Reilly..... | 1099 |
| Some Effects of Certain Solvents on Tars in the "Free Carbon" Determination. G. S. Monroe and H. J. Broderon..... | 1100 |
| The Estimation of Phenol in Crude Carbolic Acid and in Coal-Tar Oils. F. W. Skirrow..... | 1102 |
| Analytical Control of the Ammonia Oxidation Process. Guy B. Taylor and Jos. D. Davis..... | 1106 |
| A Volumetric Method for the Determination of Formic Acid or Formates in the Presence of Hydroxides, Carbonates, Oxalates and Acetates. F. Tsiropinas..... | 1110 |
| A Study of the Estimation of Fat in Condensed Milk and Milk Powders. C. H. Biesterfeld and O. L. Evenson..... | 1111 |
| A Rapid Method for the Determination of Lime as Calcium Sulfate. L. G. Willis and W. H. MacIntire..... | 1114 |
| A Modified Method for the Determination of Fluorine with Special Application to the Analysis of Phosphates. Cary R. Wagner and William H. Ross..... | 1116 |

| | |
|---|------|
| A Wool Fat (Lanolin) Substitute and the Preparation of Cetylic Alcohol. Sol. Axelrad..... | 1123 |
| The Rennetic Properties of Pepsin. Howard T. Graber..... | 1125 |
| A Method for the Determination of Alcohol. C. J. Haines and J. W. Marden..... | 1126 |

ADDRESSES:

| | |
|--|------|
| "Doing Our Bit." Bernhard C. Hesse..... | 1128 |
| Merchandise Control Laboratories. Ellwood Hendrick..... | 1133 |
| The Production of Scientific Knowledge. C. E. Kenneth Mees..... | 1137 |
| France and America in Scientific Union. Prof. Victor Grignard..... | 1142 |

CURRENT INDUSTRIAL NEWS:

| | |
|--|------|
| Estimation of Tin in Low-Grade Stuff; Coconut Industry; Starch Substitutes in Germany; Saltpeter Production in India; Ceramics; British Board of Trade; Manganese Steel; Hardening of Aluminum Bronze; Potash from Flue Dust; A New Test Paper; Ferro-Concrete Ships; Russian Cottonseed Oil Industry; Japanese Paper-Making Industry; Application of Radio-Active Substances for Batteries; Lining White Metal Bearings; Artificial Wood; Paints and Varnishes for Siam; Cotton Trade in Japan..... | 1143 |
|--|------|

NOTES AND CORRESPONDENCE:

| | |
|---|------|
| Hydrogenation of Oil; The American Coal-Tar Products Industry Production to be Ascertained by the United States Tariff Commission; Sampling Fats and Oils—Correction; Concerning the Manufacture of Phthalic Acid and Phthalic Anhydride; Chicago Chemical Exposition Plans Abandoned; Nitric Acid Sophistication—Correction; The Determination of Sulfur Dioxide—Correction..... | 1146 |
|---|------|

| | |
|------------------------|------|
| WASHINGTON LETTER..... | 1149 |
|------------------------|------|

| | |
|---------------------|------|
| PERSONAL NOTES..... | 1150 |
|---------------------|------|

| | |
|-----------------------|------|
| INDUSTRIAL NOTES..... | 1151 |
|-----------------------|------|

| | |
|------------------------------|------|
| GOVERNMENT PUBLICATIONS..... | 1153 |
|------------------------------|------|

| | |
|-------------------|------|
| BOOK REVIEWS..... | 1155 |
|-------------------|------|

| | |
|-----------------------|------|
| NEW PUBLICATIONS..... | 1159 |
|-----------------------|------|

| | |
|--------------------|------|
| MARKET REPORT..... | 1160 |
|--------------------|------|

| | |
|------------|------|
| INDEX..... | 1161 |
|------------|------|

EDITORIALS

USELESS WORK FOR THE TARIFF COMMISSION

At the request of the Chairman of the Tariff Commission there is printed on page 1148 of this issue a statement from the Commission concerning the information it is now seeking from manufacturers of crudes, intermediates and finished dyestuffs as to production of these materials within the United States during the year 1917.

This action is evidently a tuning up of the extensive machinery which will be necessary to determine whether or no at the end of the five-year period following the enactment in September 1916 of the Dyestuff Section of the General Revenue Act there is being produced in this country sixty per cent of the values of domestic consumption of these products. Failing such a development within that five-year period the special, but not the ad valorem, duties, are, by the terms of the Act, to be at once removed by Presidential proclamation rather than by the sliding scale of a twenty per cent annual reduction during the following five-year period.

The early beginning of this work of compilation is clearly indicative of the technical difficulties the Commission foresees. It is equally evident that the dyestuff manufacturers, at present about the busiest set of men in America, are to have another annual burden imposed upon their present overtaxed forces. Stronger and stronger is growing the appeal for a concentration of the nation's energies on necessary industries at the sacrifice, if need be, of unnecessary industries. Let the movement apply also to matters of legislation.

The sixty per cent clause of the Revenue Act admits of only one interpretation—doubt as to the good faith or ability of American manufacturers of dyestuffs.

Is there any fair-minded person in this country who is not proud of the accomplishments in this line during the brief period of scarcely more than one year since the legislation was enacted? Consumers have been supplied with the full tonnage of pre-war days and the variety of dyestuffs is constantly increasing. The progress made is the talk of the street.

Highest endorsement of these achievements has been given by a distinguished member of the Tariff Commission itself, the Hon. William S. Culbertson. In an address at the recent National Exposition of Chemical Industries [THIS JOURNAL, 9 (1917), 1015], Mr. Culbertson said of the dyestuff industry:

"The rapidity of its progress has amazed the world. The record of its achievement reads like a fairy tale and will prove an imperishable monument to American chemists and business men."

In view of such generally acknowledged progress and in the interest of economy of effort, we appeal to the Tariff Commission to recommend to the Congress, about to convene, the removal of this sixty per cent clause from our statutes.

EXPANDING NITRATE PLANS

The successful offense along the Flanders front within the last two months, resulting from the use of seemingly unlimited amounts of high explosives, has revolutionized prevailing views concerning the stalemate results of trench warfare.

During this same period we have become aware that while T. N. T. is the preferred high explosive, nevertheless our army must depend upon the gas works for toluol, the basis of this explosive, and this source, at its maximum output, is sufficient for only one half of the toluol needed for an army of one million men. In such a situation the officials of the War Department have naturally turned to ammonium nitrate, for use with T. N. T. Abundant confirmation of the high value of such a mixed explosive has been given by British experts recently visiting America.

The plans of our Government for independence in nitrate supply have necessarily undergone a rapid expansion, for in addition to nitric acid for explosives and ammonia salts for fertilizers, there must now be quickly available still larger quantities of ammonia for the explosive ammonium nitrate.

The immediate need of ammonia can be met by drawing temporarily upon the supplies of coke-oven ammonia without serious detriment to agriculture. We are informed by officials of the War Department that good progress is being made at Muscle Shoals in the installation of the synthetic method for manufacture of ammonia from air nitrogen. Much of the machinery is completed and the remainder is ordered and will be delivered as rapidly as completed. Materials for the buildings have been contracted for and three hundred and fifty laborers are engaged in the work of construction.

It is sincerely to be hoped that this synthetic plant will soon be greatly enlarged. The investigation of this method on April 20 by Col. C. B. Wheeler and Col. C. C. Keller of the War Department, Dr. Charles L. Parsons of the Bureau of Mines and Dr. A. A. Noyes of the Nitrate Supply Committee, showed clearly that a decided improvement had been made over the Haber process, now so largely employed in Germany, that the method had passed the experimental stage, and was capable of producing ammonia at lower cost than any other known method. As the process was immediately available for use without recompense by the Government it was recommended by the Nitrate Supply Committee to the Secretary of War as most adequately meeting the terms of the National Defense Act, namely, "the best, cheapest and most available means for the production of nitrates," etc.

The situation has become suddenly so acute, however, that the officials have wisely decided that all possible sources of ammonia should be utilized, regardless of the relative merits of the individual processes or of cost of the product. They have naturally turned therefore to the cyanamide process, the only other

available source of ammonia through nitrogen fixation. At this writing no official statement of plans has been published by the War Department, but it is understood that a cyanamide plant will also be located at Muscle Shoals, utilizing surplus power of adjacent hydroelectric developments and supplementing this by a steam plant.

We are confident that the entire Nation will support the policy of the War Department in leaving no stone unturned to secure ammonia from every possible source. Meanwhile, the operation of the two methods, the synthetic and the cyanamide, side by side at Muscle Shoals, will furnish abundant facts as to the relative merits of each for nitrogen fixation under American conditions.

THE PLATINUM SITUATION

From one who is in close touch with all phases of the platinum situation we have learned that a decrease of about forty per cent in the use of platinum for certain lines of bulky jewelry has resulted from the patriotic stand taken last spring by the jewelers. That is fine as far as it goes.

Our Washington correspondent points out in this issue that there is a possibility of complications in shipments of platinum from Colombia. This gives rise to apprehensions.

Platinum jewelry is now being extensively advertised in many periodicals. Without any attempt at a systematic survey we have read recently the advertisements of the Charles L. Trout Company in the *New York Times* of November 18, 1917, Daniel Low and Company in *Scribner's Magazine* for November, 1917, Sallan's touchingly illustrated advertisements of platinum engagement rings in the illustrated section of the *Detroit Free Press* of November 11, 1917, the James R. Armiger Company's well displayed advertisement of "Fine Platinum Jewelry" in the *Baltimore Sun* of November 6, 1917, etc. These advertisements seem to indicate an aggressive sale of platinum jewelry.

Meanwhile war developments of the last two months point clearly to the fact that chemical activities involving the use of platinum, both within and without Government circles, must be enormously expanded if the great army we are now beginning to raise is to be thoroughly supplied with essential war materials. In spite of all efforts to remedy the situation, platinum is bringing to-day (November 19, 1917) \$98 per ounce. These are facts.

Assuming the correctness of the decrease by forty per cent of the use of platinum in bulky articles, this continued high price is indicative of either diminishing imports (we have no figures at hand), absorption by the expanding chemical industries, increased manufacture of platinum jewelry (not included in the list of the Jeweler's Committee), or perhaps hoarding of platinum.

Whatever the explanation, it would seem that we are rapidly approaching the point where our Government may be compelled to follow the example of England in taking over all domestic supplies of platinum and apportioning them to the various industries in conformity with the interests of the national welfare.

THE CHEMIST, THE DRAFT, AND PATRIOTISM

In the June issue of THIS JOURNAL we wrote under the title "In the Light of Experience," urging upon all in authority to conserve for the best interests of the country the chemically trained men, using them in, or not calling them from, work for which their chemical training fitted them. May we now address a word to those chemically trained young Americans within the age limits subjecting them to the operations of the selective draft?

We have no desire to criticize and we sympathize fully with the fine spirit which prompts every young man to wish to get to the front and offer his life for the cause of his country. Nevertheless we know, personally, chemically trained men who have avowedly hurriedly sought commissions in whatever line of the service offered a chance for such, rather than risk serving as a private through the selective draft law.

If this country had a surplus supply of chemists, and if chemistry played no especial rôle in this war, such action would be purely personal and not rightly subject to comment. In view, however, of the present great dearth of chemists, of the practical exodus of all advanced students of chemistry from our universities, of the recognized vital importance of the work of the chemist both in the government service and in the industries, we do not hesitate to say that such abandonment of opportunity for chemical service for the sake of insuring a commission is not patriotism but selfishness. This may sound harsh, but it is a time for plain speaking.

The events of the last few weeks have convinced all that we must prepare for a long war and throw into the scales the full resources of this great country. The selective draft is the officially adopted method for raising our army. We have believed in its principles from the first. The Nation is indebted to President Wilson for his foresight and broad grasp of the part America is to play in the war when he so consistently and persistently urged the adoption by Congress of the selective draft rather than the volunteer principle. Only through this means can this country contribute its maximum share.

To those chemists, therefore, who have asked our advice, we repeat, and to those who will soon be subjected to the second call under the draft law we urge: "Wait for the operation of the draft law! Do not sacrifice the right of our country to your chemical training for the sake of a commission in the field service. Be prepared to serve wherever and in whatever capacity your country may most need you!"

AN APPEAL TO THE NATIONAL ASSOCIATION OF RETAIL DRUGGISTS

The spirit of coöperation is so keenly alive at the present that the time seems appropriate to make an appeal which we have long had in mind. Will not the National Association of Retail Druggists coöperate with the chemists by discouraging the use of the word "chemist" on the signboards of retail drug stores?

The request may seem trivial but there is a deeper significance than appears on the surface, and the request carries with it no suggestion of the relative values of the two classes of men. It is made simply for the sake of clarity of thought by the public at large of what the functions of the chemist really are in our national existence.

During the past two years much sincere effort has been made to acquaint the nation with the work of its chemists, and to bring about a more cordial and sympathetic relationship between chemists as a class and our American people. The lack of an adequate understanding of the work of the chemist was partly responsible for some of the shortages the country suffered from at the outbreak of the war. Much progress has been made in this campaign of understanding. It should be complete through all classes of our citizens.

The sign "Chemist" above a drug store, however, still leads to confusion or misunderstanding. Many in all walks of life still think of the druggist whenever the chemist is mentioned. An artist recently called in to design, for a Liberty Loan Bond parade, a float illustrative of the contribution of chemists to the winning of the war, at once began the delineation of a mortar and pestle as the central theme.

True it is that in the iatro period chemistry had chiefly to do with drugs and equally true it is difficult, even to-day, if contentiously inclined, to define precisely the term chemist; nevertheless the work of the chemist and that of the retail druggist are now so clearly differentiated that there can be no real justification for the retention by our modern druggists of the term chemist, a heritage of English practice.

Moreover, the druggists have such an abundance of choice in the terms druggist, apothecary and pharmacist that they can well afford to dispense with any further designations. May we not hope, therefore, that this appeal may meet with a sympathetic response on the part of the members of the National Association of Retail Druggists?

WONDERS WILL NEVER CEASE

The spirit of the times is not conducive to frivolous thoughts, yet from the quarter least expected, the Congress of the United States, frivolity is thrust upon us. Doubtless it was unwittingly the rebound from intense war debate and prolonged consideration of appropriation bills mounting into the billions which led both Senate and House to pass with all due dignity the joint resolution of acceptance for test of the proposed gift to the United States on the part of citizen Garabed T. K. Giragossian of Boston, Mass., of the "Garabed," an appliance which, in the printed words of House Joint Resolution 101 of the 65th Congress, 1st Session, embodies a principle through which or by means of which (we don't know which which), "unlimited energy can be generated without expense"—all of this in exchange for the slight courtesy of the "Government protecting the said discoverer, his heirs and assigns,

in the use and disposition of the said discovery or invention."

To administer this remarkable transaction the Secretary of the Interior was specifically designated as the trusted agent of the Government. If this was an attempted joke upon the proverbially genial Secretary of the Interior, it was shameful. Mr. Lane has always proved himself ready, willing and abundantly able to throw himself into any old breach for the public good, but this is carrying matters too far, especially as Section 2 is to the effect that Mr. Lane is not to begin the job until he shall have approved "a commission of five eminent scientists to be appointed by the said Garabed T. K. Giragossian" which high commission should certify to "the entire practicability of his (Garabed T. K. Giragossian's) discovery," pursuant to a demonstration.

We remember the interesting remarks by Dr. A. D. Little at the smoker during the recent Boston Meeting of the American Chemical Society in which he assembled in brief narrative some of the more striking scientific fakes for which Boston inventors had readily fallen: the extraction of gold from sea water, the manufacture of artificial rubber by a real new process, etc., etc. Perhaps the Bostonians have at length gotten wise and in a spirit of revenge decided to pass the buck to Congress. At any rate President Wilson saved the day by declining to sign the bill.

We realize fully the dangers run by scoffing at anything new—and yet there is a difference, which leads us unhesitatingly to congratulate the President for saving the dignity of the nation and allowing the Secretary of the Interior to go on about his regular business.

AN A. C. S. PIN FOR EVERY MEMBER

It was a happy thought that led to the adoption of an official emblem for the American Chemical Society. As a decorative feature of programs, stationery, dinner menus and for official decoration in general, this now well-known emblem has contributed largely to that increased esprit de corps which characterizes the present organization.

Particularly noticeable is the steadily increasing number of members of the Society who constantly wear the official pin, generally on the lapel of the coat. Thus worn it serves as an introduction and produces at once a feeling of community of effort and ideals.

The pins at present available, however, are expensive—needlessly so for these days of necessary economy of personal expenditures. Correspondence has been shown us recently which assures the ability to produce, at a cost of one dollar each, rolled-gold pins conforming fully to the design and beauty of the official pin. We hope the Directors at their December meeting will authorize the manufacture and sale of such inexpensive pins, under order of course from the Secretary, as is now required. Their availability would undoubtedly result in a largely increased use of the emblem by the members of the Society.

THE SCHOOL OF CHEMICAL ENGINEERING PRACTICE A YEAR'S EXPERIENCE

By WILLIAM H. WALKER, Professor of Chemical Engineering, Massachusetts Institute of Technology

The School of Chemical Engineering Practice of the Massachusetts Institute of Technology announced in THIS JOURNAL last summer has, by the results achieved in the year just closed, proved that the basic principles upon which it was founded are sound, and that the practical operation of these principles is entirely feasible when applied to selected men who have already had at least three years of preparatory scientific instruction. The year just closed has been most successful.

The aims of the course as enumerated in our original outline have been in great measure realized, and other advantages not anticipated have appeared. Extracts from some letters written by the students to their fellows at the Institute are appended, which reflect, more clearly than could be dictated, the advantages they have enjoyed. The thirty students who made up the School are enthusiastic regarding the manifold benefits received, while the manufacturing companies which are coöperating in carrying out the plan are well satisfied, not only with the results obtained from the research work of the organized staff, as part of the coöperative idea, but with the advantages which have accrued from large scale test work carried on by the students.

It will be recalled that the School was made up of five stations located at the plants of The Eastern Manufacturing Co., Bangor, Maine; The New England Gas & Coke Co., Everett, Mass.; The Carborundum Co., Niagara Falls, N. Y.; The American Synthetic Color Co., Stamford, Conn.; and The Atlas Portland Cement Co., Northampton, Pa. At each station there was provided a conference and library room for the students, and a research laboratory for the factory. A complete line of books, measuring instruments and other equipment selected with reference to the work to be done at each station was supplied. As Director of each station a man of enthusiasm and enviable record of achievement was obtained, who in turn was supplied with an assistant of energy and ability. This staff became a part of the Institute faculty, and it is largely to the ability and enthusiasm of each and all of the members of this staff that the great success of the plan is due.

The underlying principles of the Course may be made clear by the following considerations. A great advance in educational methods was made when laboratory work was introduced into the curriculum of science courses. By this means the principles of science were emphasized, clarified and made an integral part of the student's knowledge and experience. But such applications of scientific facts and principles are of necessity limited to the facilities of the laboratory, or, as we say, experimentation on a laboratory scale. There are many fundamental principles of science which possess a different interest and value when

studied under factory conditions, and there are also many problems susceptible of a scientific solution, which assume unfamiliar shape when viewed through the hazy atmosphere of large scale production.

Again there is a great gulf fixed in the minds of most students between the applications of science in the laboratory, where the thermodynamic environment is such as to make relationships quantitative and hence calculation comparatively easy, and the factory, where conditions are such as to make necessary at best a scientific guess or a rational assumption. And yet, if we involve our scientific knowledge in the solution of our problems only when a rigorously quantitative treatment is possible, we must in the majority of cases revert to a "rule of thumb" method of solution.

Therefore, the first general object of the School of Chemical Engineering Practice was to introduce the laboratory method of instruction into a study of factory operations and processes, to make the factory a chemical engineering laboratory. This was based upon the tenet that it is entirely possible to study the performance of a piece of apparatus or the progress of a reaction or process, without interfering with production in either quantity or quality.

The advantages gained by this method of study are twofold. First, the men get a personal first-hand knowledge of the unit operations involved in chemical industry, and the part played by such unit operations in the success of a chemical-manufacturing process; and second, they acquire a knowledge of men and the organization of men necessary to carry on a coördinated and interdependent plant. The students mix with the laboring men, coöperate with the foremen and observe the method of control from those high in authority to those with none.

It is interesting to note that the rock on which nearly every one predicted our educational ship would most probably be wrecked was this one of relations between the students and the factory organization. I am glad to be able to state that not the slightest difficulty of any description has been experienced. On the contrary, the superintendents have been interested and uniformly anxious to make our stay at the plant both pleasant and profitable, while the laboring men have been most helpful in every way.

The second general object of the School was to allow the student to realize the opportunities which exist in industry for the application of science, provided first, the student can detect the presence of the problem and diagnose the difficulty, and second that he has the training necessary to apply that knowledge of science which he possesses. In other words, to show him that two things are necessary for success: first, a knowledge of science; and second, a training in its applications.

In organizing the work at the several stations it

was classified roughly under heads providing for the following objects:

I—*To study the chemical control of industrial processes through the laboratory, and to acquire ability in the interpretation of laboratory data in terms of factory practice.*

Instruction in analytical chemistry to prospective engineers is handicapped, in that it is difficult to combine in the student's work the necessary accuracy with that speed on which depends his effectiveness as part of a laboratory organization. The average student is generally either accurate and painfully slow or rapid and unreliable. When placed in a cement mill, however, he learns that the composition of the rock from the quarry must not only be accurately determined, but it must be known by the time the rock has passed through the rough crushers and driers. The importance of the analytical work now strikes him with its full significance. To reap the benefit of life in an active industrial laboratory where both wonderful speed and accuracy are obtained, each student spent five days in the laboratory of Station *E*, where raw material and finished product were analyzed according to the methods of the Atlas Portland Cement Co., and his work checked, both as to result and time consumed, against the standard practice of the laboratory.

Special methods of analysis employing a wide variety of instruments are involved in controlling the factory experimental work at the different stations. Two types of optical pyrometers, and a variety of thermal junctions are used in the heat balance run on the cement kilns. Gas analysis in all forms is in use at Station *B* and elsewhere; polarizing and petrographic microscopical work at Station *C*, and so on. Analytical chemistry takes on an unexpected attractiveness when it becomes the most important source of knowledge by which the progress of a reaction or a process must be determined.

II—*To acquire a first-hand knowledge of the processes of the plant and the machines with which it is equipped.*

A process or a machine may be studied in two ways: first, by making a quantitative run or test upon it, in which input of energy and material is balanced against output; and second, by operating the unit machine and determining how well it does the work for which it was designed, how resistant it is to both mechanical and chemical wear and tear, how easily cleaned and repaired, and how nearly perfect the product is when viewed from its various commercial standpoints.

Both of these methods were used at the different stations. For example, the squad of six men were placed in the electrolytic bleach plant of Station *A* and directed to decide what mechanical measurements must be made, what data secured, what and where samples for analysis must be drawn, and in short, to outline in detail a test run of 36 hours, which would furnish answers to the following type of questions:

What per cent of the energy supplied to the bus bars is converted into calcium hypochlorite as delivered to the storage tanks?

What per cent of the salt drawn from the storage bins appears as caustic soda in the concentrated liquor tank?

Same question as to lime consumption, and so on.

From two to three days were consumed in deciding all the details and making necessary arrangements for withdrawing samples, recording measurements and doing the necessary analytical work. A 36-hour run was then made and calculated very completely. The daily practice of the plant relative to temperature, current density, concentration of feed liquor, rate of flow, composition of cell effluent, resistance of diaphragm and other working conditions were then studied and interpreted in the light of the laws of electrochemistry already learned in earlier years of the Course. Each squad then tested the accuracy of the predictions in reference to one variable. For example, the influence of the rate of flow of the brine through the diaphragm on the efficiency, for cells of different ages, was determined. Incidentally many data of service to the company were obtained.

This method of applying the principles of science to industrial problems under factory conditions was found to adapt itself to almost every important operation, and when applied to the widely differing conditions of the five stations, a most comprehensive experience was obtained.

The second method of studying a process and machine is so obvious as to need no example. It was found that much valuable experience was obtained by putting the students, one at a time, on the regular factory repair gang for a period of 3 to 6 days. In some cases, for example in the routine repair of the Huntington Mills of the Cement Plant, the work was so heavy that but few students could take an active part in it: but in the majority of cases a student can do the work of a helper and learn how most quickly to do the thing which is needed to be done.

III—*To obtain the wider view-point which comes from contact with those who are employed to superintend or carry on the factory operations, and to acquire the degree of confidence in handling industrial processes and large sized apparatus which comes from actual participation in the active work of the plant.*

No part of the plan has received more hearty endorsement on the part of the students than the opportunity to mix with the operations of the factory and to share in the work of the plant. For example, at Station *A* each student was for a time assistant to the assistant cook in the digester house; at *B* he helped run the ammonia stills and the sulfate recovery; at *C* he operated both the magnetic and electrostatic separators, and made runs on large scale electric furnaces; at *D* he worked on the phenol plant, from the sulfonation to the final distillation; at *E* he fired the cement kilns, and so on. Although at few times was the entire responsibility for operation placed on the student, yet he was at most times sufficiently in charge to gain a fair measure of self-confidence in handling industrial processes. He realized the importance of the human element in industry, and observed the efforts being made at the different companies toward welfare work, task and bonus systems, and other methods by which

the workman is made to share in the profits of the industry.

IV—*To acquire that inspiration for further work in science and research which intimate contact with large progressive industries inevitably affords.*

This is a somewhat less tangible object than the other, but one which we have steadily striven to accomplish by constantly bringing out in relief the dependence of industrial progress upon the application of science. The results have been entirely satisfactory. In none of our efforts have we been more successful than along these broad lines of development.

It is a truism to say that it is easier to acquire a knowledge of science than it is to apply intelligently and successfully this knowledge to the solution of technical problems. The first is definite and self-contained; the laboratory experiments of instruction are chosen with reference to the law or principle under consideration and the conditions of temperature, pressure, concentration, and so on, are so chosen that

the validity of the law may be demonstrated. In practice, however, the problem is generally the very difficult one of analyzing the situation into its essential factors, the determination of the controlling conditions, and finally the application of scientific laws in a thermodynamic environment where such laws and principles cannot be expected to hold quantitatively.

The most far-reaching benefit accruing from the school of Chemical Engineering Practice is, therefore, an introduction into that fascinating field which, for want of a better name, we call applied science. This introduction carries to the student these convictions:

1—That he must acquire a sounder knowledge of existing science;

2—That he must aid in creating or enlarging the field of science;

3—That he must continue to apply science to industry for the ultimate good of mankind.

CAMBRIDGE, MASS., November 7, 1917

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RANDOM EXTRACTS FROM LETTERS OF MEMBERS OF THE SCHOOL OF CHEMICAL ENGINEERING PRACTICE TO THEIR FRIENDS

"* * * * * The Cement Works offered a splendid opportunity to get a line on plant design, power distribution, conveyor systems, grinding machinery, and the procedure of commercial laboratories. We had a free run of the place, and the workmen were invariably friendly and anxious to help us. Each fellow had to spend a week with the repair gang, and that meant getting up at five every morning for the 6 o'clock train. The fine cement powder got pretty well onto everything and hardened on rainy days, but being dirty means nothing at all to us by this time."

"Every member of the group is impressed with the change from the theoretical view-point of the classroom to the practical view-point of this Course. Especially those of the group who have had no previous practical training often remark how greatly this Course has added to their ability both to attack problems and to accomplish their solution. In short, the greatest contribution of this Course seems to be that of obtaining self-confidence and the ability to do things."

"It is very interesting in this connection to watch and analyze the men who hold the bigger, the more responsible positions. What qualities has this one leading to success? What gives that one his position of command? Comparisons arise unconsciously between the methods of this man here, and that one of the plant we last left, in his different relation to the organization as a whole, and to the men working with him. Likewise the part a man's technical training plays in his advancement as compared with other factors is of import to us."

"Conveying systems, transmission of power by shafting and the use of the belt, rope and other drives are details of mechanical engineering not usually obtained by students in chemical engineering. Industrial practice in the field of electrical engineering has been illustrated at practically every plant visited. Generating machinery for power and electro-chemical work, transmission systems, motors adapted to various uses, especially those of the induction type, are but a few applications that have been studied."

"The writing of detailed reports must be considered of the utmost importance in this course not merely for the preservation and classification of actual data but also for the training obtained in expressing one's thoughts logically, accurately, and rapidly."

"Study of plant organization and experience obtained by working side by side with laborers is of great value to us."

"The general principles of chemical engineering calculations including such valuable methods of attack as the pound-mol system and the principles of fluid flow, are impressed much more vividly by using data obtained by ourselves during plant operations. Not only is experience obtained in calculation, but valuable training is secured in the planning and execution of tests of apparatus and processes. Efficiency in time and labor is obtained by applying the principles of precision before the performance of a test."

"One of the most far-reaching effects of this Course is the help gained from personal contact with the men who have been

in the profession into which we are about to enter. The personal experiences of the Directors and Assistants, together with the influence of their personalities form no small part of the Course in Chemical Engineering Practice."

"* * * you can hardly realize what a difference there is between a picture or drawing, and the real piece of apparatus itself. An electric furnace or a scrubber are now old friends to us, instead of being somewhat awesome objects. We are beginning to see how varied chemical industries are."

"At Everett the facilities for handling great quantities of gas strongly impressed us—8,000,000 cubic feet of gas a day means something to us now. We can yet see the size of those intake pipes from the batteries."

"The Cochrane Chemical Plant is a wonderful place. Here for the first time I saw and understood how acids are conveyed and handled. The immense towers and chambers in the sulfuric acid plant are indelibly impressed on my memory: for, to say a Gay-Lussac Tower is x feet high is one thing but to climb to the top of it is another."

"At Niagara Falls our work is mostly electrical. . . . The other day we ran a test on a small Aloxite furnace. We kept Aloxite at a temperature of 1600° C. for 5 hours with an electrical expenditure of only 550 kw. hours. I had no idea before that so much heat was contained in 100 kw.; but after standing over that furnace for an hour one has an idea, and a very different idea it is, as to the meaning and value of 100 kw. * * * Tomorrow we run a test on a 1,000 H. P. carborundum furnace. Electricity, that name which in the past I have usually associated with a shock, or when I was very ambitious with a motor, is beginning to take on a new significance—that of energy easily convertible into very high temperatures."

"The friendliness of the workmen in the various plants is noteworthy. We have yet to receive our first rebuff. They are willing to help us on all occasions and to tell us all they know, in fact even eager. That is the trouble, they sometimes tell a good deal more than they know."

"We have learned much as to what is essential and what is negligible in a commercial test, and much about the complete interpretation of test data."

"We have close contact with the commercial operations; we live in the atmosphere and think in the terms of profit and loss; and yet our time is our own. We can idealize without wasting the company's time. I believe that this is an immensely important feature of our work."

"To sum up the student's point of view, we feel that we are gaining a working knowledge of chemistry and of engineering. We are gaining an interest in our work which has never been equalled. We are learning our weaknesses and our strong points, and we are put in a position where with the proper kind of efforts they may both be improved. We are gaining a friendship with men of importance in our profession, and we are learning the value of such friendship."

ORIGINAL PAPERS

COMPARATIVE TESTS OF CHEMICAL GLASSWARE¹

By PERCY H. WALKER AND F. W. SMITHER

Received October 23, 1917

The cutting off of imports from Germany and Austria has forced us to rely upon American manufacturers for practically our entire supply of glass beakers and flasks. In order to give chemists some information as to the quality of this ware, the Bureau of Standards has examined five brands of American-made ware in comparison with the two best known wares of European make.

The tests included chemical analysis, determination of coefficient of expansion, refractive index, condition of strain, resistance to repeated evaporation, to heat, and to mechanical shock, and resistance to chemical reagents.

In all cases beakers and flasks approximating in size the 400-cc. Jena beaker and flask were used. All

ers, consisted in repeated evaporation to dryness of sodium chloride solution with examination for cracks after each evaporation. None of the wares developed cracks after twelve evaporations.

One of the heat shock tests consisted in filling the beakers with cold water, which was then rapidly heated to boiling. Other tests included the plunging into ice water of vessels containing boiling water, paraffin at 150° C., and paraffin at 200° C., and the dropping of beakers bottom down upon a thick board from heights increased by intervals of 5 in.

The solubility tests were made by determining the loss in weight of pieces of the wares upon treatment with water and various solutions commonly used in the laboratory. With water on beakers the action was continued about 72 hrs., the water being heated about 24 hrs.; on flasks, the action was continued about 17 hrs., keeping the water boiling during 5

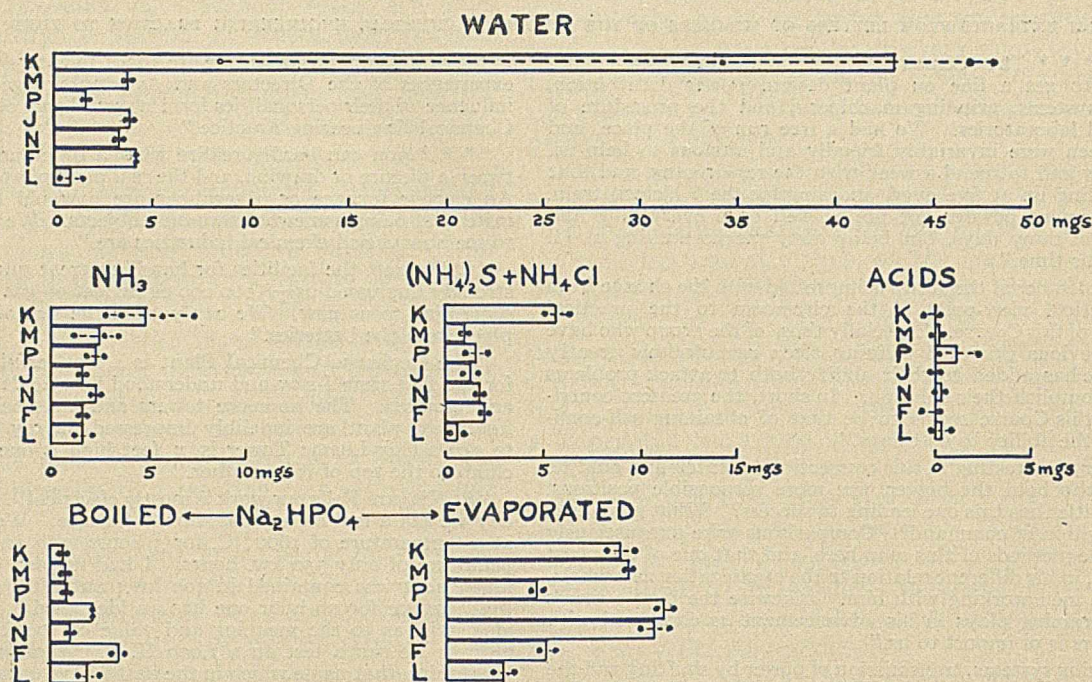


FIG. 1.—LOSS IN WEIGHT OF BEAKERS WITH WATER, AMMONIA, AMMONIUM SULFIDE AND CHLORIDE, ACIDS AND SODIUM PHOSPHATE SOLUTIONS

the ware tested bore permanent trade marks. From 45 to 50 beakers and flasks of each ware were secured for this series of tests.

Table I gives the composition of the different wares tested.

Details regarding the methods of analyses, weight and size of pieces tested, coefficient of expansion, refractive indices, and condition of strain will appear in a publication of the Bureau of Standards and are not given here, since little information bearing on the suitability of the various glasses for laboratory use can be obtained from these results. The Pyrex ware has low coefficient of expansion and refractive index.

The evaporation test, which was made only on beak-

ers; with mineral acids, solutions containing sodium chloride and sodium nitrate were mixed with a large

TABLE I—ANALYSES

| WARE | Kava-M. E. G. | | | | | | | |
|--------------------------------------|---------------|------------|--------------|-------------|------------|---------------|------------|---------------|
| | Beaker | Co. Beaker | Pyrex Beaker | Jena Beaker | Jena Flask | Nonsol Beaker | Fry Beaker | Libbey Beaker |
| Al ₂ O ₃ | 0.14 | 1.0 | 2.0 | 4.2 | 4.2 | 2.5 | 2.7 | 2.1 |
| Fe ₂ O ₃ | 0.08 | 0.35 | 0.25 | 0.25 | 0.27 | 0.23 | 0.22 | 0.44 |
| ZnO..... | ... | 5.6 | ... | 10.9 | 10.9 | 7.8 | 3.6 | ... |
| PbO..... | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.03 | 0.03 |
| MnO..... | 8.7 | 0.66 | 0.29 | 0.63 | 0.56 | 0.79 | 2.6 | 0.42 |
| CaO..... | 0.17 | 4.3 | 0.06 | 0.21 | 0.25 | 3.4 | 2.6 | 0.08 |
| Na ₂ O..... | 7.1 | 10.8 | 4.4 | 7.5 | 7.8 | 10.9 | 9.8 | 8.2 |
| K ₂ O..... | 7.9 | 0.30 | 0.20 | 0.37 | 0.31 | 0.30 | 1.5 | 0.67 |
| SiO ₂ | 75.9 | 73.0 | 80.5 | 64.7 | 64.7 | 67.3 | 68.6 | 75.9 |
| B ₂ O ₃ | ... | 3.6 | 11.8 | 10.9 | 10.6 | 6.2 | 8.1 | 10.8 |
| P ₂ O ₅ | 0.08 | ... | ... | ... | ... | ... | ... | ... |
| SO ₃ | 0.20 | 0.02 | ... | ... | ... | ... | ... | ... |
| As ₂ O ₃ | Trace | 0.02 | 0.70 | 0.14 | 0.19 | Trace | 0.18 | 0.36 |
| Sb ₂ O ₃ | ... | 0.60 | ... | ... | ... | 0.62 | ... | ... |
| TOTAL..... | 100.29 | 100.27 | 100.21 | 99.81 | 99.79 | 100.05 | 99.93 | 100.00 |

Selenium and fluorine were not found, but lithium was detected spectroscopically by Mr. Paul W. Merrill in all the samples.

¹ Published by permission of the Director of the Bureau of Standards. An abridgement of a longer and more complete publication to be issued by the Bureau of Standards.

TABLE II—HEAT AND MECHANICAL SHOCK TESTS
No. refers to Number Tested. U, Unaffected. F, Failed. b, Broken. c, Cracked

| WARE | Water at 4° C. Heated to Boiling over Direct Flame | | Boiled Water and Plunged into Ice Water | | Paraffin Heated in Vessel to Indicated Temperature and Vessel Plunged into Ice Water Heated to 150° C. | | Heated to 200° C. | | DROP TEST—BEAKERS ONLY (6 of Each Ware Tested) | | | | | | | |
|------------------|--|--------|---|--------|--|--------|-------------------|--------|--|--------|--------|--------|--------|--------|------|---------|
| | BEAKERS | FLASKS | BEAKERS | FLASKS | BEAKERS | FLASKS | BEAKERS | FLASKS | 5 in. | 10 in. | 15 in. | 20 in. | 25 in. | 30 in. | Note | |
| Kavalier..... | 4 | 1 3c | 0 | .. | 2 2 0 | 0 | .. | 2 1 1c | 0 | .. | 4 0 4b | 0 | .. | .. | 4 2 | .. |
| M. E. G. Co..... | 2 | 2 0 | 4 | 2 2c | 2 2 0 | 2 | 2 0 | 2 1 1c | 4 | 3 1c | 4 0 4b | 2 | 0 2b | .. | 3 3 | .. |
| Pyrex..... | 2 | 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 4 4 0 | 5 | 3 2c | .. | .. | 1 1 (m) |
| Jena..... | 2 | 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 2 2 0 | 4 | 1 3b | 4 1 3b | 4 | 1 3b | .. | .. | .. |
| Nonsol..... | 2 | 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 2 2 0 | 4 | 4 0 | 4 0 4b | 4 | 0 4b | .. | .. | .. |
| Fry..... | 2 | 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 4 3 1c | 4 | 3 1c | 4 4 0 | 4 | 0 4b | .. | .. | .. |
| Libbey..... | 2 | 2 0 | 2 | 2 0 | 2 2 0 | 2 | 2 0 | 4 4 0 | 4 | 4 0 | 4 4 0 | 4 | 0 4b | .. | .. | .. |

(m) One broke on bound at 25 in. and 2 did not break at 45 in. (n) One broke on bound at 20 in.

excess of sulfuric acid, boiled and heated for an hour after fumes of SO₂ appeared. With sodium and potassium carbonates and hydroxides and sodium phosphate half-normal solutions were boiled for 20 mins. in the vessels and in the case of beakers fresh half-normal solutions were subsequently evaporated in the same beakers. With ammonia, strong ammonia was allowed to stand 24 hrs. in the vessel, then diluted and boiled for 30 mins. With ammonium sulfide and chloride, mixtures of twice normal salts were allowed to stand in the vessels 24 hrs., then boiled for 30 minutes.

Table II shows the results of heat and mechanical shock tests. Figs. I to IV show the effects of the various reagents on the wares tested. In these figures

individual accepted determinations are shown by dots, determinations which are believed to be in error and therefore omitted from the averages by circles. The lengths of the rectangles indicate the averages of accepted values. The letters K, M, P, J, N, F, and L indicate Kavalier, M. E. G. Co., Pyrex, Jena, Nonsol, Fry, and Libbey, respectively.

Table III gives a general summary of the resistance to the various solutions and to mechanical and heat shock of the wares tested. In this table the numerical exponents indicate the minor differences in resistance, the lowest number being the most resistant. The absence of an exponent indicates that the differences in resistances are too small to justify any differentiation between the wares graded in the same group.

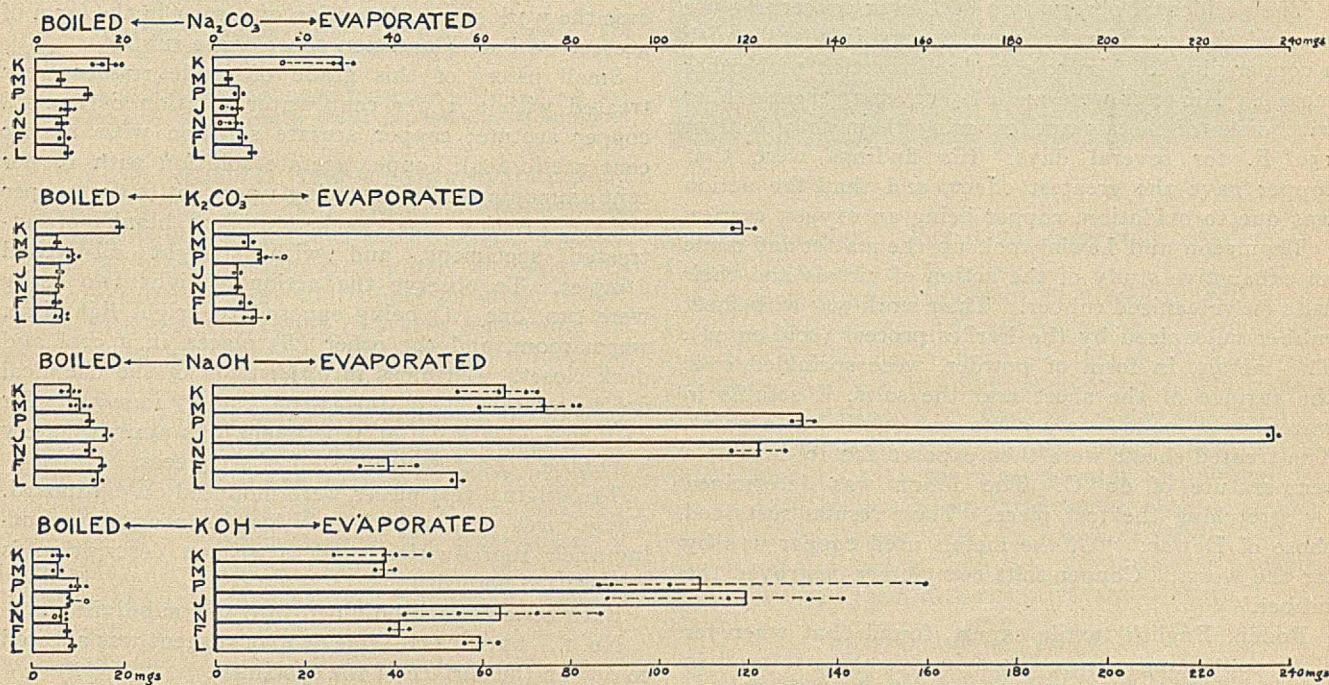


FIG. II—LOSS IN WEIGHT OF BEAKERS WITH SODIUM CARBONATE, POTASSIUM CARBONATE, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE SOLUTIONS

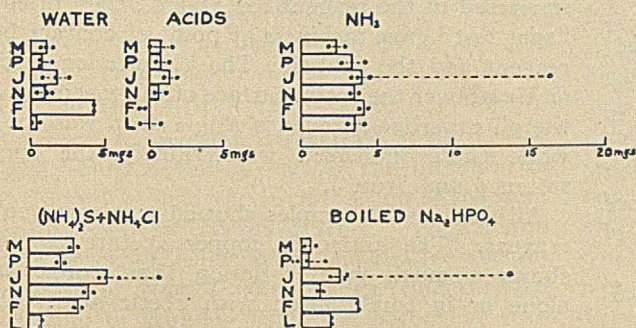


FIG. III—LOSS IN WEIGHT OF FLASKS WITH WATER, ACIDS, AMMONIA, AMMONIUM SULFIDE AND CHLORIDE, AND SODIUM PHOSPHATE SOLUTIONS

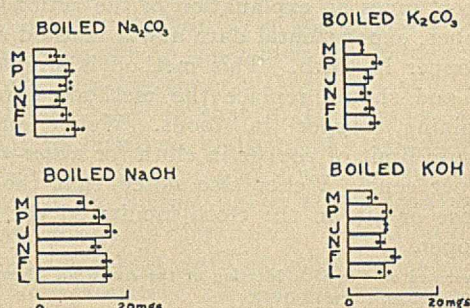


FIG. IV—LOSS IN WEIGHT OF FLASKS WITH SODIUM CARBONATE, POTASSIUM CARBONATE, SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE SOLUTIONS

TABLE III—GENERAL SUMMARY OF TESTS

| RESISTANCE TO: | Water | Car- | | Ammo- | | Heat Shock | Mechanical Shock |
|------------------|-------------------|---------------|-------------------|-------------------|-------------------|-------------------|------------------|
| | | bonated Acids | Alkalies | ni-um Salts | nia and | | |
| Kavalier..... | Poor | Good | Poor | Good ² | Good ² | Poor | Poor |
| M. E. G. Co..... | Good ² | Good | Good ¹ | Good ¹ | Good | Poor | Poor |
| Pyrex..... | Good ² | Good | Good ² | Fair | Good | Good ¹ | Good* |
| Jena..... | Good ⁴ | Good | Good ² | Fair | Good | Good ² | Fair |
| Nonsol..... | Good ² | Good | Good ¹ | Fair | Good | Good ² | Fair |
| Fry..... | Good ⁴ | Good | Good ² | Fair | Good | Poor | Good |
| Libbey..... | Good ¹ | Good | Good ² | Fair | Good | Good ² | Good |

* Far superior to any of the other wares.

In the rating of resistance to caustic alkalies the boiling tests only have been considered. These results indicate that all the American-made wares tested are superior to Kavalier and equal or superior to Jena ware for general chemical laboratory use.

BUREAU OF STANDARDS
WASHINGTON, D. C.

EFFECT OF COPPER ON CRUDE RUBBER¹

By CHAS. P. FOX

Manufacturers of rubber goods, following the teachings of Pearson,² have carefully avoided the use of copper salts in their compounds. Coppered iron was used to a limited extent in vulcanizing rubber to iron. Copper in this operation has recently been superseded by a plating of other metals.

The accidental observation of Dewar concerning the marked change of a rubber gasket used in contact with a copper pipe led him to compare its action with other metals. His tests were made by covering sheet rubber with disks of metals and exposing them to a heat of 150° F. for several days. His findings were that copper gave the greatest effect, and that the action was due to oxidation, copper being an oxygen carrier.

Thompson and Lewis³ took up the matter and made an exhaustive study of the action of metals and their salts on vulcanized rubber. Their work was with sheet rubber vulcanized by the Parkes process (cold-cured). The metals, in form of powder, were sprinkled over the surface of the sheet and the salts, if soluble in water, were made into a paste and applied as a paint. The treated sheets were then exposed for 10 days at a temperature of 60° C. The action was determined by stretching the test piece. Their results sustained those of Dewar: "Of the metals used copper was by far the worst. Copper salts completely destroyed the rubber."

Foden, English textile expert, found that wherever cloth containing copper (used in dyeing) was used in *water-proofing*, the rubber became hardened and was soon destroyed.

Weber⁴ gives an explanation of the action of copper on rubber, experimental data and a method of estimating copper in cloth. This method is simple and reliable, and should replace the methods now used in determining copper in foods. Weber places the maximum limit of copper in cloth for *water-proofing* at 0.005 per cent. Weber also noted that the presence of grease or oils in the cloth facilitated the action of the copper.

¹ Presented at the 55th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917.

² "Crude Rubber and Compounding Ingredients."

³ *Abstract Journal, Soc. Chem. Ind.*, 10 (1891), 717-718.

⁴ "Chemistry of Rubber."

Esch¹ attributes the action of copper to the formation of copper chloride which acts as an accelerator.

Morgan² states that the presence of copper compounds may cause "*tackiness*" in crude rubber, and strongly advises against the use of copper vessels in the preparation of crude rubber, and even against the use of copper insecticides or fungicides on trees during the tapping operation.

By experiments made by adding copper salts to rubber latex, Morgan concludes that the rate at which tackiness is induced is dependent upon the amount of copper salts used.

The formation of resins is the main factor in the *copper-induced* tackiness. Schidrowitz³ says that tackiness is due to a physical degradation of the rubber molecule and not to a change in its chemical composition.

There seems to be a distinct difference between "*perished*" or "*decayed*" rubber (Thompson and Lewis), and the "*tackiness*" observed by Morgan. Tackiness as understood by the practical rubber-worker is a soft sticky condition affecting crude rubber.

Several years ago I became interested in the action of copper on dry crude rubber. Some of these experiments have recently been repeated. In this particular case the work shows the action of copper in the form of acetate on Pale Plantation sheet crude rubber.

Small pieces of this grade of crude rubber were treated with a 1 per cent water solution of neutral copper acetate; copper acetate solution with 10 per cent acetic acid; copper acetate solution with 10 per cent ammonia; and oil carrying 1 per cent of dry copper acetate. Action was checked against blanks of untreated specimens, and with straight oil-treated samples. To observe the action of light two series were run, one (A) being exposed to bright light in a warm room, and the other (B) placed in a cool and dark closet. Extremes in *application* of the chemical are represented by a *single* spot, and by *immersion* for 24 hours. Duration of experiment was approximately 3 months. Each set consisted of six pieces.

The original test pieces were mounted on cardboard. These cards were unavoidably lost in transit, preventing their reproduction, and a written description is substituted herewith.

Each series was subdivided into two subdivisions:

NO. I. DROP TEST—One drop of reagent was allowed to dry on the surface of the specimen.

NO. II. IMMERSION TEST—The entire specimen was immersed in the reagent for 24 hrs., then dried. The "spot test" gave *tackiness* at point of contact between reagent and the rubber. The "immersion test" gave *tackiness* over the entire surface of the specimen. With the oil experiments even a single drop was too much, while those immersed were ruined (the specimens softened and "run").

All the treated samples showed *tackiness* due to the reagent. The ammonia copper acetate combination shows a much greater action than copper acetate alone or in combination with acetic acid. The oil-

¹ "Manufacture of Rubber Goods."

² "Preparation of Plantation Rubber."

³ "Rubber."

REPORT ON TESTS

No. 1 was the control or check, untreated. The checks showed no change in color or texture (a good index of the character of this grade of crude rubber).

No. 2 was treated with a 1 per cent water solution of copper acetate (neutral). The reagent produced *tackiness*.

No. 3 was treated with copper acetate solution made acid with 10 per cent glacial acetic acid. The reagent produced *tackiness*, but not materially greater than in No. 2.

No. 4 was treated with copper acetate solution made alkaline with 10 per cent of strong ammonia. It reacted strongly with the rubber, giving a hard surface which easily cracked. The product resembled "perished rubber" (Spiller's resin).

No. 5 was treated with lubricating oil (containing 25 per cent of rancid vegetable oil) carrying 1 per cent of dry powdered copper acetate.

No. 6 was treated with the same lubricating oil as No. 5 but without copper acetate.

In Nos. 5 and 6 the "immersion" test pieces were spoiled. The test was too severe, the specimens being destroyed (dissolved in oil). The "drop" tests in both Nos. 5 and 6 showed much action, the oil spread over the entire surface. Those of No. 5 (with copper) showed stronger action than those of No. 6 (without copper).

OBSERVATIONS

- 1—Copper acetate will produce *tackiness* in crude rubber.
- 2—The action is proportional to amount of reagent and time of contact.
- 3—Influence of light and heat is not as great (compared with darkness and a lower temperature) as expected.
- 4—The ability of the check samples to "stand up" under the light conditions indicates the value of Pale Plantation Crêpe variety of crude rubber.
- 5—The presence of acetic acid did not materially aid in the production of *tackiness*.
- 6—The presence of ammonia exerted a pronounced influence. The specimens, however, exhibited a much different appearance, the surface hard and cracked.
- 7—Lubricating oil (containing rancid vegetable oil) with 1 per cent of dry copper acetate gave a greater action than the same oil when used alone.

treated samples should be considered in a separate group as they show results that may arise from washing-mills in bad order. While oils alone exert a powerful action on crude rubber, the presence of copper magnifies this action. Results with oil and copper on crude rubber coincide with the observation of Weber concerning the presence of oil in cloth aiding the action of copper on rubber.

The action of the reagent is proportional to the time of application. The influence of light and heat is not as great as expected. This feature of the experiment emphasizes the fact that copper salts induce tackiness in crude rubber independently of the usual causes of this trouble.

Considered as a whole the work sustains the views of Dr. Morgan.

CLEVELAND, OHIO

COPPER IN SEWAGE AT THE NEW HAVEN SEWAGE EXPERIMENT STATION

By F. W. MOHLMAN

Received September 21, 1917

REASONS FOR INVESTIGATIONS

In the summer of 1916 representatives of the United States Public Health Service, under the direction of Dr. H. S. Cumming, made an investigation of the sanitary condition of New Haven Harbor. They found that it was seriously polluted by the sewage and industrial wastes of New Haven. They recommended that the taking of shellfish from the harbor be prohibited, that bathing be prohibited, and that the city take steps to insure the proper disposal of the sewage.

Following these recommendations, the City Council appropriated a sum of money for the establishment of a sewage experiment station, and a citizens' committee was appointed to take charge of the work. Prof. C. E. A. Winslow, of Yale University, is the chairman of this committee and the director of the experiments. During his absence in Russia with the Red Cross Commission, Mr. Henry B. Sargent is chairman of the committee. The plant was designed by Prof. S. E. Barney, of Yale University, assisted by Mr. R. H. Skelton. The writer is chemist and engineer-in-charge of the station, with Mr. W. S. Sturges

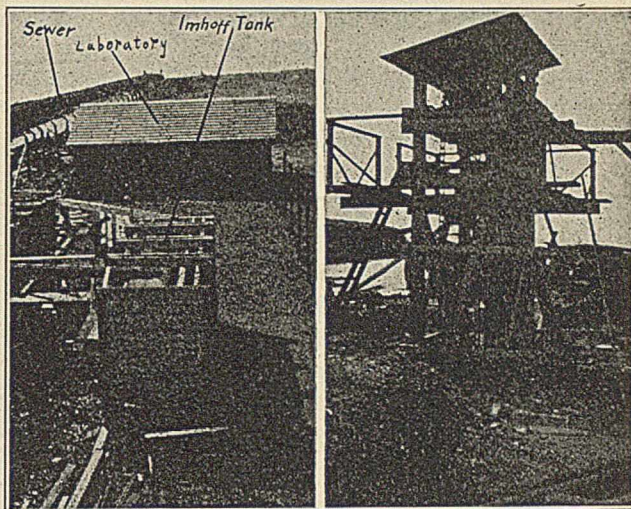


FIG. I—EXPERIMENT STATION

FIG. II—BUCKET ELEVATOR

as bacteriologist. Continuous operation started in June of this year.

New Haven is an important manufacturing city of 150,000 inhabitants. The sewerage is on the combined system. Wastes from most of the larger factories are discharged into the East Street sewer, which has an average dry-weather flow of 13,000,000 gallons per day. Since it was thought that trade-wastes might interfere with the treatment of this sewage it was decided to locate the Experiment Station at the outfall of this sewer (Fig. I). The sewer discharges into tide-water and at high tide the sewage is backed up in the sewer for a distance of several blocks.

DESCRIPTION OF THE PLANT

The sewage for the testing station is pumped by a bucket-elevator, which was erected in a concrete fore-bay at one side of the sewer (Fig. II). The sewage is deflected into the forebay by a galvanized-iron deflector built out nearly to the center-line of the sewer, and flows back into the sewer at the lower end of the forebay. It was believed that a fair sample of the sewage could be obtained in this way, including the floating solids and grease, and that the suspended solids would not be broken up to as great an extent as if a centrifugal pump were used. Operation of the elevator has shown that it fulfills these expectations. It delivers approximately 150,000 gallons of sewage per day into a hopper-shaped receptacle, from which it flows over to the station through a wooden flume

supported by wooden bents. Before flowing into the weir-box, where it is measured, the sewage passes through a grit chamber 15 ft. long, 12 in. deep at the inlet end, 4 in. deep at the outlet end, and 4 in. wide, with a detention period of 0.24 minute. The velocity of the sewage is checked to 0.7 ft. per sec. at the inlet end, increasing to 2.1 ft. per sec. at the outlet end. This velocity is so high and the detention period so short that very little grit has been removed from the sewage.

Following the grit chamber there is a butterfly valve in the flume which is automatically controlled by a float in the weir-box. This butterfly valve keeps the sewage at a constant level in the weir-box, the excess sewage being deflected over weirs 4 ft. long cut in the sides of the flume. The apparatus for maintaining a constant level was constructed by Wallace and Tiernan, of New York City.

From the weir-box the sewage flows to the various tanks over adjustable weirs, small amounts of 10,000 gallons per day being measured by 60° V-notch weirs, a larger amount, 100,000 gallons per day, by a rectangular weir 7½ in. long.

PROCESSES UNDER INVESTIGATION

The processes being studied are:

(1) Activated Sludge, (2) Imhoff, (3) Miles Acid, (4) Screening, (5) Disinfection by Liquid Chlorine.

(1) THE ACTIVATED-SLUDGE EXPERIMENTS are on the continuous-flow basis. The aerating tank is 16 ft. long, 4 ft. wide and 8 ft. deep. At the bottom of the tank the sides slope at 45° to a trough 1 ft. wide, which runs the full length of the tank. An iron frame in which are cemented 15 filtros plates is cemented into this trough. The air is admitted at the inlet end of the trough, and the water which filters through the plates can be drawn off at the outlet end. The air is compressed to 3.5 lbs. pressure by a Nash Hydro-turbine having a capacity of 20 cu. ft. of free air per minute. It is measured by means of a Venturi tube.

The settling tank is 4 ft. × 4 ft. in plan, and 12 ft. deep to the bottom of the hopper. This hopper slopes at 60° to a sump in which is cemented a 3-in. ell connected to the suction of an air-lift pump. Sludge is pumped back to the aerating tank, where it is measured in an orifice box. A baffle 7½ ft. deep extends across the center of the settling tank. This baffle was first placed 3 ft. from the inlet weir and 1 ft. from the outlet weir, but the upward velocity of the effluent carried particles of sludge over the outlet weir. Since placing it in the center of the tank no sludge has been lost in this way. The theoretical upward velocity is now 2.4 in. per min. and was formerly 4.8 in. per min. The capacity of the aerating tank is 3100 gallons, the settling tank 1150 gallons. At present, while treating 17,000 gallons of sewage per day with 50 per cent as much sludge returned, the aeration period is 3 hrs., the settling period 66 min.

(2) THE IMHOFF TANK is 16 ft. long × 4 ft. 6 in. wide × 11 ft. 6 in. deep. The flowing-through chamber extends the full length of the tank, with gas vents 8 in. wide on each side. Its capacity is 840 gallons,

giving a detention period of 2 hrs., when treating 10,000 gallons of sewage per day.

(3) THE MILES TANK is 16 ft. long × 3 ft. 6 in. wide × 4 ft. deep, having a capacity of 1680 gallons. When treating 10,000 gallons per day the theoretical detention period is 4 hrs. Liquid sulfur dioxide in cylinders is used for acidifying the sewage, supplemented at times by gas produced by a sulfur burner.

(4) SCREENING EXPERIMENTS were planned with the expectation that an experimental Riensch-Wurl screen could be obtained, which was to be operated at the rate of 100,000 gallons per day. In view of the impossibility of obtaining this screen, experiments with a mechanically operated screen had to be abandoned. Fixed screens of 30-mesh Monel metal wire cloth are used in a screen chamber through which raw sewage flows at the rate of 100,000 gallons per day. The screens are removed when the loss of head reaches 2 ft., and are cleaned by hand. The operation of the screens is discontinuous, approximately 3,000 gallons of sewage being screened for one experiment.

(5) The effluents from the Imhoff tank, activated-sludge tank, and screening chamber run through baffled tanks where they are treated with LIQUID CHLORINE. The periods of detention are from 2 to 5 mins.

ANALYSES OF SAMPLES COLLECTED HOURLY

Four-ounce samples of raw sewage and effluents are collected every hour and combined into composites for chemical analysis. Samples are collected for bacterial analysis as often as time permits. On May 7-8, 24 samples were collected, one each hour, and a complete analysis made of each sample (Table I).

TABLE I—ANALYSES OF SAMPLES OF RAW SEWAGE COLLECTED HOURLY, MAY 7-8, 1917

| Time | PARTS PER MILLION | | | | | | Bacteria per cc. 20° C. | Gas Formers per cc. 37° C. | | |
|---------|-------------------|------------|--------------------|---|------------|-----------|----------------------------|-------------------------------|---------|---------|
| | Chlorine | Alkalinity | AS NH ₃ | Total Organic NO ₂ +NO ₃ | O Consumed | (SOLIDS) | | | | |
| | | | | | | Suspended | | | | |
| | | | | | | Total | | | | |
| 8 A.M. | 2075 | 76 | 10.4 | 17.6 | 3.8 | 50 | 165 | 4430 | 4,200 | 100 |
| 9 | 2750 | 94 | 7.6 | 14.0 | 2.6 | 49 | 445 | 6178 | ... | ... |
| 10 | 2725 | 70 | 6.0 | 11.0 | 2.4 | 50 | 230 | 5880 | 4,500 | 100 |
| 11 | 2875 | 90 | 4.0 | 13.6 | 2.4 | 50 | 122 | 5057 | ... | ... |
| 12 | 2775 | 104 | 4.2 | 12.6 | 2.5 | 51 | 133 | 5872 | 70,000 | 1,000 |
| 1 P.M. | 2675 | 98 | 4.0 | 13.6 | 2.2 | 50 | 189 | 5440 | ... | ... |
| 2 | 2675 | 66 | 3.4 | 11.0 | 2.5 | 45 | 155 | 4313 | 97,000 | 1,000 |
| 3 | 2100 | 72 | 3.2 | 10.4 | 3.2 | 51 | 107 | 5583 | ... | ... |
| 4 | 1600 | 80 | 3.6 | 10.8 | 3.8 | 42 | 87 | 3325 | 33,000 | 1,000 |
| 5 | 1350 | 48 | 3.4 | 11.0 | 3.2 | 37 | 97 | 2840 | ... | ... |
| 6 | 100 | 56 | 4.8 | 12.8 | 2.4 | 48 | 126 | 540 | 25,000 | 1,000 |
| 7 | 47 | 108 | 4.2 | 13.4 | 1.4 | 52 | 90 | 433 | ... | ... |
| 8 | 38 | 72 | 4.6 | 15.4 | 1.3 | 50 | 97 | 342 | ... | ... |
| 9 | 36 | 80 | 5.8 | 10.2 | 1.2 | 49 | 80 | 312 | ... | ... |
| 10 | 37 | 72 | 5.4 | 9.0 | 1.6 | 35 | 65 | 262 | ... | 10,000 |
| 11 | 32 | 70 | 5.6 | 9.4 | 1.1 | 33 | 47 | 230 | ... | ... |
| 12 | 29 | 64 | 4.8 | 7.2 | 1.0 | 22 | 42 | 170 | ... | 10,000 |
| 1 A.M. | 23 | 56 | 3.2 | 5.6 | 1.1 | 15 | 21 | 108 | ... | ... |
| 2 | 21 | 48 | 2.0 | 5.2 | 1.0 | 14 | 18 | 115 | ... | 1,000 |
| 3 | 17 | 46 | 1.8 | 3.0 | 1.3 | 15 | 9 | 93 | ... | ... |
| 4 | 14 | 42 | 1.6 | 2.4 | 1.2 | 9 | 14 | 92 | 150,000 | 10,000 |
| 5 | 17 | 42 | 2.0 | 3.6 | 1.4 | 15 | 17 | 122 | ... | ... |
| 6 | 20 | 56 | 3.6 | 10.0 | 1.3 | 24 | 42 | 182 | 51,000 | 100,000 |
| 7 | 1350 | 68 | 5.4 | 17.0 | 1.2 | 34 | 87 | 2655 | 362,000 | 10,000 |
| AVERAGE | 1058 | 70 | 4.4 | 10.4 | 2.0 | 37 | 104 | 2275 | 88,500 | 12,100 |

These results indicate that some trade-waste containing large amounts of chlorides is discharged into the sewer from 7 A.M. to 6 P.M. The nitrogen determinations show that the sewage is very fresh, the ratio, *Ammonia-Nitrogen* : *Total-Organic-Nitrogen*, being unusually low. The presence of large amounts of nitrite and nitrate nitrogen also testifies to the fresh-

ness of the sewage. The alkalinity, oxygen consumed, and suspended solids are unusually low. The dilute character of the sewage is due largely to the high consumption of water in New Haven, amounting approximately to 180 gallons per capita per day.

The most unusual features of the analyses are the large amounts of chlorides and total solids, and the low bacterial content during the daytime. During the week of July 9-16, samples collected at the plant during the daytime had the bacterial content indicated in Table II. These results clearly show the

TABLE II—BACTERIAL CONTENT OF SEWAGE, WEEK JULY 9-16

| DAY | TOTAL COUNT, AGAR, 20° C. | | | | GAS FORMERS, 37° C. | | | |
|--------------|---------------------------|-----------|-----------|-----------|---------------------|----------|---------|----------|
| | 8 A. M. | 10 A. M. | 1 P. M. | 4 P. M. | 8 A. M. | 10 A. M. | 1 P. M. | 4 P. M. |
| Mon..... | 1,500,000 | 225,000 | 59,000 | 16,000 | 100,000 | 1,000 | 1,000 | 100 |
| Tues..... | 1,080,000 | 128,000 | 5,000 | 7,500 | 100,000 | 100 | 1,000 | 100 |
| Wed..... | 1,670,000 | 81,000 | 7,000 | 100,000 | 100,000 | 100 | 100 | 1,000 |
| Thurs..... | 1,100,000 | 148,000 | 1,500 | 12,000 | 100,000 | 10,000 | 100 | 10 |
| Fri..... | 1,125,000 | 42,000 | 9,000 | 9,000 | 100,000 | 100 | 100 | 100 |
| Sat..... | | 68,500 | 7,100 | 800,000* | | 100 | 10 | 100,000* |
| Average..... | 1,295,000 | 115,400 | 14,700 | 159,000 | 100,000 | 1,900 | 385 | 17,000 |
| Sun..... | | 3,355,000 | 2,275,000 | 2,535,000 | | 100,000 | 100,000 | 100,000 |

* Factories shut down at noon Saturday.

presence of some disinfecting substance in the week-day sewage. Although the sewage is found to be acid at times, the composite samples are never acid, and it is believed that none of the above samples for bacterial analysis was acid.

SOURCE OF COPPER IN SEWAGE

The ignited residue from the mat of suspended solids deposited in a Gooch crucible was usually of a brilliant red color, quite similar to the residue of cuprous oxide obtained in the determination of reducing sugars with Fehling's solution. Qualitative tests of the mat for copper were positive. This led to the conclusion that the disinfection of the sewage is due to copper salts.

The bactericidal action of the copper ion is well known. Copper sulfate was first proposed as a disinfectant for water and sewage by B. Kröhnke¹ in 1892. It was first used in America by Moore² and Kellerman in 1903. Extensive studies were made by Johnson³ and Copeland in 1904 at the Columbus Testing Station on the use of copper sulfate as a disinfectant for sewage. By treating Columbus sewage with copper sulfate they obtained the results given in Table III. These data indicate that 5.0 p. p. m. of copper in solution in sewage are sufficient to exert a marked disinfecting action. Quantities as low as 2.5 p. p. m. were almost as effective as 5.0 p. p. m. when treating the effluents from a contact bed.

In order to find the source of the copper and the high chlorides in New Haven sewage, samples were collected from manholes at various places in the sewer from the source to the outfall (Table IV). Copper was determined by evaporating the sample to dryness with 2 cc. of concentrated nitric acid, taking up the residue in distilled water, filtering, and adding 2 cc. of concentrated sulfuric acid. This solution was electrolyzed between platinum electrodes for 3 hrs. at 70° C., using 3 dry cells as a source of current. Experiment showed that all the copper was deposited in this time. The cathode was removed, the copper

dissolved in nitric acid, the acid driven off on the steam bath, and the residue dissolved in distilled water. An aliquot portion of this solution was diluted to 50 cc. in a Nessler tube, and 10 cc. of alkaline sodium sulfide added. The color developed was compared with that produced by known quantities of a copper-sulfate solution containing 0.2 mg. of copper per cc., when treated with 10 cc. of the alkaline sodium sulfide. This method is similar to that in "Standard Methods of Water Analysis" with a few modifications.

The entrance of the high chlorides is clearly shown

TABLE III—EFFECT OF COPPER SULFATE ON BACTERIA IN COLUMBUS SEWAGE

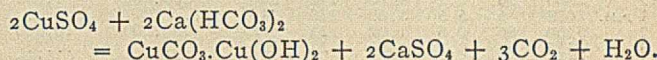
| Johnson and Copeland, 1904 | | | | |
|----------------------------|----------------------------------|-------------------|-----------|------------|
| COMPOSITION OF SEWAGE | | | | |
| Organic Nitrogen | Alkalinity | Bacteria | | |
| 6.3 P. p. m. | 376 P. p. m. | 1,200,000 per cc. | | |
| P. p. m. | TOTAL COUNT ON GELATIN AT 20° C. | 24 hrs. | | |
| Cu CONTACT: | 0 | 1 | 6 | 24 hrs. |
| 0 | 1,200,000 | 1,200,000 | 6,000,000 | 14,000,000 |
| 5 | 1,200,000 | 14,000 | 700 | 3,400,000 |
| 25 | 1,200,000 | 9,500 | 250 | 200 |
| 250 | 1,200,000 | 3,000 | 190 | 35 |

to be between Samples 6 and 7. Inquiry showed that a large rubber factory in this vicinity was pumping 2,000 gallons of sea-water per minute for condenser purposes, all of which was discharged into the sewer.

TABLE IV—SOURCE OF COPPER AND CHLORIDES IN NEW HAVEN SEWAGE

| DESCRIPTION OF SAMPLE | PARTS PER MILLION | | | Bacteria per cc. 20° C. | Gas Formers per cc. 37° C. |
|---------------------------|-------------------|------------|------------|-------------------------|----------------------------|
| | No. linity | Alka- line | Chlor- ine | | |
| Near source of sewer..... | 1 | 54 | 67 | 0.0 | 990,000 |
| Below munitions factory.. | 2 | 90 | 144 | 8.8 | 3,000 |
| | 3 | 165 | 74 | 5.6 | 3,000 |
| Small branch sewer..... | 4 | 134 | 72 | 0.0 | 559,000 |
| Main sewer..... | 5 | | | | 70,000 |
| | 6 | 156 | 71 | 1.9 | 380,000 |
| Below rubber factory..... | 7 | 90 | 2700 | 3.5 | 65,000 |
| Experiment Station..... | 8 | 130 | 2500 | | 53,000 |

Between the places where Samples 1 and 2 were collected there is a large munitions factory which employs 15,000 people. This factory manufactures brass cartridges and cannon shells. In stamping out these shells the brass must be annealed several times, and after each annealing the scale must be removed. The shells are washed with hot water and dilute sulfuric acid after each annealing, 1600 lbs. of acid and 120,000 gallons of water being used per day for this purpose. The waste goes into catch basins, in which some of the solid particles are removed, but the residual acid wastes, containing copper and zinc sulfates, go into the sewer. Here the acid is neutralized by the bicarbonates in the sewage, and the copper sulfate is changed to the basic carbonate:



This basic carbonate is gradually changed to the hydroxide:



Ellms¹ has shown that the presence of carbon dioxide and organic matter greatly retards the precipitation. He found that quantities as great as 5 p. p. m. of copper may be retained in solution by organic matter for long periods of time. Since the sewage from the munitions factory reaches the Experiment Station in approximately 1 hour, it is probable that most of the copper is still in solution. Its germicidal power is in-

¹ J. Gasbel. und Wasservers., 36 (1893), 513.

² U. S. Bur. of Plant Industry, Bull. 64 (1904).

³ J. Infect. Dis., Sup. 1 (1905), 327.

¹ J. N. Eng. Water Works Assoc., 19 (1905), 499.

creased by the high temperature of the sewage, averaging 84° F. during August.

There is a noticeable correlation between the number of bacteria and the amount of copper, as shown in Table III. In order to determine whether the disinfecting action is greatest at the time when the copper content is greatest, samples were collected at the Experiment Station from 6 A.M. to 9 P.M., on August 10. Four-ounce samples were incubated at 20° C. with

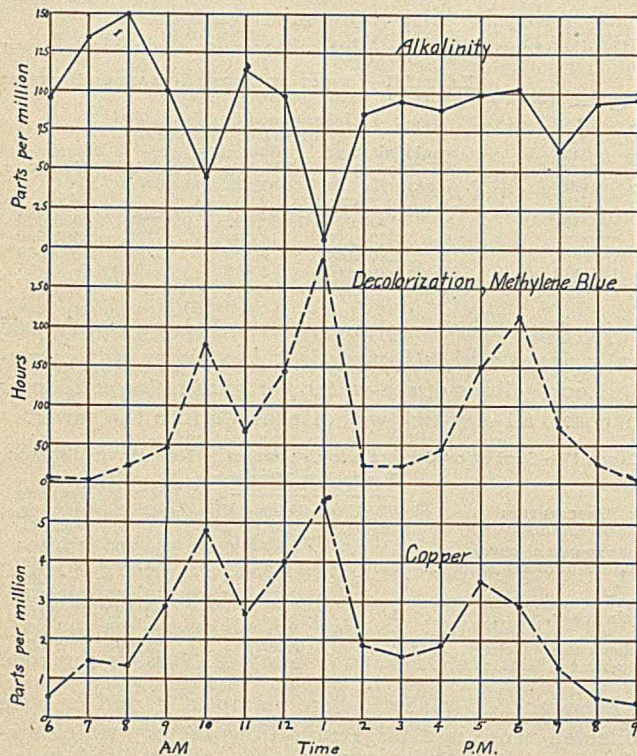


FIG. III

methylene blue, the time required for decolorization being a rough measure of the strength of the disinfecting action. Diluted samples were also incubated, and bacterial counts made (Table V and Fig. III).

TABLE V—DISINFECTION OF SEWAGE BY COPPER, AUG. 10, 1917

| Time | PARTS PER MILLION | | | | HOURS | | Bacteria per cc. 20° C. | Gas Formers per cc. 37° C. |
|--------|-------------------|------------|------|--------|--------------------------|------------------------|-------------------------|----------------------------|
| | Chlorine | Alkalinity | Iron | Copper | Methylene Blue Undiluted | 1 sewage luted 2 water | | |
| 6 A.M. | 30 | 94 | 0.1 | 0.56 | 6 | 120 | 3,700,000 | 100,000 |
| 7 | 3750 | 136 | 0.2 | 1.52 | 6 | 24 | 6 | 24 |
| 8 | 3100 | 160 | 5.0 | 1.36 | 24 | 72 | 2,500,000 | 1,000,000 |
| 9 | 2900 | 101 | 1.8 | 2.88 | 48 | 120 | 19,000 | 100 |
| 10 | 2800 | 43 | 0.3 | 4.80 | 168 | 192 | 559,000 | 1,000 |
| 11 | 2750 | 114 | 0.4 | 2.72 | 60 | 144 | 187,000 | 10,000 |
| 12 | 2800 | 98 | 0.2 | 4.00 | 144 | 168 | 39,000 | 100 |
| 1 P.M. | 3075 | 6 | 5.5 | 5.60 | 240 | 240 | 45,000 | 1,000 |
| 2 | 3200 | 86 | 0.6 | 1.92 | 24 | 72 | 33,000 | 1,000 |
| 3 | 3325 | 91 | 0.7 | 1.60 | 24 | 120 | 39,000 | 100 |
| 4 | 3375 | 88 | 0.2 | 1.92 | 48 | 96 | 144 | 144 |
| 5 | 3450 | 98 | 0.1 | 3.52 | 150 | 144 | 100 | 100 |
| 6 | 130 | 103 | 0.4 | 2.88 | 216 | 100 | 80 | 80 |
| 7 | 95 | 63 | 1.4 | 1.28 | 72 | 80 | 96 | 96 |
| 8 | 52 | 92 | 0.2 | 0.64 | 24 | 96 | | |
| 9 | 50 | 96 | 0.0 | 0.44 | 6 | 24 | | |

The time of decolorization varies directly and the alkalinity and bacterial content vary inversely, with the amount of copper. The physical appearance and tests showed markedly the effect of the copper. The samples collected at 6 A.M., 8 P.M., and 9 P.M. became septic within a few days, developed a strong odor and lost their colloidal appearance. The remaining samples, with the exception of the one collected at 1 P.M., retained their original odor, that of fresh sewage,

and remained colloidal and opalescent. The relatively high iron content of the one o'clock sample produced a floc of iron hydroxide which coagulated the suspended matter and clarified the sewage. The results obtained by incubating diluted samples show that in some cases, notably at 5 P.M. and 6 P.M., the diluted samples were decolorized before the undiluted ones. This shows how impossible it is to apply the "dilution method" for the determination of the oxygen demand of this sewage. By incubating the composite sample of raw sewage with methylene blue, however, it is possible to obtain a rough measure of the amount of germicide present. The Sunday sewage will reduce the methylene blue to the leuco-base within 6 hrs.; some week-day composites have not produced the colorless compound for more than 20 days.

The effect of the copper on the various processes being studied remains to be seen, since operation has not been continued sufficiently long to allow any conclusions to be drawn. The company producing the copper-bearing wastes has investigated the recovery of the copper and acid, and claims that such recovery would not be profitable because of the great concentration necessary. If the wastes interfere seriously with the solution of the sewage disposal problem, their removal will probably be considered again.

The writer wishes to express his thanks to Mr. Sturges for the bacterial data contained herein, and to Prof. Winslow for suggestions and advice.

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TANNIN CONTENT OF PACIFIC COAST TREES

By H. K. BENSON AND FRANK M. JONES

Received August 28, 1917

In a previous article it was shown¹ that the tannin content of Douglas fir slabwood when properly selected contained sufficient tannin to be considered a suitable raw material for the extract industry. In order to ascertain what other species common to the Pacific Northwest might be available for extract manufacture this study was undertaken.

METHODS OF EXTRACTION AND ANALYSIS—The samples in each case were taken from four or five trees of the same species, were first chipped in a Mitts & Merrill "hog", carefully quartered and the final sample finely ground in a Koerner drug mill. The extractor was of the same type as used in the previous study, extraction carried on for 16 hours and analyzed according to the method of the American Leather Chemists' Association (1914). All calculations are made on a moisture-free basis.

EFFECT OF SEASONING ON DOUGLAS FIR

The sample of sawmill slab reported in the previous study (*l. c.*) was still available, having been kept in a loosely stoppered jar. It was thought of interest to ascertain its tannin content after a year's storage. The average of seven analyses is given in Table I for comparison with previous results.

From these results, it would seem that the effect of seasoning is to bring about hydrolysis and possibly

¹ THIS JOURNAL, 7 (1915), 915.

TABLE I—EFFECT OF SEASONING ON TANNIN CONTENT OF DOUGLAS FIR

| PERCENTAGES | FIR SLABWOOD | |
|---------------------|---------------------------------|---|
| | Analyzed by Thompson in 1914 | Same sample analyzed by Jones one year later |
| Total Solids..... | 14.92 | 15.8 |
| Soluble Solids..... | 13.02 | 13.7 |
| Reds..... | 1.90 | 2.1 |
| Non-Tannins..... | 7.10 | 6.2 |
| Tannins..... | 5.92 | 7.5 |
| Moisture..... | 6.91 | 10.0 |

oxidation, thereby increasing the tannin content by 1.6 per cent (27 per cent of the former). The total solids are increased and the non-tannin decreased, each 0.9 per cent.

PART I—CONIFERS

WESTERN LARCH (*Larix occidentalis*)—The sample was taken from four trees, averaging 28 in. in thickness, growing in the Whitman National Forest in Oregon. The trees were felled in December, 1910, and transported by skidding and log train to the station. The cross-sections were cut 18 in. from the ground and showed a very wet and pitchy surface. The wood is dull red in color and the bark averaged 2¹/₄ in. in thickness. The sample was dried for one week at 40° C. before extraction. The analyses were made in March, 1916.

The tannin content of this, as well as of the other species tested, is given in Table II.

The wood extract was bright red in color and unimportant from the standpoint of either tannin content or dye. The extract from the bark was a dull red and gave a pleasing light red color to the tanned hide.

Inasmuch as this species ranks ninth in the order of most prevalent trees in the states of Oregon and Washington, often occurring in pure forests in North-eastern Washington, Northern Idaho, and North-western Montana, is a prolific seeder and well adapted to reforest burned-over areas, its importance as a source of tannin must not be overlooked. Investigations carried on in the U. S. Forest Products Laboratory also show¹ that this species produces a high yield of alcohol by hydrolysis.

Considering the high tannin content of its bark and the exceptional yield of alcohol, it would seem that this species might be especially adapted to chemical utilization, rather than for lumber and timber purposes.

TABLE II—TANNIN CONTENT OF PACIFIC COAST SPECIES

| PERCENTAGES: | | Total Solids | Soluble Solids | Reds | Non-Tannins | Tannins | Moisture |
|---------------------|----------------|--------------|----------------|-------|-------------|---------|----------|
| | | | | | | | |
| Western Larch | { Wood(a)..... | 28.9* | 27.6* | None* | 23.9* | 6.7* | 7.8* |
| | { Bark(b)..... | 20.5 | 17.0 | 3.5 | 6.4 | 10.6 | 11.0 |
| Western Yellow Pine | { Wood(c)..... | 19.6 | 16.9 | 2.7 | 8.0 | 8.9 | |
| | { Bark(c)..... | 22.3 | 19.3 | 3.1 | 8.3 | 10.9 | 4.0 |
| Western Hemlock | { Wood(c)..... | 4.2 | 4.1 | 0.1 | 3.1 | 1.0 | 9.5 |
| | { Bark(c)..... | 20.8 | 19.5 | 1.3 | 8.57 | 10.93 | 9.8 |
| Dogwood | { Wood..... | 8.3 | 7.1 | 1.2 | 5.8 | 1.3 | 5.0 |
| | { Bark..... | 8.3 | 7.9 | 0.4 | 6.2 | 1.7 | 5.0 |
| Cottonwood | { Wood..... | 10.8 | 9.1 | 1.7 | 7.3 | 1.8 | 6.5 |
| | { Bark..... | 25.3 | 24.3 | 1.0 | 19.6 | 4.7 | 2.0 |
| Alder | { Wood..... | 3.5 | 3.3 | 0.2 | 2.6 | 0.7 | 6.8 |
| | { Bark..... | 10.2 | 9.6 | 0.6 | 6.2 | 3.3 | 9.8 |

(a) Results are averages of 2 extractions. * Analysis by W. E. Gailey.

(b) Results are averages of 8 extractions.

(c) Results are averages of 4 extractions.

YELLOW PINE (*Pinus ponderosa*)—This sample was obtained from the Whitman National Forest, the cross-sections being cut 18 in. in diameter. The bark averages 2 in. in thickness. The trees were felled 4 months before extraction.

¹ THIS JOURNAL, 7 (1915), 922.

This species ranks second in quantity of the standing timber of Oregon and Washington. The bark on old trees is often 3 to 4 in. thick. The yellow pine is chiefly used in making boxes, but both the quantity of the bark and of the tannin in the bark and wood make the use of the sawmill waste of this species feasible for tannin extract manufacture.

WESTERN HEMLOCK (*Tsuga Heterophilla*)—Various published analyses of the western hemlock bark show that the tannin content of the western species is equal to or exceeds that of the eastern species. The bark of the western hemlock has been regularly used by tanneries on the Pacific Coast. Inasmuch as considerable second growth hemlock occurs on the logged off lands of the Northwest, a composite sample of four trees taken from the University campus was prepared. One tree was 18 in. in diameter and the other three averaged 9 in. The bark was 1/2 in. thick. The trees were felled 9 months before extraction. The tannin content is less than that found by other investigators, due probably to the difference in the ages of the trees.

PART II—DECIDUOUS SPECIES

DOGWOOD (*Cornus nuttalli*)—The western dogwood is essentially the same as that of the East. The wood is a dull pink and the bark a reddish black. Its dye possibilities have been utilized by the Pacific Coast Indians for coloring clothing and moccasins deep red. It ranges from the southern coast of British Columbia through Washington, Oregon and California, usually thriving in low altitudes and damp soils and mixed singly or in groups under all the trees of the Pacific slope except the yellow and sugar pines.

For the sample, cross-sections of five trees on the University campus were cut 3 ft. from the ground. They ranged from 8 to 24 in. in diameter, and were air-dried for 6 months. The bark averaged less than 1/2 in. in thickness and was not easily peeled. The extract is reddish brown in color and imparts a light reddish brown color to the tanned hide in the case of the wood extract and a deeper red from the bark. It is believed that dogwood extract might be used with other tanning extracts to furnish the dye property.

COTTONWOOD (*Populus trichocarpa*)—The cottonwood tree is found growing in damp, sandy land from Alaska to Mexico. It is a very rapid grower, a tree growing to 15 in. in as many years. The sample was obtained from a tree 2 ft. in diameter, felled 3 months before extraction. The bark ranged from 1/2 to 3/4 in. in thickness.

ALDER (*Alnus Oregona*)—This species occurs to a considerable extent as a second growth on the logged off lands of Oregon and Washington. Four trees were cut on the University campus 9 months before extraction. Cross-sections were taken about 2 ft. from the ground. The average diameter of the tree was 10 in., the bark averaging 1/4 in. in thickness. The quality of the tannin is of doubtful value.

CONCLUSIONS

I—Douglas fir slabwood, selected for tanning extraction, can advantageously be seasoned for one year.

II—In addition to the western hemlock bark, that of the western larch and western pine seems to yield extract satisfactory both in quantity and quality.

III—Of the deciduous species examined, the dogwood alone appears suitable for use in extract manufacture but only as a dye.

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SATURATED HYDROCARBONS IN BASKING-SHARK LIVER OIL

By MITSUMARU TSUJIMOTO

Received July 25, 1917

Basking-shark (Japanese: "Uba-zamé"), *Cetorhinus maximus* (Gunner), (*Cetorhinidae*), is the largest of all living sharks and indeed of all fishes. It reaches a length of 14 meters and has an enormous weight. This shark is a dull and sluggish animal of the arctic seas, being occasionally found off the coast of Japan. The liver of basking-shark is very heavy, often weighing as much as 1 ton and yielding some 5 cwt. of oil.¹

Three authentic samples of basking-shark liver oil examined by the writer were pale yellow to orange-yellow liquids of low specific gravity and contained 41.92–55.51 per cent of unsaponifiable matter. They contained squalene, $C_{30}H_{50}$, a highly unsaturated hydrocarbon found by the writer in certain Japanese shark liver oils.² This is important as an instance showing that the occurrence of squalene is not limited to the liver oils from the sharks belonging to the family *Squalidae*. The experimental details concerning squalene will, as the writer hopes, be published shortly in another paper, together with the results of the experiments performed on the liver oils obtained from some twenty-three species of Japanese sharks. In the present paper, the writer describes the remarkable occurrence of saturated hydrocarbons in a sample of basking-shark liver oil.

Of the three samples of the oil above referred to, the one from the Province Hidachi had the following properties:

| | |
|------------------------------------|----------------|
| Specific gravity at 15°/4° C..... | 0.8839 |
| Acid value..... | 1.09 |
| Saponification value..... | 102.45 |
| Iodine value (Wijs)..... | 178.30 |
| Refractive index at 20° C..... | 1.4773 |
| Butyro-refractometer at 20° C..... | 78.2 |
| Unsaponifiable matter..... | 41.92 per cent |

The unsaponifiable matter was, for the most part, a liquid. One hundred grams of the oil were distilled under 5 mm. pressure. At the temperature of 170–190° C. (the temperature of the oil bath, 250–270° C.), 10 g. (or 10 per cent) of a pale yellow liquid distilled over. It had the refractive index 1.4775 at 20° C. This substance was, therefore, different from squalene. On changing the receiver and raising the temperature

of the oil bath to 290–315° C., a further distillate was obtained at the boiling temperature of 244–260° C., amounting to 25 g., or 25 per cent of the original oil. This latter distillate was found to consist mainly of squalene.

The first distillate was washed with aqueous NaOH solution to remove free fatty acids, and then 8 g. of this purified substance were distilled under 13 mm. pressure. It distilled over at 160–166° C., mainly at 164° C. (the temperature of the oil bath, 200–205° C.), leaving a small residue. The distillate was a colorless, mobile liquid which did not solidify even when cooled to below 0° C. It had the specific gravity 0.7868 at 15° C., 0.7815 at 20° C., 0.7789 at 28° C. (water at 4° C. = 1), and the refractive index 1.4398 at 20° C. Its iodine value was determined to be only 4.40, so that it was nearly saturated. It dissolved in alcohol; when mixed with concentrated sulfuric acid, the acid layer turned brown, and on raising the temperature to about 100° C., the coloration became darker, but the distillate on the upper layer was not readily attacked. No insoluble hydrochloride was formed by passing dry HCl into the well-cooled ethereal solution of the substance.

When heated under 766 mm. pressure, the substance began to boil at about 294° C., and mainly distilled over at 296° C. The distillate thus obtained had the refractive index 1.4395 at 20° C., which was nearly identical with that of the original substance.

0.2011 g. original substance (distilled under 13 mm. pressure) gave 0.6223 CO₂ and 0.2700 H₂O:

C = 84.39 per cent; H = 15.02 per cent.

Molecular weight determined by the depression of the freezing point of benzene solution, (1) 265, (2) 252, mean 259.

| | C | H | Mol. wt. |
|---|----------------|----------------|----------|
| C ₁₇ H ₃₆ requires..... | 84.89 per cent | 15.11 per cent | 240.3 |
| C ₁₈ H ₃₈ requires..... | 84.96 | 15.04 | 254.3 |
| C ₁₉ H ₄₀ requires..... | 84.98 | 15.02 | 268.3 |

The substance was, therefore, a hydrocarbon or a mixture of hydrocarbons, the percentage of carbon and hydrogen amounting to 99.4 per cent. Its elementary composition corresponded to any of the above-mentioned three paraffins. It is not safe to say that the substance was a single chemical compound, but judging from its boiling point and molecular weight, it appears to be very probable that it consisted mainly of C₁₈H₃₈ or an octadecane. But as the normal octadecane is a solid at the ordinary temperatures, the substance must be at least an iso-octadecane. Its comparatively low boiling point may be attributed to this cause. A quite similar relation has already been observed between solid triacontane and the hydrogenation product of squalene, C₃₀H₆₂, a liquid not solidifying even at –20° C.¹

| COMPOUND | Melting Point ° C. | Boiling Point ° C. (mm.) | Specific Gravity –/4° C. |
|--|--------------------|--------------------------|--------------------------|
| Normal Heptadecane, C ₁₇ H ₃₆ .. | 22.5 | 303 (760) | 0.7768 (22.5° C.) |
| Normal Octadecane, C ₁₈ H ₃₈ .. | 28 | 181.5 (15) | 0.7768 (28° C.) |
| | | 317 (760) | |
| Normal Nonadecane, C ₁₉ H ₄₀ .. | 32 | 193 (15) | |
| | | 330 (760) | 0.7774 (32° C.) |

¹ Loc. cit.

¹ L. E. Andes, "Animal Fats and Oils," 1898, p. 194.
² THIS JOURNAL, 8 (1916), 889. Spinacene, a hydrocarbon found by C. Chapman [J. Chem. Soc., 56 (1917), 111], in a Portuguese shark liver oil appears to be identical with squalene. The writer has already prepared squalene hexahalogen hydrates of the general formula C₃₀H₅₀6HX, which crystallize well and serve for the convenient identification of squalene.

Employing the n^2 formula, the specific refraction of the saturated hydrocarbon of the basking-shark liver oil is 0.3283, and the molecular refraction (adopting the formula $C_{18}H_{38}$) 83.4. The calculated molecular refraction for $C_{18}H_{38}$ (adopting Eisenlohr's numbers) is 85.3.

The saturated hydrocarbons in the sample of the basking-shark liver oil were not due to some adulteration, inasmuch as their properties differed considerably from petroleum or other hydrocarbons, more especially from Japanese petroleum which consists chiefly of naphthenes. Then, the occurrence of about 10 per cent of saturated hydrocarbons in a shark liver oil is a fact hitherto unknown. However, the hydrocarbons appear not to be the essential constituents of basking-shark liver oil, since they were not found in the other two samples of the oil examined by the writer.

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SOME DATA ON SPERM OILS USED FOR BURNING PURPOSES

By ABRAHAM G. BLAKELEY AND EDMUND A. REILLY

Received September 10, 1917

A considerable quantity of sperm oil is used as a burning oil in Miners' Safety Lamps of the Davy type. Some trouble experienced with a shipment of supposedly pure sperm oil led the writers to conduct an investigation, results of which are given in Table I.

TABLE I

| DESCRIPTION OF SAMPLE | Abbreviations: N W, Natural Winter; B W, Bleached Winter; E W B, Extra Winter Bleached | | | | | | | | | | | | | | | |
|--|--|--------|--------|--------|--------|--------|----------|----------|--------|--------|------------------|--------|--------|--------|--------|--|
| | SAMPLE NO.: | R-1 | R-2 | R-3 | F-1 | F-2 | F-3 | N-1 | N-2 | N-3 | N-4 | S-1 | F-4 | T-1 | T-2 | |
| Kind of Oil: | N W | B W | B W | N W | B W | B W | N W | B W | B W | B W | B W ¹ | E W B | (a) | (b) | (b) | |
| "Cold Test": | 45 | 45 | 38 | 45 | 45 | 38 | Below 38 | Below 38 | 42 | 42 | | | | | | |
| Specific Gravity at 15.6° C. | 0.882 | 0.876 | 0.877 | 0.881 | 0.879 | 0.879 | 0.883 | 0.881 | 0.882 | 0.879 | 0.883 | 0.879 | 0.884 | 0.881 | 0.881 | |
| Refractive Index at 15.6° C. | 1.4649 | 1.4649 | 1.4649 | 1.4665 | 1.4661 | 1.4665 | 1.4649 | 1.4650 | 1.4650 | 1.4644 | 1.4669 | 1.4665 | 1.4593 | 1.4600 | 1.4600 | |
| Flash Point, ° C. | 245 | 260 | 260 | 245 | 255 | 250 | 260 | 255 | 265 | 255 | 265 | 250 | 250 | 270 | 270 | |
| Fire Point, ° C. | 285 | 295 | 300 | 285 | 295 | 290 | 290 | 295 | 295 | 295 | 300 | 295 | 285 | 300 | 300 | |
| Saponification Value. | 142.1 | 128.9 | 130.2 | 136.1 | 130.1 | 130.6 | 142.2 | 135.0 | 139.6 | 127.7 | 133.8 | 130.8 | 145.7 | 142.7 | 142.7 | |
| Iodine Value (Hanus). | 86.6 | 86.4 | 89.6 | 83.1 | 86.3 | 85.7 | 89.3 | 87.9 | 87.1 | 88.1 | 85.3 | 85.6 | 64.7 | 62.4 | 62.4 | |
| Per cent Free Acid (calculated as oleic) | 3.60 | 0.21 | 0.20 | 2.28 | 0.46 | 0.14 | 1.34 | 0.03 | 0.58 | 0.04 | 0.19 | 0.23 | 1.42 | 1.37 | 1.37 | |
| Flake Test, ° F. | 52 | 51 | 42 | 50 | 43 | 39 | 39 | 38 | 38 | 37 | 43 | | | | | |
| Cloud Test, ° F. | 46 | 46 | 35 | 45 | 39 | 34 | 36 | 34 | 35 | 34 | 38 | | | | | |
| Pour Test, ° F. | 35 | 30 | 25 | 36 | 31 | 25 | 31 | 29 | 30 | 24 | 38 | 29 | 37 | 37 | 37 | |
| Viscosity (Tagliabue): at 70° F. | 110 | 107 | 105 | 112 | 108 | 105 | 109 | 106 | 112 | 116 | 114 | | 111 | | | |
| at 120° F. | 91 | 93 | 94 | 93 | 90 | 88 | 93 | 97 | 93 | 92 | 96 | | 86 | | | |
| Viscosity (Saybolt): at 100° F. | 117 | 110 | 111 | 117 | 110 | 111 | 127 | 118 | 120 | 119 | 118 | | | | | |
| at 130° F. | 82 | 82 | 83 | 79 | 76 | 76 | 80 | 74 | 80 | 74 | 88 | | | | | |
| at 210° F. | 52 | 48 | 48 | 49 | 50 | 48 | 47 | 47 | 49 | 47 | 46 | | | | | |
| PERCENTAGES: Fatty Anhydrides | 63.1 | 59.8 | 59.6 | 55.5 | 61.3 | 56.3 | 63.0 | 52.4 | 64.1 | 58.0 | | 63.7 | 60.1 | 59.9 | 59.9 | |
| Alcohols | 35.2 | 39.1 | 39.9 | 43.3 | 37.1 | 43.2 | 35.4 | 46.2 | 33.6 | 41.4 | 33.6 | 35.2 | 36.3 | 37.8 | 37.8 | |
| FATTY ACIDS: | | | | | | | | | | | | | | | | |
| Specific Gravity at 15.6° C. | 0.899 | 0.896 | 0.897 | 0.897 | 0.895 | 0.894 | 0.896 | 0.899 | 0.896 | 0.894 | 0.895 | 0.893 | 0.895 | 0.895 | 0.895 | |
| Refractive Index at 15.6° C. | 1.4623 | 1.4609 | 1.4600 | 1.4595 | 1.4595 | 1.4595 | 1.4587 | 1.4600 | 1.4585 | 1.4580 | 1.4609 | | | | | |
| Neutralization Value. | 216.2 | 208.9 | 206.2 | 201.6 | 201.2 | 194.3 | 204.3 | 198.8 | 201.3 | 188.6 | 197.7 | 186.8 | 224.8 | 222.8 | 222.8 | |
| Iodine Value (Hanus). | 88.8 | 82.2 | 86.5 | 86.6 | 87.7 | 88.1 | 86.0 | 85.6 | 84.8 | 85.9 | 91.8 | 86.7 | 64.9 | 66.2 | 66.2 | |
| Titer Test, ° C. | 13.6 | 11.5 | 10.5 | 12.9 | 10.6 | 10.1 | 7.9 | 7.7 | 9.6 | 6.2 | 13.2 | 11.0 | 12.0 | 12.0 | 12.0 | |
| ALCOHOLS: | | | | | | | | | | | | | | | | |
| Refractive Index at 60° C. | 1.4475 | 1.4450 | 1.4455 | 1.4495 | 1.4490 | 1.4490 | 1.4461 | 1.4484 | 1.4465 | 1.4464 | 1.4383 | | | | | |
| Iodine Value (Hanus). | 67.4 | 65.9 | 70.2 | 68.9 | 72.3 | 73.2 | 71.4 | 74.1 | 74.1 | 72.5 | 71.6 | 63.9 | 41.4 | 39.3 | 39.3 | |
| Melting Point, ° C. | 27.0 | 25.5 | 25.0 | 23.5 | 24.0 | 22.5 | 24.0 | 20.0 | 23.5 | 25.0 | 23.2 | 24.0 | 34.0 | 35.0 | 35.0 | |
| Saponification Value of Acetate. | 193.2 | 216.0 | 203.3 | 202.9 | 193.4 | 200.1 | 204.6 | 197.9 | 197.3 | 215.4 | 189.6 | 189.5 | 198.3 | | | |

¹ Low acidity.

(a) Sample representing shipment. (b) Oil which gave trouble.

The Flake Test indicates the temperature at which occurs a separation of solid matter. This test corresponds to the "cold test" of the sperm oil manufacturer. The cloud test indicates the temperature at which the lower half of the sample becomes opaque. The pour test indicates the temperature at which a sample of oil in cylindrical form of specified diameter and length will just flow under specified conditions.¹ The iodine values were determined by the Hanus method. The melting points were determined by the ordinary capillary tube method.

¹ Proceedings of the A. S. T. M., 15 (1915), Part 1, pp. 281-282.

No glycerol was found in any sperm oil tested.

Samples R-1, R-2, and R-3 (received Dec. 1, 1916) were supplied by the same manufacturer. The manufacturer stated that the oil was probably taken from one or two different lots of Atlantic Ocean Sperm Oil. The oil was all from the Sperm or Cachalot Whale. The head and body oils were thoroughly mixed. The "boats catch this oil in moderately warm waters, say from about as far north as the Azores to as far south as the coast of Brazil." Samples R-2 and R-3 were entirely satisfactory as burning oils. Sample R-1, the Natural Winter Oil, was not satisfactory for burning.

Samples F-1, F-2, and F-3 (received December 11, 1916) were all supplied by a second manufacturer. The oils were from the Sperm or Cachalot Whale, and were mixtures of head and body oils. No further information was available. Samples F-2 and F-3 were entirely satisfactory as burning oils. Even Sample F-1, the Natural Winter Oil (containing 2.28 per cent free oleic acid), gave fairly good results, although showing a slight tendency to incrust the wick.

Samples N-1, N-2, N-3, and N-4 (received January 4, 1917) were supplied by a third manufacturer. The manufacturer stated that the oils were all from the same cargo. The oil is bought from the whalers in original casks. The oil in these casks, in refining, is put into a press, and in one pressing there may be three or four different casks of oil. These casks may contain head and body oil from two or three different

whales. The cargo from which the four samples were prepared consisted of some 16,000 gallons of oil of "very fine quality." The oil is all strictly pure sperm oil from the Sperm or Cachalot Whale. Sample N-1 represents the Natural Winter Oil. Sample N-2 represents the same oil after "caustic" bleaching to reduce free acid. Sample N-3 represents Sample N-1 bleached by filtering through fuller's earth to make it of light color. Sample N-4 represents Sample N-3 "caustic" bleached; that is, this sample had been treated both to reduce color and to reduce acidity. Samples N-3

and N-4 gave entirely satisfactory results in burning. Sample N-2 was satisfactory but inferior to samples N-3 and N-4. Sample N-1, the Natural Winter Oil, was fairly good as a burning oil.

Sample S-1 represents an oil sample submitted by a fourth company. No information was furnished with this oil. The oil gave satisfactory results as a burning oil.

Sample F-4 represents an oil shipment which was entirely satisfactory. Samples T-1 and T-2 are from two different barrels of the shipment which caused considerable trouble. These oils encrusted the wicks very badly and were altogether unsatisfactory.

The nature of the adulteration in the unsatisfactory oils has not been determined. The table shows abnormal figures for refractive index (saponification value) and iodine value of the oil as well as for iodine values of fatty acids and alcohols, and for melting point of alcohols.

Results for the constants of the genuine sperm oils agree, in the main, with results given in the literature. For some constants, the writers have found a somewhat wider variation than is generally noted in the technical literature (*see* Table II).

TABLE II

| | Data given in Literature | Data from Authors' Tests |
|--------------------------------------|--------------------------|--------------------------|
| SPERM OILS: | | |
| Refractive Index (15.6° C.) | 1.4664 to 1.4673 | 1.4649 to 1.4669 |
| FATTY ACIDS: | | |
| Specific Gravity (15.6° C.) | 0.899 | 0.893 to 0.899 |
| Neutralization Value..... | 183 to 199 | 186.8 to 216.2 |
| Titer Test, ° C..... | 11.1 to 11.9 | 6.2 to 13.6 |
| ALCOHOLS: | | |
| Iodine Value..... | 64.6 to 65.8 | 63.9 to 74.1 |
| Melting Point, ° C..... | 25.5 to 27.5 | 20.0 to 27.0 |
| Saponification Value of Acetate..... | 161 to 190 | 189.5 to 216.0 |

In connection with the writing of Specifications for Sperm Oil it has been the general custom to include requirements as to the maximum percentage of free acid allowed. In order to determine the effects of free acid upon the burning properties of sperm oil, experiments were made with sperm oil to which had been added varying amounts of pure oleic acid. The oil was in each test burned in a Davy Miners' Safety Lamp. It was found that sperm oil containing 1, 2, 3 and up to 4 per cent added oleic acid caused a slight crust to form on the wick, but that oil with even 4 per cent oleic acid gave fairly satisfactory results. The addition of 5 per cent oleic acid caused heavier crust, while the addition of 6 per cent made the sperm oil entirely unsatisfactory for burning in a Davy Safety Lamp. It must be admitted that free acid has a harmful effect upon a burning oil, but it seems also that this effect has been somewhat overestimated in the case of sperm oil.

In judging the suitability of a sperm oil for burning purposes, one would do well to consider the iodine value and refractive index as well as the other constants and the free acid.

Some of the work above tabulated was done by Mr. Donald Thorn, to whom the authors would acknowledge indebtedness.

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SOME EFFECTS OF CERTAIN SOLVENTS ON TARS IN THE "FREE CARBON" DETERMINATION

By G. S. MONROE AND H. J. BRODERSON

Received July 2, 1917

The work to be described was carried out in order to obtain some additional data which might throw some light on the probable condition of free carbon in tars, and the extent to which it or other substances in the tar might react with solvents used in the free carbon determination. There is much uncertainty as to the physical and chemical nature of free carbon as it exists in the original untreated tar. The fact that only part of the free carbon existing in tars, as shown by analysis, can be removed by filtration suggests the probability that it is present in a finely divided state. According to Abderhalden¹ this free carbon exists in the tar as an emulsion, the emulsifying agent being the pitch oils present in the tar.

The first series of determinations was made to show the effect on the free carbon content of tars when the latter are allowed to stand in contact with the solvent at room temperature for different periods of time. The results showed a gradual increase in free carbon when benzene, bromobenzene, and chloroform were used. The numerical data are not given for this series of determinations as the results were of the same general nature as those recorded by Weiss.²

The next series of experiments was made to show the effect on the free carbon content of tars by digesting the tars with the solvent for different periods of time. In each determination 10 g. of tar were added to 100 cc. of solvent in an Erlenmeyer flask and digested on the water bath for a certain period of time, after which the tar solution was filtered through a weighed extraction thimble. This thimble was then placed in a Soxhlet extractor, extracted with the same solvent as that used in digestion, then dried and the insoluble residue weighed as free carbon. When chloroform was used as solvent, analyses were made for halogen in the free carbon residues by the peroxide method.³ These analyses were not made, however, in case of water-gas tar because the free carbon residues obtained were too small to work with conveniently. The results obtained by hot extraction are given in Table I.

TABLE I—FREE CARBON BY HOT EXTRACTION

| MATERIAL TREATED | SOLVENT USED | Period of Digestion | Per cent Free Carbon | Per cent Cl in Free Carbon Residue |
|------------------|--------------|---------------------|----------------------|------------------------------------|
| Water-Gas Tar | Benzene | 1 hr. | 1.06 | .. |
| | | 4 hrs. | 1.33 | .. |
| | | 7 hrs. | 1.13 | .. |
| | | 43 hrs. | 1.17 | .. |
| Gas-House Tar | Benzene | 1 hr. | 4.28 | .. |
| | | 4 hrs. | 4.47 | .. |
| | | 40 hrs. | 5.16 | .. |
| | | 96 hrs. | 4.68 | .. |
| Coke-Oven Tar | Benzene | 1 hr. | 6.13 | .. |
| | | 4 hrs. | 6.73 | .. |
| | | 50 hrs. | 9.33 | .. |
| | | 98 hrs. | 9.46 | .. |
| | | 8 days | 11.83 | .. |
| Water-Gas Tar | Chloroform | 1 hr. | 0.77 | .. |
| | | 4 hrs. | 0.68 | .. |
| | | 45 hrs. | 0.97 | .. |
| Gas-House Tar | Chloroform | 1 hr. | 3.77 | 0.55 |
| | | 42 hrs. | 4.63 | 1.34 |
| | | 3 days | 5.76 | 2.64 |

¹ *J. Gas Light.*, 123 (1913), 46-47.

² *THIS JOURNAL*, 6 (1914), 279-83.

³ J. F. Lemp, "A Method for the Determination of Halogens in Organic Compounds," Senior Thesis, University of Illinois, 1917.

The results given above show that in case of water-gas tar and gas-house tar the free carbon percentages gradually approached a maximum value and then decreased when benzene was used as solvent. The same general behavior was observed in determination of free carbon in gas-house tar when toluene was used as solvent. In case of coke-oven tar, however, no maximum point was reached. This is due perhaps to the possibility that digestion was not continued long enough to reach the maximum point. It hardly seems wise to theorize as to the explanation of this maximum point until more data of this kind are available.

In the determination of free carbon made with chloroform as solvent no maximum value was observed, but the amount of free carbon gradually increased. This variation in free carbon which takes place when benzene, toluene, chloroform, etc., are used as solvents has been thought to be due to chemical reactions¹ producing insoluble compounds which are continuously precipitated. That chemical reaction does take place in case of chloroform is shown conclusively by the fact, as observed by Weiss, that small crystals of amber

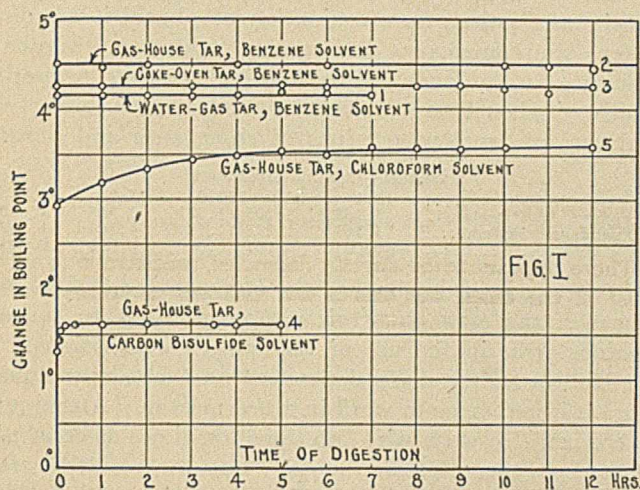


FIG. I

color were found throughout the free carbon residue when gas-house tar was digested with this solvent for three days. The amount, however, of this substance was too small to account for the observed increase in weight. The probability of chemical reaction in the tar solution in case of chloroform is also indicated by the presence of chlorine in the free carbon residues from gas-house tar, although the same might be explained in part on the basis of adsorption of some of the solvent by the free carbon present in the tar. This is especially true when it is considered that there is no definite relation between the amount of chlorine found and the total amount of so-called free carbon.

If the theory of chemical reaction is to explain partly, if not completely, the variations observed in the free carbon content of tars by continued digestion, there should be a fluctuation in the boiling temperatures of such solutions on digestion due to the change in the chemical nature of the constituents in the tar solution. The following experiments were not designed to predict

the nature of the chemical reactions, if such take place, but to show whether such chemical changes do occur. The experiments were performed in the following manner: In each case 5 g. of tar diluted with 50 cc. of solvent were placed in a standard type of apparatus used in determining the molecular weights of compounds by the boiling point method. To prevent the escape of solvent the condenser attached to the inner tube was closed with a mercury seal. The boiling points of solutions of tars with different solvents were observed at different intervals with a Beckmann thermometer. The barometric pressure was observed at the different intervals but was not found to be great enough to make any appreciable difference in the boiling temperature. The actual boiling temperatures were not observed but simply the changes in such temperatures. The results are shown by the curves in Fig. I. The Curves 1, 2, 3, representing the digestions of water-gas tar, gas-house tar, and coke-oven tar, respectively, are horizontal and show no fluctuations, hence no appreciable chemical reaction takes place between the tars and benzene. The experiment using carbon bisulfide as solvent shows the same probability as mentioned in case of benzene (Curve 4). The rapid rise observed in the first portion of the curve is perhaps due to the possibility that temperature equilibrium was not reached between the tar solution and the surroundings.

In the case where chloroform was used as solvent the boiling point showed a continuous rise, thus showing that chemical reaction took place appreciably in the tar solution (Curve 5). Unfortunately, only one tar (gas-house tar) was investigated using chloroform as solvent, but it is reasonable to suppose that other tars would give similar results.

CONCLUSIONS

The results thus far obtained are not sufficient to warrant any general conclusion as to what happens between the tars or parts of the tar and the solvent but the following are some of the indications:

I—Variations in percentages of free carbon for different periods of digestion should not be entirely attributed to chemical reactions between tar and solvent, thereby producing insoluble material which is gradually precipitated. It may be that due to dilution some of the free carbon which may have been in the colloidal condition has been precipitated.

II—While it is very probable that chemical reactions take place between tar and chloroform when the latter is used in determining free carbon in tars, such reactions cannot account completely for the gradual increase in free carbon on continued digestion.

III—If the selection of a solvent which when added to tar will not give rise to chemical reactions is the proper criterion in devising a method for the determination of free carbon, benzene, toluene, and carbon bisulfide should be selected in preference to chloroform.

¹ Weiss, THIS JOURNAL, 6 (1914), 279-83.

THE ESTIMATION OF PHENOL IN CRUDE CARBOLIC ACID AND IN COAL-TAR OILS

By F. W. SKIRROW

Received September 5, 1917

Until quite recently no satisfactory method was to be found in the literature for the estimation of phenol in tar oils or in crude carbolic acid. In a recent paper, Masse and Leroux¹ give a method based on preliminary fractionation of the crude carbolic acid and subsequent estimation of the phenol from determinations of the solidifying point. This method suffers from the disadvantage that the cresols and other higher boiling bodies may vary in the fraction containing the phenol, while they assume a constant and arbitrary ratio of the cresols to be present.

More recently Weiss and Downs² have published a method in which the crude carbolic acid is fractionated in such a way as to obtain the whole of the phenol in a fraction supposed to contain only phenol and the cresols, and in this fraction the phenol is then estimated by simultaneous determination of the specific gravity and the solidifying point, whence by reference to graphs the amount of phenol present is deduced. These graphs also are drawn up with fixed ratios of meta- and para-cresol.

In 1909 the author worked out a method for the estimation of phenol in coal tar which depended on quite other properties of the constituents for their estimation, and which gave a fair indication of the amount of the cresols also present. The method gave satisfactory results and was used in the author's laboratory for some years, but was not at that time published. It is thought that the method of attack may not be without interest at the present time, and the author desires to thank the Directors of Messrs. Hardman and Holden, Ltd., of Manchester, England, for permission to publish the results.

In a paper on the determination of phenols in gas liquor,³ the author determined the "Oxygen Absorption" due to the various constituents of the effluent from a sulfate of ammonia works and incidentally of the phenol and cresols, respectively, in that effluent. This suggested the possibility that the oxygen absorption might furnish a means to estimate the amount of phenol in a mixture of phenolic bodies.

OXYGEN ABSORPTION OF PHENOL *o*-, *m*- AND *p*-CRESOL Solutions Required

| | |
|---|-----------------------------|
| Standard Potassium Permanganate.. | 0.79 g. in 2 liters |
| Standard Sodium Thiosulfate..... | 7.00 g. crystals in 1 liter |
| Dilute Sulfuric Acid (1 : 3) faintly tinged with Permanganate | |
| Potassium Iodide Solution..... | 10 per cent |
| Starch Solution..... | 4 g. in 1 liter |

The phenol, etc., was diluted so that 50 cc. of the solution contained 0.002 g. of the particular phenol or cresol.

METHOD

Portions (50 cc.) of the permanganate were measured into stoppered bottles and 15 cc. of the dilute sulfuric acid added to each. These bottles were placed in a rack

in a thermostat which was maintained at 23° C. The solutions of the tar acids were also brought to the temperature of the thermostat: 50 cc. of the tar acid solution were then run into the permanganate solution from a pipette also warmed to 23° C., and the time noted when the first drop entered the permanganate. When the whole had been added, the bottle was quickly shaken to insure uniformity. At the end of 3 min. the action was stopped by quickly adding 1 cc. of the potassium iodide solution. The liberated iodine was then titrated with the thiosulfate solution. Sufficient excess of permanganate was used so that 30 to 40 per cent of the permanganate remained at the end. The results were then calculated to grams of oxygen absorbed by 1 g. of the respective tar acid. The concordance of the results is shown in the case of the phenol, the others being equally good.

TABLE I—GRAMS OXYGEN ABSORBED

| | | | | | |
|-------------|-------|-----------------|-----------------------|-------|------------------|
| Phenol..... | 1.435 | } Mean 14.34 | <i>o</i> -Cresol..... | 1.170 | } Mean Values |
| | 1.434 | | <i>m</i> -Cresol..... | 1.156 | |
| | 1.434 | | <i>p</i> -Cresol..... | 1.062 | |

OXYGEN ABSORPTION OF MIXTURES

In order to see if any considerable difference would be found in the rate of oxidation of phenol if cresols were simultaneously undergoing oxidation, known mixtures were made up containing varying proportions of phenol to cresols, the cresol taken being a mixture of equal proportions of *ortho*, *meta* and *para*.

TABLE II—OXYGEN ABSORBED

| | | | | | |
|------------------------|--------|--------|-------|--------|--------|
| Per cent Phenol..... | 11.1 | 25.0 | 50.0 | 75.0 | 88.9 |
| OXYGEN { Calculated.. | 1.163 | 1.205 | 1.281 | 1.358 | 1.400 |
| ABSORBED: { Found..... | 1.167 | 1.212 | 1.281 | 1.364 | 1.405 |
| Difference..... | +0.004 | +0.007 | 0.000 | +0.006 | +0.005 |

There appears to be slightly increased oxidation in most of the cases, but this is not sufficient to cause serious error in the use of the oxygen absorptions.

The rate is naturally dependent on the temperature and it is necessary to work in a thermostat. Attempts were made to work with solutions ten times as concentrated as the solutions quoted, but the results were much less steady owing no doubt partly to the considerable temperature disturbance due to the increased heat of reaction.

The phenol can thus be estimated with reasonable accuracy provided that the ratio of the cresols to one another be known. The difference in the rate of oxidation of the three cresols from one another, while much less than the difference between the rate of oxidation of any one cresol and the rate of oxidation of phenol, is still much too great to allow of estimation in this way unless the ratio of the cresols present is known. It is thus necessary to get some idea as to the ratio of cresols present in order to proceed.

FRACTIONATION EXPERIMENTS

It is obvious that in dealing with a mixture of phenol, cresols and higher boiling phenolic bodies, which are present in a crude carbolic acid, preliminary fractionation would have to precede any attempt at titration, and experiments were carried out in this direction on crude carbolic acid, which was the average from a very large amount of tar from widely differing sources. This crude carbolic acid was fractionated

¹ *Compt. rend.*, **165** (1916), 361.

² *THIS JOURNAL*, **9** (1917), 569.

³ *J. Soc. Chem. Ind.*, January, 1908.

through still heads of various types and the progress of the fractionation observed by taking the oxygen absorption of the fractions.

OXYGEN ABSORPTION OF HIGHER BOILING BODIES

A large sample of higher boiling bodies was obtained which had had most of the phenol and cresols removed in a works column still. This was freed from H₂S and was fractionated several times in the laboratory to remove any phenol and cresols which might still remain. Fractions were then collected and their oxygen absorption measured with the results given in Table III.

TABLE III

| FRACTION..... | 205 to 210° C. | 210 to 215° C. | 215 to 220° C. |
|-----------------------|----------------|----------------|----------------|
| Oxygen Absorption.... | 0.942 | 0.879 | 0.831 |

The oxygen absorption decreases steadily with increasing boiling point and will thus throw light on the progress of the fractionation.

COMPARISON OF THE EFFICIENCY OF STILL HEADS

The two still heads giving the best results with crude carbolic acid were found to be the "LeBel" bulbs and the "Pear" bulbs. The Hempel column was not so efficient and had the disadvantage that a large amount of liquid is held up in the glass beads. The Young dephlegmator, although excellent for lower boiling liquids, did not give as good results in the author's hands as did the Pear bulbs.

COMPARISON OF A 4-BULB LEBEL WITH A 12-BULB PEAR STILL HEAD—The total length of the two columns to the side tube was practically the same. In both cases 1000 cc. of the crude carbolic acid was taken in a copper flask and distilled through the respective head. An air condenser was used leading into receivers closed with a calcium chloride tube. Any moisture was first distilled off and the temperature carried to 180° C. The phenol was recovered from this, dehydrated, and returned to the distilling flask and the fractionation then proceeded with. The rate of distillation was regulated carefully to one drop per second, a seconds pendulum being placed behind the receiver. The flask was protected by a shield of asbestos paper and the column enclosed in one thickness of glazed paper to prevent draughts and to diminish somewhat the radiation from the column. Under these conditions extremely steady conditions were easily maintained. A small Anschütz thermometer graduated in tenths was used and this was compared with a standard "N. P. L." thermometer.

The oxygen absorption of each fraction was measured and the fractions then submitted to a second and to a third systematic fractionation. The oxygen absorption of the fractions of the second and of the third fractionations were also measured. Table IV contains the results so obtained. The two first temperature intervals in the first fractionation are different from those in the second and third fractionations, but in all subsequent work the latter intervals were used.

If we examine these fractionations we see that the oxygen absorption of the fractions is much the same whether the "Pear" or the "LeBel" column is

used, being a little to the advantage of the "Pear" form but that with the Pear a greater volume accumulates in the first fraction which contains the largest proportion of phenol. The use of the Pear head is further to be preferred on account of the smaller amount of liquid remaining after a distillation. In all subsequent work the Pear form was used. This superiority of the Pear still head was also established by Weiss and Downs.¹

It will further be seen by comparing the second and the third fractionations, confining our attentions now to the values for the Pear head only, that the "quality" of the fractions does not alter very materially after the second fractionation, but that the chief difference is in the volume of the first fraction. From this it was inferred that more than two fractions would not bring any commensurate advantage, and that with two fractionations a steady state of affairs had been reached which would be easily reproducible. The examination of these fractions was then proceeded with, to ascertain the amount of phenol in each.

The oxygen absorption of the fractions obviously gives us no quantitative measure of the amount of phenol which they contain as we have no information as to the ratio in which the cresols exist in each.

MATCHING EXPERIMENTS

In order to establish definitely the percentage of phenol, ortho-, meta- and para-cresol in these fractions, use was made of a fact previously observed by the author in the course of work on the phenols in gas liquor¹ but not at that time alluded to, *viz.*, that if the Messinger and Vortman method for the estimation of phenol be applied to solutions of *o*-, *m*- and *p*-cresol, respectively, the end-product obtained (tri-iodophenol, etc.) has widely different colors in each case. The colors of these end-products are extremely characteristic and may be described as follows:

| | | | |
|------------------|------------------|------------------|------------------|
| PHENOL | <i>o</i> -CRESOL | <i>m</i> -CRESOL | <i>p</i> -CRESOL |
| Bright Rose-Pink | Brown | Slate-Blue | Dirty Yellow |

Preliminary experiments showed that if a known mixture of phenol and the cresols be taken, the percentage of each constituent could be determined with good accuracy by first measuring the oxygen absorption of the mixture and then making up mixtures with the same oxygen absorption, forming the iodo-compounds, and by the method of trial and failure gradually approaching the exact shade of the so-called tri-iodo-compound of the mixture to be analyzed. (The end-product in the case of the cresols is by no means exactly the tri-iodo compounds.)

The iodo compound was prepared in each case as follows: 200 cc. of water and 3.5 cc. *N* NaOH were mixed; 1 g. of the tar acid was dissolved in 500 cc. of water and 25 cc. of this solution were added to the dilute sodium hydroxide solution. This was heated to 70° C. in a stoppered flask and 25 cc. of 0.02 *N* iodine solution added and well shaken. After standing for 5 mins. the flask was cooled under the tap, the mixture slightly acidified with sulfuric acid and the excess of iodine removed with a slight excess of sodium

¹ *Loc. cit.*

TABLE IV—COMPARISON OF 4-BULB LEBEL WITH A 12-BULB PEAR STILL HEAD

| (1)—FIRST FRACTIONATION | | | | | (2)—SECOND FRACTIONATION | | | | | (3)—THIRD FRACTIONATION | | | | | | | |
|-------------------------|-------------------|---------------------------|----------------|-----------|--------------------------|-------------------|---------------------------|----------------|-----------|-------------------------|-------------------|---------------------------|----------------|-----------|-------|-----|-------|
| No. | Temperature C. | 12-BULB PEAR 4-BULB LEBEL | | | No. | Temperature C. | 12-BULB PEAR 4-BULB LEBEL | | | No. | Temperature C. | 12-BULB PEAR 4-BULB LEBEL | | | | | |
| | | Vol. Cc. | Phenol Abs. | O Abs. | | | Vol. Cc. | Phenol Abs. | O Abs. | | | Vol. Cc. | Phenol Abs. | O Abs. | | | |
| 1 | To 185.5 | 26 | 1.293 | 27 | 1.292 | 1 | 180 to 184 | 143 | 1.342 | 124 | 1.337 | 1 | 180 to 184 | 202 | 1.351 | 165 | 1.340 |
| 2 | 185.5 to 187 | 155 | 1.305 | 112 | 1.300 | 2 | 184 to 187 | 179 | 1.293 | 174 | 1.299 | 2 | 184 to 187 | 100 | 1.297 | 126 | 1.297 |
| 3 | 187 to 190 | 234 | 1.257 | 243 | 1.266 | 3 | 187 to 190 | 75 | 1.233 | 114 | 1.236 | 3 | 187 to 190 | 87 | 1.240 | 90 | 1.236 |
| 4 | 190 to 193 | 103 | 1.204 | 130 | 1.214 | 4 | 190 to 193 | 78 | 1.188 | 79 | 1.189 | 4 | 190 to 193 | 56 | 1.183 | 64 | 1.185 |
| 5 | 193 to 196 | 69 | 1.159 | 81 | 1.166 | 5 | 193 to 196 | 65 | 1.133 | 66.5 | 1.139 | 5 | 193 to 196 | 69 | 1.099 | 53 | 1.140 |
| 6 | 196 to 199 | 61 | 1.117 | 62 | 1.125 | 6 | 196 to 199 | 66 | 1.098 | 69 | 1.099 | 6 | 196 to 199 | 85 | 1.104 | 67 | 1.094 |
| 7 | 199 to 202 | 67 | 1.074 | 69 | 1.079 | 7 | 199 to 202 | 61 | 1.068 | 54 | 1.060 | 7 | 199 to 202 | 71 | 1.060 | 71 | 1.058 |
| 8 | 202 to 205 | 57 | 1.037 | 51 | 1.036 | 8 | 202 to 205 | 62 | 1.028 | 44 | 1.022 | 8 | 202 to 205 | 23 | 0.972 | 23 | 0.978 |
| 9 | 205 to 208 | 35 | 1.003 | 31 | 0.999 | 9 | 205 to 208 | 23 | 0.972 | 23 | 0.978 | 9 | 205 to 208 | 23 | 0.972 | 23 | 0.978 |

thiosulfate solution. The precipitated iodo compound was allowed to settle, washed once by decantation and placed in a small clear glass weighing bottle for comparison. It is essential that the compound be freshly prepared as it becomes lighter in color after standing one or two hours. The method is clearly cumbersome but it was used only to establish the percentages present in the fractions once and for all, *i. e.*, as a method of standardization.

In this way the percentages of phenol, *o*-, *m*-, and *p*-cresol were determined in the fractions through the Pear still head for the second and third fractionations quoted in Table IV, (2) and (3).

TABLE V—RESULTS OF MATCHING EXPERIMENTS

| No. | 1—SECOND FRACTIONATION | | | | | 2—THIRD FRACTIONATION | | | | | |
|-----|------------------------|-------------|-------------|------|------|-----------------------|-------------|-------------|------|------|------|
| | Vol. Cc. | Phenol % | Cresol % | | | Vol. Cc. | Phenol % | Cresol % | | | |
| 1 | 143 | 71.0 | 14.8 | 14.2 | 0 | 1,117 | 202 | 73.5 | 14.5 | 12.0 | 0 |
| 2 | 179 | 56.0 | 20.8 | 23.2 | 0 | 1,114 | 100 | 57.1 | 21.4 | 21.4 | 0 |
| 3 | 75 | 40.5 | 18.7 | 40.8 | 0 | 1,096 | 87 | 40.5 | 25.5 | 34.0 | 0 |
| 4 | 78 | 30.0 | 22.2 | 47.8 | 0 | 1,083 | 56 | 25.0 | 25.0 | 50.0 | 0 |
| 5 | 65 | 15.9 | 18.7 | 65.4 | 0 | 1,076 | 53 | 15.4 | 21.1 | 63.5 | 0 |
| 6 | 66 | 6.9 | 18.6 | 65.7 | 8.8 | 1,073 | 85 | 3.2 | 19.8 | 68.5 | 9.0 |
| 7 | 61 | 0 | 11.3 | 72.8 | 15.9 | 1,068 | 70 | 0 | 11.3 | 72.8 | 15.9 |

The mixtures were made up to have the same oxygen absorptions as the respective fractions with the exception of the higher fractions—where it was found that better matches could be obtained by making mixtures with slightly higher oxygen absorptions than the fractions. This was probably due to the small amounts of higher boiling bodies in the higher fractions. (The color of the "iodo-compounds" of the higher boiling bodies is not pronounced, while their oxygen absorptions are progressively less than the cresols.) Table V gives the results of these matching experiments. The last column gives the mean oxygen absorption of everything except phenol in the fractions, calculated from the oxygen absorption of the fraction, the oxygen absorption of pure phenol and the found percentage of phenol in the fraction. Here we see more definitely that the percentage of phenol

in the third fractionation has not changed very materially from that in the second fractionation.

RESULTS OBTAINED WITH OTHER MATERIALS

The preceding results were obtained with a large stock sample of crude carbolic acid representing the total extract from a very large amount of tar. Similar experiments were then carried out with other materials as follows:

- A—For comparison: Material already quoted
- B—Sample of Refined Cresylic Acid
- C—Sample of "60's" Carbolic Acid
- D—Another sample of Refined Cresylic Acid of different origin
- E—Another sample of Crude Carbolic Acid of different origin to that quoted in "A"

These were submitted to preliminary purification to free them from H₂S, etc., and were then fractionated twice in the manner described. In A the volume of the fractions was measured; in all subsequent operations the fractions were weighed to the nearest decigram. Results are given in Table VI.

In Table VII is given the mean oxygen absorption of everything except the phenol in the fractions, calculated as before indicated from the oxygen absorption of the fraction, the oxygen absorption of pure phenol and the found percentage of phenol in the fraction. From these data we see that the mean oxygen absorption of the cresols, etc., in the fractions is very constant for one and the same fraction and varies very little with the nature of the material distilled. Thus it seems evident that the larger variation of the oxygen absorption of the fractions themselves is caused principally by variation in the percentage of phenol present.

METHOD OF ANALYSIS ADOPTED

Thus the method adopted for the analysis of any unknown sample of crude carbolic acid was to fractionate about a liter of the sample in the manner outlined and then determine the oxygen absorptions of the fractions of the second fractionation. The per-

TABLE VI—RESULTS WITH VARIOUS MATERIALS

| No. | 1. AMOUNT OF FRACTIONS | | | | | 2. OXYGEN ABSORPTIONS | | | | | | |
|-----|------------------------|----------|---------|---------|---------|-----------------------|-----|-------|-------|-------|----------|-------|
| | Temp. C. | A Cc. | B G. | C G. | D G. | E G. | No. | A | B | C | D | E |
| 1 | 180 to 184 | 143 | 41.6 | 377.3 | 7.4 | 44.9 | 1 | 1.342 | 1.332 | 1.355 | 1.272(a) | 1.327 |
| 2 | 184 to 187 | 179 | 173.8 | 152.1 | 58.3 | 183.0 | 2 | 1.293 | 1.294 | 1.297 | 1.287 | 1.302 |
| 3 | 187 to 190 | 75 | 200.6 | 68.7 | 171.2 | 104.3 | 3 | 1.233 | 1.235 | 1.238 | 1.245 | 1.251 |
| 4 | 190 to 193 | 78 | 115.5 | 45.1 | 151.1 | 76.0 | 4 | 1.188 | 1.175 | 1.172 | 1.195 | 1.207 |
| 5 | 193 to 196 | 65 | 109.6 | 37.7 | 128.3 | 70.1 | 5 | 1.133 | 1.132 | 1.130 | 1.147 | 1.150 |
| 6 | 196 to 199 | 66 | 104.2 | 23.5 | 125.5 | 56.9 | 6 | 1.098 | 1.099 | 1.087 | 1.103 | 1.101 |
| 7 | 199 to 202 | 61 | 106.1 | 22.6 | 147.4 | 63.7 | 7 | 1.068 | 1.065 | 1.070 | 1.071 | 1.066 |

| No. | 3. MATCHING EXPERIMENTS | | | | | | | | | | | | | | | |
|-----------------|-------------------------|---------|------|------------------|--------|------------------|-------|--------|------------------|-------|--------|---------|-------|-------|-------|-------|
| | FRACTIONS FROM B | | | FRACTIONS FROM C | | FRACTIONS FROM D | | | FRACTIONS FROM E | | | | | | | |
| PERCENTAGES IN: | Phenol | Cresols | | | Phenol | Cresols | | Phenol | Cresols | | Phenol | Cresols | | | | |
| 1 | 67.5 | 17.5 | 15.0 | 0 | 75.0 | 13.0 | 12.0 | 0 | 50.0(a) | 22.2 | 27.8 | 0 | 66.5 | 16.1 | 17.4 | 0 |
| 2 | 55.6 | 23.1 | 21.3 | 0 | 57.3 | 20.1 | 22.6 | 0 | 54.2 | 21.5 | 24.3 | 0 | 58.6 | 20.3 | 21.1 | 0 |
| 3 | 40.5 | 18.7 | 40.8 | 0 | 40.9 | 17.5 | 41.6 | 0 | 44.0 | 23.3 | 32.7 | 0 | 45.4 | 18.7 | 35.9 | 0 |
| 4 | 26.7 | 18.2 | 55.1 | 0 | 26.7 | 18.2 | 55.1 | 0 | 31.0 | 28.1 | 40.9 | 0 | 35.5 | 23.3 | 41.2 | 0 |
| 5 | 15.2 | 17.6 | 61.4 | 5.8 | 15.0 | 26.7 | 33.3? | 25? | 18.1 | 23.1 | 51.9 | 6.9 | 20.6 | 14.1 | 61.9 | 3.4 |
| 6 | 5.8 | 17.1 | 60.5 | 16.6 | 4.7 | 19.2 | 57.3 | 18.8 | 9.4 | 17.5 | 61.8 | 11.3 | 10.6 | 21.2 | 59.9 | 8.3 |
| 7 | 0 | 9 | 62 | 29 | | | | | | | | | | | | |

(a) On the first fractionation the volume of the first fraction was so small that it could be distilled only through a 3-bulb Pear-head.

TABLE VII—MEAN OXYGEN ABSORPTION OF THE CRESOLS, ETC.

| No. | A | B | C | D | E | Mean |
|--------|-------|-------|-------|---------|-------|-------|
| 1..... | 1.117 | 1.120 | 1.118 | (1.110) | 1.114 | 1.117 |
| 2..... | 1.114 | 1.119 | 1.113 | 1.113 | 1.115 | 1.115 |
| 3..... | 1.096 | 1.099 | 1.102 | 1.097 | 1.099 | 1.099 |
| 4..... | 1.083 | 1.081 | 1.077 | 1.088 | 1.082 | 1.082 |
| 5..... | 1.076 | 1.078 | 1.076 | 1.084 | 1.076 | 1.078 |
| 6..... | 1.073 | 1.078 | 1.070 | 1.069 | 1.062 | 1.070 |

centage of phenol in each fraction was then calculated from the oxygen absorption of pure phenol and the oxygen absorption of the cresol, etc., in that fraction as given in Table VII. In Table VIII comparison is made of the percentages of phenol found in the materials A, B, C, D and E.

(1) By direct matching of the fractions.

(2) By calculation, as described, from the mean oxygen absorptions of the cresols, etc., in the respective fraction.

These results are not, of course, independent, as the results in the second case also depend on the matching experiments, but the result indicates how far the mean oxygen absorption of the cresols, etc., in the fractions may be regarded as fixed points, thus avoiding the necessity for the tedious matching experiments in each case dealt with.

TABLE VIII—PERCENTAGES PHENOL

| Material | By Direct Matching | By Calculation |
|----------|--------------------|----------------|
| A..... | 30.0 | 30.0 |
| B..... | 27.7 | 28.0 |
| C..... | 44.0 | 43.9 |
| D..... | 20.5 | 20.7 |
| E..... | 24.6 | 24.5 |

SOURCES OF ERROR IN THE PRECEDING WORK

1—It has been noted that in the case of the higher boiling fractions better matches were obtained when mixtures were made up having slightly higher oxygen absorption than the fractions to be matched, and it was pointed out that this was probably due to increasing amounts of higher boiling bodies in these fractions. It would undoubtedly have been better to have taken some of this higher boiling material as well as phenol and the cresols in the matching experiments.

2—It was found after the method had been in use for some time that in practically all experiments with crudes a disturbing factor was present in the form of small amounts of pyridine.

3—It was further observed that crude carbolic acid tenaciously retains small amounts of dissolved sodium phenate when water is also present. Thus water is much more soluble in crude-tar acids in presence of sodium phenate, and, on the other hand, sodium phenate is considerably soluble in tar acids in presence of water. This sodium phenate remains in the distilling flask when the mixture is distilled. It was found necessary to treat the crude carbolic acid with successive washes of dilute sulfuric acid, followed by washes of water to remove pyridine and decompose the dissolved sodium phenate. The tar acids in the acid and water washes were recovered and returned to the bulk.

When these disturbing factors were discovered, time was not available to repeat the work herein recorded, but the effects were partially eliminated by using the constants already determined on a series of synthetic mixtures with known amounts of phenol

and varying and known amounts of the cresols and higher boiling bodies. In that way a correction was found to be applied to all results as so obtained.

The resulting corrections when plotted against the percentage of phenol found gave a smooth curve. Typical points from this curve are given in Table IX.

TABLE IX

| Per cent Phenol Taken..... | 10.00 | 25.00 | 50.00 | 75.00 |
|----------------------------|-------|-------|-------|-------|
| Found..... | 9.62 | 23.98 | 47.50 | 70.54 |
| Correction (per cent)..... | 0.38 | 1.02 | 2.50 | 4.46 |

Duplicate determinations when carried out with the precautions mentioned on the same sample of material gave results with a maximum variation of not more than about 0.2 to 0.3 per cent and with the above corrections applied were not very much farther than that from the truth.

OXYGEN ABSORPTION OF THE FRACTIONS OF TAR ACIDS FROM VARIOUS KINDS OF TAR

The method was also used to estimate the phenol in the tar acids from inclined retorts, vertical retorts, blast furnace creosote and producer gas tar. In Table X are quoted the oxygen absorption of the fractions of the second fractionation of these materials. The first column contains results already given which were largely for the material from horizontal retorts. With the exception of the first column the tar acids received the preliminary treatment with dilute sulfuric acid, and were further carefully freed from any neutral oils by conversion to phenate and extraction with benzene, with all necessary precautions to recover any phenol which was so washed out.

It will be seen that these oxygen absorptions all lie in much the same range.

TABLE X—OXYGEN ABSORPTION OF FRACTIONS

| No. | Horizontal | Inclined | Vertical | Blast | Producer |
|--------|------------|----------|----------|---------|----------|
| 1..... | 1.342 | (1.288) | ... | ... | ... |
| 2..... | 1.293 | 1.293 | (1.256) | ... | ... |
| 3..... | 1.233 | 1.244 | 1.243 | (1.198) | (1.187) |
| 4..... | 1.188 | 1.202 | 1.201 | 1.175 | 1.195 |
| 5..... | 1.133 | 1.155 | 1.152 | 1.123 | 1.128 |
| 6..... | 1.098 | 1.102 | 1.105 | 1.095 | 1.101 |

The figures given in parentheses were for very small fractions which could not be handled through the 12 bulbs.

REMARKS

It will be noted from the matching experiments that the fraction from 199 to 202° always contains definite and easily detectable percentages of phenol, but that in the fraction above 202° no phenol was ever detected. Weiss and Downs also distilled twice, but collected only two fractions, *viz.*, "to 190°" and "190 to 202°" on the first fractionation, while on the second they collected everything up to 197°. It seems certain that under these conditions some phenol must have been left in the distilling flask, while some of the higher boiling bodies must have inevitably appeared in the distillate.

Another point which is of interest in connection with the work of Weiss and Downs is to be found in the amount of *m*-cresol present. In the materials investigated by the author the amount of *m*-cresol in the fractions up to 202° was invariably far less than the amount of *o*-cresol or of *p*-cresol. Thus from the figures in Tables IV, V and VII the following

that about one liter of gas was taken into each sample in about one hour. The excess acid in *K* was titrated with $N/5$ alkali for the determination of the value of *a*. The gas in *K'* was displaced with oxygen into *H'*, noting the total volume of water drawn therefrom. The two tubes *H H'* were then detached and immersed in a large tank of water, a manometer attached and the temperature and pressure noted. The gas in *H'* was analyzed for nitrogen by absorbing the oxygen in alkaline pyrogallol. The composition of the air in *H* was taken as 79 per cent nitrogen. This furnished the data necessary for the calculation of the values *b* and *d*.

For determination of the value *c* the contents of *K''* were washed into a small Erlenmeyer flask and boiled for about 5 minutes, then thoroughly cooled and the excess alkali titrated with $N/5$ NaOH, methyl orange indicator and a companion flask. The nitrite present tended to destroy the indicator in acid solution, turning the color a permanent yellow, unaffected by either acids or alkalis. By taking care not to run over the end-point, noting the first change in shade from the color of the companion flask, this titration was accurate and satisfactory. The boiling and cooling was found to be absolutely necessary in order to recognize the end-point at all. Carpenter¹ condemned the alkali H_2O_2 reagent for absorbing nitrous gases on account of the difficulty

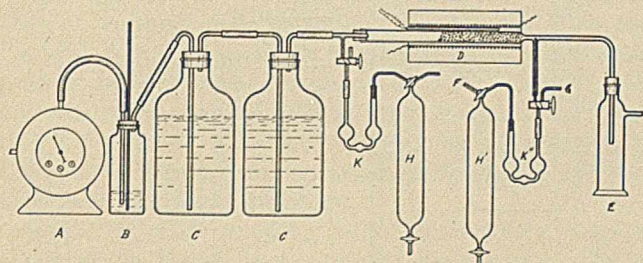


FIG. I.—ANALYTICAL CONTROL OF AMMONIA OXIDATION

of the end-point and proposed the use of a solution of hydrogen peroxide alone, but we have not found it as efficient as the alkali, when the gas is bubbled through it.

When methyl red or sodium alizarine sulfonate is used as an indicator, the boiling is not necessary, both indicators working fairly well in the presence of nitrites. Sodium alizarine sulfonate is rather the better indicator to use, being more sensitive. Methyl red is destroyed to some extent by the nitrite but the end-point is sufficiently sharp even when $N/10$ solutions are used.

Since no appreciable ammonia escaped oxidation in tests where this method was used, the value of *f* is zero. The absorption of the acid in *K''* was practically complete. The water drawn from *H'* was never acid and that remaining in the tube was titrated after shaking when especial accuracy was required. This rarely increased the value of *c* more than one per cent.

METHOD II—This method was essentially the same as Method I, except that the nitrogen-oxygen mixture, after absorption of the acid, was drawn over hot copper to remove the oxygen, thus eliminating the analysis of the gas collected in *H'*. A small Meyer sulfur bulb was used as an absorber and a 4-liter aspirator bottle substituted for *H'*, Fig. I.

¹ "Note on Some Condition Affecting the Oxidation of Nitrous Acid to Nitric Acid." *J. Soc. Chem. Ind.*, 5 (1886), 287.

The above methods were especially useful in small scale experiments where sampling into evacuated bottles as described below would have seriously interfered with the constancy of the gas flow through the catalyzer tube.

METHOD III—For larger scale experiments samples taken into evacuated bottles have been found convenient. This is the only method permitting determination of the ammonia escaping oxidation, *f*. Bottles of known volume, 1 to 2.5 liters capacity, were provided with single capillary stopcocks and evacuated to less than 2 mm. pressure. Ground glass stoppers were more satisfactory but soft rubber stoppers served well enough when the samples were drawn immediately after evacuating.

Sufficient $N/5$ H_2SO_4 was admitted to the ammonia sample and a measured volume of water, after absorbing the ammonia, until the residual air was at atmospheric pressure.

Enough condensation occurred in the acid sample to permit sucking in a measured volume of water containing hydrogen peroxide to absorb the acid fumes. The volume of the bottle minus that of solution introduced gave the volume of the oxygen-nitrogen gas which, together with its analysis, furnished the necessary data for calculating the free nitrogen. The acid solution was titrated with $N/5$ NaOH for free acid and then distilled with caustic into $N/5$ H_2SO_4 for determination of ammonia *f*. Since this ammonia was present as nitrate, its equivalent was added to the free acid already found for the calculation of *c*. While this method requires rather more manipulative skill than the average works chemist possesses, the authors consider it the best available and have used it quite extensively for control work with very satisfactory results. Duplicate determinations on samples taken at the same instant should agree within 1 per cent, but in practice agreement so close will hardly be consistently obtained unless the gas flow is very uniform. It is desirable to check the analysis method and the standard solution used by the analysis of gas samples containing a known amount of nitric oxide. The NO required may be conveniently prepared by means of a nitrometer.

It is often desirable to know whether or not there has been a leak between the point where the NH_3 sample was taken and the point where the nitrous gases were sampled. To determine this it is only necessary to measure the amount of oxygen admitted to the sample of nitrous gases and use water to which a known amount of standard H_2O_2 has been added for absorption. All the combined nitrogen in the sample will now be present as nitric acid. After the excess oxygen gas has been determined the liquid is divided into two parts. In one part the acid is determined by titration with standard alkali and in the other part the excess H_2O_2 is determined by titration with permanganate. The oxygen used is now known and the amount required for the oxidation of the ammonia converted may be calculated, any excess being due to leakage. Obviously, the yield may be calculated from a knowledge of the relation of combined nitrogen to oxygen in both the NH_3 air sample and the sample of nitrous gas. A few such calculations

were made with results agreeing fairly well with those by the regular method of calculation.

The vacuum method offers a convenient means of following the reactions in an absorption system; for example, it is a simple matter to determine the efficiency of a given tower by sampling and analyzing the gas on both sides of it. Ordinarily the leakage will not be great enough to interfere.

OTHER METHODS—Analysis of the ammonia-air intake gas may be made by ordinary gas analysis methods by taking proper precautions. In common gas analysis practice it is customary to make all volume readings with the gas saturated with water vapor. When mercury is used as a confining liquid, the walls of the burette are always kept wet. This precaution is essential because of the very different vapor pressures of the solutions used as selective absorbents.

In dealing with ammonia gas it is obviously necessary to have the walls of the burette dry and to absorb the ammonia in a reagent whose vapor tension is equal to the partial pressure of the water vapor in the sample. Now this result is accomplished if the gas is thoroughly dried and the absorption made in a reagent whose vapor tension is practically zero.

The apparatus employed consisted of a special bulb form of compensated burette with graduations extending from 140 to 165 cc., easily readable to ± 0.02 cc. Clean, dry mercury was used as a confining liquid and the ammonia was absorbed in concentrated sulfuric acid. The sample was introduced into the burette through a U-tube filled with pieces of solid potassium hydroxide, which thoroughly dried it.

This method proved very satisfactory in practice, and checked the vacuum bottle method. Its advantages are ease of manipulation and simplifying of the calculation, since no temperature or barometer observations are required and no titrations are made. The calculation follows:

$$a = \text{contraction in volume of the sample}$$

$$b = \text{volume after contraction} \times 0.79 \times 2.$$

An equally simple method suggested itself for analysis of the nitrous gases. It was thought that a sample of the nitrous gases drawn into a nitrometer containing mercury and sulfuric acid, and then shaken, would convert all the nitrogen oxides to NO and cause the excess oxygen to disappear. Analysis of the remaining mixture of nitrogen and nitric oxide would give the values for *c* and *d* in volumes as in the burette method for the NH_3 -air mixture.

In experiments with this method it was found that a concentrated solution of chromic acid¹ rapidly absorbed NO and effected quantitative separation of this gas from artificially prepared mixtures of nitrogen and nitric oxide. When the method was applied to the nitrous gases the results were always low. A series of experiments was then made by introducing a measured volume of air into the decomposition bulb of a duPont nitrometer and adding a known quantity of nitric acid dissolved in concentrated sulfuric acid. After shaking several minutes the residual gas was measured, transferred to a gas analysis burette and the NO absorbed

by passing into a pipette containing the chromic acid reagent. Mercury was used as a confining liquid and the walls of the burette were kept wet. The results in every case showed that the residual gas measured corresponded to that calculated, assuming disappearance of the oxygen in the volume of air used and evolution of nitric oxide from the nitric acid introduced. However, analysis of this gas always showed a considerably less percentage of NO than that calculated as well as a small amount of oxygen as determined by absorption in alkaline pyrogallol. Evolution of the NO in the nitrometer bulb in the presence of nitrogen instead of air gave more nearly the correct percentage of NO in the residual gas. In view of these results the nitrometer method appeared unavailable.

A second method for eliminating titrations was devised. Fig II shows the essential details of the apparatus. The ammonia air sample is drawn into the gas burette (2) through the drying tube (1) containing pieces of solid potassium hydroxide. Burette (2) is provided with a right angle two-way stopcock at the top and a leveling tube below not shown in figure. It is filled with

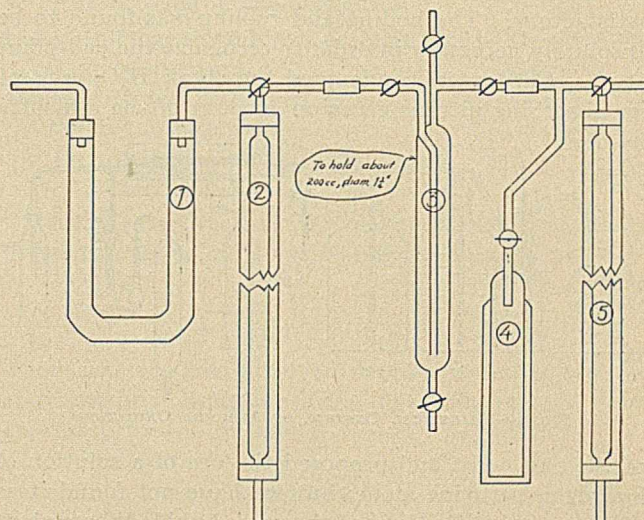


FIG. II—ANALYTICAL CONTROL OF AMMONIA OXIDATION

dry mercury. Bulb (3) is detached from the apparatus and completely filled with water containing hydrogen peroxide and indicator.¹ A small leveling bottle is attached by means of a flexible rubber tube at the bottom. About 10 cc. of pure oxygen, which need not be measured, are introduced into the bulb through one branch of the T tube. The nitrous gases are then drawn from the oxidizer into the bulb through the same tube by allowing 70 to 80 cc. of water to run out into the leveling bottle. This can be done without loss of acid since the indicator shows plainly the diffusion of any acid through the water while the sample is being taken. The bulb is then shaken until all the nitrogen oxides are absorbed. It is then restored to its position (Fig. II) and the residual gas transferred to the mercury-filled burette (5). The walls of this burette are kept wet. The gas is now passed into alkaline pyrogallol in the Williams pipette (4), the residual nitrogen brought back into the burette and measured. This volume is called *d*, and is discarded. The ammonia sample in (2) is

¹ Bohmer. *Z. anal. Chem.*, 21 (1882), 212.

¹ Methyl red or sodium alizarine sulfonate.

now bubbled slowly into the acid liquid in (3) until neutral, noting the volume required. The air from (3) is measured in burette (5) and this volume multiplied by 0.79 corresponds to the nitrogen volume b .

In calculating the yield by the general formula

$$\frac{c(a+b)}{a(c+d+f)}$$

neglecting f , since by the above procedure a and c are equal, we have

$$\frac{a+b}{a+d}$$

The volume of dry gas introduced from (2) into (3) corrected to moisture saturation, minus the volume of air measured, gives the volume of ammonia. This volume must be divided by two to obtain the corresponding volume of nitrogen, a , to be applied in the formula. When the yield is known to be in the neighborhood of 90 per cent approximate results may be obtained by simple division of the measured nitrogen volumes, *i. e.*, b/d .

While the method has not been thoroughly tested experimentally, it is presented here because the principle involved offers possibilities for development of a rapid method of works control.

DISCUSSION

It was realized at the beginning of this investigation that no method of determining the efficiency of an industrial process appeals to a manufacturer more than pounds put in to pounds taken out. In order to put our analytical results upon an unquestionable foundation, the method was checked by experiments in which the ammonia input was determined by weight and the total acid produced absorbed.

These experiments were carried out as follows: two tared flasks containing a known weight of carefully analyzed ammonia solution were connected in series so that air could be blown through them, the air-ammonia mixture passing over a catalyzer in a glass tube. The acid gases were absorbed in a series of wash bottles containing water and finally in the last ones 10 per cent NaOH solution. The ammonia was determined by weighing the flasks and re-analyzing; the acid, by titrating the HNO₃ absorbed in the water and analyzing the alkaline solutions for nitrate and nitrite. Although the absorption system was quite elaborate some acid passed through unabsorbed. This was estimated by frequent samples of the issuing gas. Method II was used for checking the above outlined procedure because the time in drawing the samples could be made to coincide more nearly with the length of the run. The results follow:

| Time | Condi- tions | Liters Air Room Taken | Grams NH ₃ | GRAMS | | | Grams Total HNO ₃ | PER CENT | |
|------|-----------------|--------------------------------|--------------------------|------------------|--|------------------------------|------------------------------------|---------------|---------------------|
| | | | | Water Bottles | —HNO ₃ RECOVERED— Alkali as Nitrate | End Loss from Train | | By Weights | By Analy- sis |
| 144 | 200 | 10.82 | 24.40 | 1.40 | 4.90 | 0.90 | 31.60 | 79.0 | 82.5 |
| 180 | 270 | 13.44 | 33.00 | 1.40 | 6.80 | 1.05 | 42.25 | 85.1 | 87.0 |
| 172 | 187 | 8.74 | 22.70 | 0.60 | 3.15 | 0.60 | 27.05 | 83.8 | 85.5 |

There is no doubt in our minds that the analysis method gives the true efficiency of conversion. The complete absorption of the acid gases was exceedingly difficult and losses undoubtedly occurred through leaks at rubber connections. These facts account for the

slightly lower results of the total absorption method. Had we cared to elaborate the train, no doubt all the acid could have been absorbed and the agreement would have been better.

In a recently published article Fox¹ has raised the question of possible oxidation of ammonia to ammonium nitrite by hydrogen peroxide. This point was carefully tested in a number of experiments and no evidence secured of any such oxidation in significant quantity under the conditions obtaining in the above outlined procedures. The following experiment seems to be conclusive.

A sample of the nitrose gases was drawn into a 2-liter evacuated bottle from an experimental converter running at low velocity so that no unchanged ammonia passed the catalyzer. A solution containing 40 cc. *N/5* NaOH, 15 cc. 3 per cent hydrogen peroxide and 3.5 cc. *N/5* NH₄OH was introduced into the bottle immediately, followed by 100 cc. distilled water. The NaOH was in excess of that needed to neutralize the acid present. After vigorous shaking the bottle was allowed to stand several minutes. Then an excess of *N/1* H₂SO₄ was added to fix the ammonia. The contents of the bottle were transferred to a Kjeldahl distillation apparatus, made alkaline with NaOH, and the ammonia distilled into *N/5* acid. Exactly that amount of ammonia taken was recovered. No ammonia was oxidized.

We have further evidence pointing to the *fact* that under the conditions of analysis the use of H₂O₂ in alkaline solution does not affect the accuracy of the results by oxidation of NH₃ to nitrite.

Two chemists using the vacuum method described above made a number of analyses of parallel samples, one using alkali with H₂O₂ and the other using water with H₂O₂ for absorbing the nitrous gases. The results agreed very well, showing that there could not have been appreciable oxidation of NH₃ by H₂O₂ in alkaline solutions.

Moreover, Hoppe-Seyler² found no evidence of oxidation of ammonia in solutions of ammonia, or ammonium carbonate, or when a fixed alkali was present, by dilute hydrogen peroxide on 24 hrs. standing. It was necessary to concentrate such solutions by evaporation to small volume before nitrite could be detected by colorimetric methods. The statements of Schönbein, Weith, and Weber³ are not to be taken to mean that ammonia is oxidized by hydrogen peroxide "abundantly" under all conditions.

Fox's,⁴ analytical method is based on the assumption that NO in the presence of an excess of oxygen reacts immediately to NO₂ (or N₂O₄). It has been shown by a number of investigations⁵ that the reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ occurs in measurable time and that a mixture of NO₂ and NO behaves toward alkali as N₂O₃, being rapidly absorbed as nitrite. In Fox's method all the acid would be absorbed but it is

¹ THIS JOURNAL, 9 (1917), 737-43.

² *Ber.*, 16 (1883), 1917-24.

³ *Ibid.*, 7 (1874), 1745.

⁴ *Loc. cit.*

⁵ Holwech, *Z. angew. Chem.*, 21 (1908), 2131; Le Blanc, *Z. Elek.*, 12 (1906), 541; Foerster and Koch, *Z. angew. Chem.*, 21 (1908), 2161 and 2209; Foerster and Blich, *Ibid.*, 23 (1910), 2017.

extremely doubtful that the NO could go completely to NO₂ in his apparatus, in which case results calculated by the formula given would be too low.

ACKNOWLEDGMENTS

The authors have had valuable assistance, in the work on which this paper is based, from Lieut. G. A. Perley, Mr. J. H. Capps, and Mr. L. R. Lenhart; Mr. A. S. Coolidge performed many of the experiments in trying out the nitrometer method.

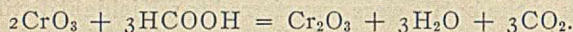
BUREAU OF MINES
WASHINGTON, D. C.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF FORMIC ACID OR FORMATES IN THE PRESENCE OF HYDROXIDES, CARBONATES, OXALATES AND ACETATES

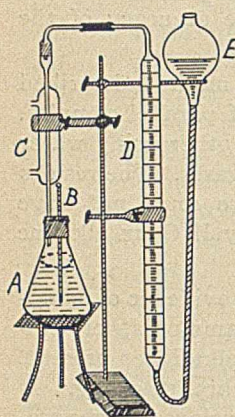
By F. TSIROPINAS

Received August 16, 1917.

This method is based upon the well-known fact that formic acid is quantitatively oxidized to carbon dioxide by chromic acid in boiling solution, and that therefore every 44 parts by weight of carbon dioxide correspond to 46 parts of formic acid according to the equation,



APPARATUS—The accompanying sketch shows the arrangement of the apparatus used: *A* is an Erlenmeyer flask of resistant glass with a capacity of about 500 cc.; *B* is a thermometer for the control of the temperature of the contents of the flask; *C* is a 15-in.



Liebig reflux condenser, for the condensation of the vapors produced during the boiling of the liquid and is connected by means of a glass tube and heavy rubber tubing to *D*, the gas collector. The latter consists of a glass tube, about 1.5 in. in diameter, having a capacity of approximately 600 cc. and is graduated in cc.'s; connected to this gas collector by means of a rubber tube is the reservoir *E*, by means of which the air in the collector may be discharged and the water level

obtained, when the CO₂ gas has been collected in the graduated tube. To prevent the absorption of gas by the water used for leveling purposes, a 1-in. layer of paraffin oil is floated upon the surface.

REAGENT—50 g. of C. P. sodium bichromate are dissolved in 500 cc. of distilled water, 80 cc. of C. P. concentrated sulfuric acid added and the liquid boiled for 5 minutes to expel all dissolved gases; then it is allowed to cool to room temperature.

PROCEDURE (1)—In the absence of other substances which give CO₂ when boiled with chromic acid, the procedure is as follows: A solution is prepared, so that 50 cc. of the same will contain from 0.5 to 1.0 g. of formic acid; 50 cc. of this solution are emptied by means of a pipette into the clean Erlenmeyer flask and if alkaline, 2 to 3 drops of methyl orange are added, and the solution made acid with dilute sulfuric acid (1 : 1); 400 cc. of the chromate solution are now

added and the flask attached to the condenser; the stopper at the top of the condenser is removed and the reservoir raised until the graduated tube is filled to the zero mark. The stopper is now firmly replaced and a reading is made upon the graduated tube for correction of the air displaced by the stopper. The reservoir is then lowered and observation is made to assure that the apparatus is air-tight. If no leakage is observed, the reservoir is again raised to a level slightly below that of the liquid in the collector, the cooling water turned on, and the contents of the flask are heated to boiling. As the gas collects, the reservoir is lowered from time to time so that atmospheric pressure is maintained. The boiling is continued until the volume of the gas is practically constant, which requires from 15 to 20 minutes. The flame is now removed and the flask placed in a water bath and cooled until the temperature is reduced to that at which the operation was started; the reservoir is brought to the same level as the liquid in the collector and the volume of the gas noted. A correction is made for the air displaced by the stopper at the beginning of the operation and atmospheric pressure and room temperature are recorded. The volume of the gas must now be reduced to normal barometric pressure and a temperature of 0° C. according to the following well-known formula,

$$V_1 = \frac{V(C - h)}{760(1 + at)}$$

where V_1 = reduced volume, V = volume actually found, C = barometric pressure, h = tension of water vapor at temperature t , $a = 0.00366$, and t = room temperature.

Taking the results of Guye, the weight of 1 cc. of CO₂ gas at 760 mm. and at 0° C. is 0.0019768 g. Therefore, the number of cc. multiplied by 0.0019768 gives the weight of carbonic acid gas generated. This result calculated to 100 g. of material and multiplied by 46/44, or 1.04545, will give the percentage of formic acid.

Trial experiments with known quantities of C. P. sodium formate (recrystallized from alcohol) gave the following results:

(0.5 Gram Sodium Formate Used in Each Case)

| Temp. ° C. | Pressure Mm. | Cc. of CO ₂ | | Difference Gram |
|------------|--------------|------------------------|--------------|-----------------|
| | | GENERATED Actual | HCOONa Found | |
| 25° C. | 747 | 187 | 163.1 | 0.4988 |
| 21° C. | 743 | 185 | 163.7 | 0.5001 |
| 26° C. | 743 | 188 | 162.2 | 0.4955 |
| 27° C. | 743 | 190 | 163.0 | 0.4979 |

PROCEDURE (2)—In the presence of carbonates, bicarbonates, oxalates and acetates, the following procedure is to be followed: take sufficient material that the formic acid content will range between 2.5 and 5.0 g. Dissolve in 50 cc. of water, boil a few minutes, make alkaline with NaOH if bicarbonates are present and add a 10 per cent solution of calcium chloride in sufficient quantity to precipitate all of the carbonates and oxalates. Allow the precipitate to settle, filter into a 250 cc. graduated flask, wash thoroughly with boiling water, cool to room temperature and fill to the mark. Take 50 cc. of the filtrate and proceed as directed under Procedure (1). Trial experiments with known quantities of C. P. sodium formate mixed with

different quantities of sodium carbonate, oxalate and acetate (which is not oxidized by the chromate solution) gave the following results:

| Temp. ° C. | Pressure Mm. | Cc. OF CO ₂ GENERATED | | Difference Gram | |
|--------------|--------------|----------------------------------|-----------|-----------------|---------|
| | | Actual | Corrected | | |
| 22° C. | 739 | 186 | 162.9 | 0.4976 | -0.0024 |
| 25° C. | 739 | 188 | 162.2 | 0.4955 | -0.0045 |
| 18° C. | 737 | 184 | 163.9 | 0.5005 | +0.0005 |
| 18° C. | 737 | 183 | 163.0 | 0.4979 | -0.0021 |
| 28° C. | 748 | 190 | 163.2 | 0.4985 | -0.0015 |
| 27° C. | 748 | 189 | 163.3 | 0.4989 | -0.0011 |
| 16° C. | 746 | 180 | 163.8 | 0.5004 | +0.0004 |
| 20° C. | 746 | 183 | 163.4 | 0.4974 | -0.0026 |
| Average..... | | | | 0.4982 | |

SUMMARY

I—From the above results it can be seen that this method is an accurate and reliable one for the technical determination of formic acid or formates in the presence of carbonates, oxalates and acetates.

II—An added advantage is that the time required for an analysis does not exceed one hour and, furthermore, it requires but little attention; and preparations for subsequent determinations can be made during the intervening time.

NOTE—Thorpe in his "Dictionary of Applied Chemistry" calls attention to a method devised by Rupp and published in the *Archiv. der Pharmazie*, 243, 69 for the determination of formates. Rupp uses sodium hypobromite as the oxidizing agent and not potassium bichromate, as stated by Thorpe.

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A STUDY OF THE ESTIMATION OF FAT IN CONDENSED MILK AND MILK POWDERS¹

By C. H. BIESTERFELD AND O. L. EVENSON

It was found by Röse² that, if whole milk was treated with ammonia and alcohol, the casein was dissolved to such an extent that the fat could be removed quantitatively by a mixture of equal volumes of ethyl and petroleum ethers. Subsequently, E. Gottlieb³ failed to corroborate the results of Röse, but found that if he extracted, after the treatment with ammonia and alcohol, first with ethyl ether and then with petroleum ether, he was able to obtain more accurate results than he could by the procedure outlined by Röse. Harding and Parkin⁴ claim that results from the application of the Röse-Gottlieb procedure to evaporated milk or milk powders show that the fat is not completely extracted. For the fat determination in evaporated milk they proposed to dissolve the protein in acetic acid and the fat in a mixture of alcohol and carbon tetrachloride before extracting the fat with petroleum ether. During shaking and centrifuging, rubber stoppers were used in contact with the solvents. The action of the solvents on the rubber stoppers would seem to be the cause of the higher results obtained by Harding and Parkin when the fat was extracted by the procedure

¹ Published by permission of the Secretary of Agriculture. Presented at the 54th Meeting of the American Chemical Society in Kansas City, Mo., April 10 to 14, 1917.

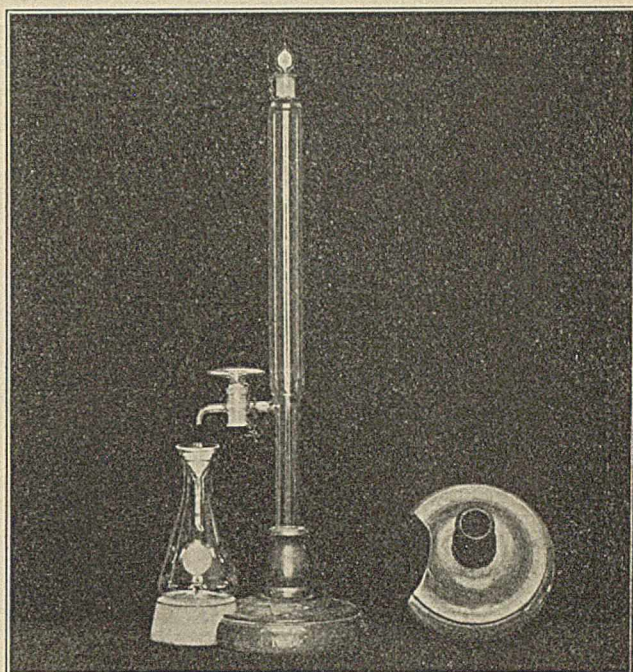
² *Z. angew. Chem.*, 1888, 100.

³ *Landw. Ver.-Sta.*, 40 (1892), 1.

⁴ *THIS JOURNAL*, 5 (1913), 131.

they outline rather than when it was extracted by the Röse-Gottlieb method. O. Laxa's¹ work on separator slime indicates that a small amount of fat adheres tenaciously to the protein. It would probably adhere none the less tenaciously in evaporated milk or milk powder. The presence of free fatty acids would not be expected in any appreciable quantity in condensed milk, but milk powder, on account of its tendency to develop rancidity, might have appreciable quantities, as shown by Eccher.² Hence, the Röse-Gottlieb method, which extracts only neutral fats, might fail to show the original fat content of the powder. Hunziker³ used dilute acetic acid to dissolve casein in condensed milk before extracting the fat with ether. It has been shown⁴ that acetic acid does not react chemically with butter fat.

In the work recorded here, the errors in the Röse-



MODIFIED RÖHRIG TUBE (Biesterfeld)

Height of tube, over all (not including stopper), 37 cm., about.
Narrow part (below spigot), 19 mm. outside diameter.
Capacity of narrow part, to middle line of spigot, 28 cc.
Upper part (above spigot), 27 mm. outside diameter.
Tube must have a tight-fitting glass stopper.
No vent hole in neck. No graduations.

Gottlieb⁵ method have been studied and the method compared directly with a modified method in which a small amount of acetic acid as an aid in separating the fat from the casein, mixtures of petroleum ether, ethyl ether and ethyl alcohol (which are recoverable for repeated use) and a modified Röhric tube, have been used.

The two mixtures, which must be kept separate, are used as solvents. The proportions for Mixture 1 are 400 cc. of petroleum ether, 200 cc. of ethyl ether and 20 cc. of 95 per cent ethyl alcohol. For Mixture 2 the

¹ *Milchwirtschaft. Zentr.*, 42 (1913), 691.

² *Arch. Chem. Mikros.*, 6 (1913), 302.

³ Purdue Univ. Agri. Expt. Station, *Bulletin* 134 (1909).

⁴ Bahlman, *THIS JOURNAL*, 7 (1915), 680.

⁵ U. S. Dept. of Agriculture, Bureau of Chemistry, *Circular* 66 (1911).

proportions are 350 cc. of petroleum ether, 280 cc. of ethyl ether and 63 cc. of 95 per cent ethyl alcohol. The ethyl ether of commerce was washed with water, and the petroleum ether redistilled slowly and the portion boiling below 65° C. was reserved for this work.

A larger tube than Röhrig's¹ is necessary because the amount of alcohol used is so much greater than has been used previously. A modification devised by Mr. Biesterfeld is shown in the accompanying photograph. Its large capacity permits vigorous and rapid mixing and affords sufficient volume for the ethers to boil quietly during the heating with little danger of mechanical loss. It may also be adapted to the Röse-Gottlieb method by increasing proportionately the quantities in that method.

To recover the ethers and use them again separately would require laborious fractionation. Mixed ethers cannot very well be used with the Röse-Gottlieb proportions, as extraction is incomplete, due to the lack of sufficient alcohol. The problem here is to obtain a

proportion in which the two are mixed. Practically, however, the mixtures prepared in the quantities stated have been used, as described below, until a volume of 50 cc. remained and such a disturbance in proportions, if it has occurred, has not produced any observed differences in the final results.

In a Biesterfeld tube, 4 to 4.5 g. of evaporated milk, or 7 to 7.5 g. of a 40 per cent emulsion of sweetened condensed milk, were diluted to a volume of 9 cc. with water and, after mixing with 1.5 cc. of concentrated ammonium hydroxide, 15 cc. of 95 per cent alcohol were added and the whole mixed again. It was then shaken vigorously for two minutes with 50 cc. of Mixture 1. After standing for 10 min. the ethers were filtered through a 4 cm. Dreverhoff No. 86 fat-free filter paper into a 100 cc. Erlenmeyer flask, previously dried and weighed with a similar flask as counterpoise. The tip of the spigot and the paper were washed with a few cc. of Mixture 1 and the funnel with the paper set aside for future use. The ethers were distilled on a hot plate, using cork stoppers

TABLE I—FAT EXTRACTION
SWEETENED CONDENSED MILK

| "SOLVENTS RECOVERED" METHOD | | RÖSE-GOTTLIEB METHOD | | Difference Per cent Fat |
|-----------------------------|--------------|----------------------|---------------------------|-------------------------|
| Weight Taken Grams | Per cent Fat | Weight Taken Grams | Ex-tractions Per cent Fat | |
| 7.2550 | 10.05 | 10.7731 | 3 10.01 | +0.04 |
| 7.4945 | 10.45 | 10.6182 | 3 10.40 | +0.05 |
| 7.5570 | 7.94 | 10.9948 | 3 7.88 | +0.06 |
| 7.6284 | 9.47 | 10.5559 | 3 9.45 | +0.02 |
| 7.9267 | 7.95 | 10.7370 | 3 7.90 | +0.05 |
| 6.7503 | 10.20 | 10.6095 | 3 10.18 | +0.02 |
| 7.1397 | 10.32 | 10.6489 | 3 10.26 | +0.06 |
| 7.2141 | 10.04 | 10.6880 | .. 9.97 | +0.07 |
| 7.0509 | 10.68 | 10.9410 | 6 10.68 | ±0.00 |
| 6.9584 | 10.03 | 10.6125 | 3 9.97 | +0.06 |
| 7.0508 | 10.22 | 10.7829 | 6 10.25 | -0.03 |
| 7.3238 | 8.21 | 10.8739 | 3 8.15 | +0.06 |
| 7.5140 | 9.94 | 10.8006 | .. 9.91 | +0.03 |
| 7.3009 | 9.13 | 10.7248 | 3 9.12 | +0.01 |
| 7.3343 | 9.00 | 10.6195 | 3 8.96 | +0.04 |
| 7.2240 | 9.64 | 10.2432 | 3 9.53 | +0.11 |
| 7.9940 | 8.00 | 10.8825 | 3 7.93 | +0.07 |
| Average, +0.04 | | | | |

TABLE II—FAT EXTRACTION
UNSWEETENED CONDENSED MILK

| "SOLVENTS RECOVERED" METHOD | | RÖSE-GOTTLIEB METHOD (3 Extractions) | | Difference Per cent Fat |
|-----------------------------|--------------|--------------------------------------|--------------|-------------------------|
| Weight Taken Grams | Per cent Fat | Weight Taken Grams | Per cent Fat | |
| 4.2443 | 8.01 | 4.4234 | 7.99 | +0.02 |
| 4.4698 | 7.98 | 4.2455 | 7.98 | +0.00 |
| 4.5526 | 8.07 | 4.4469 | 8.02 | +0.05 |
| 4.2029 | 9.05 | 4.2110 | 9.02 | +0.03 |
| 4.0204 | 7.97 | 4.1455 | 7.92 | +0.05 |
| 4.4006 | 7.56 | 4.5140 | 7.51 | +0.05 |
| 4.5701 | 6.78 | 4.5376 | 6.77 | +0.01 |
| 4.2514 | 8.05 | 4.3135 | 7.97 | +0.08 |
| 4.6008 | 7.92 | 4.5975 | 7.88 | +0.04 |
| 4.6910 | 7.89 | 4.7650 | 7.87 | +0.02 |
| 4.6818 | 8.06 | 4.4123 | 8.01 | +0.05 |
| 4.4807 | 8.30 | 4.5186 | 8.27 | +0.03 |
| 4.1328 | 8.29 | 4.6730 | 8.23 | +0.06 |
| 4.1293 | 8.26 | 4.3654 | 8.23 | +0.03 |
| 4.6575 | 7.50 | 4.7469 | 7.44 | +0.06 |
| 4.1668 | 7.89 | 4.1738 | 7.83 | +0.06 |
| 4.6525 | 8.09 | 4.5167 | 8.06 | +0.03 |
| 4.0960 | 8.40 | 4.6118 | 8.34 | +0.06 |
| 4.0236 | 8.12 | 4.3327 | 8.08 | +0.04 |
| 4.1875 | 8.45 | 4.2732 | 8.42 | +0.03 |
| Average, +0.04 | | | | |

TABLE III—FAT EXTRACTION
OLD CONDENSED MILK

| Residual Fat Obtained from Old Condensed Milk by Acetic Acid Treatment after 3 or more Röse-Gottlieb Extractions | | RESIDUAL FAT EXTRACTED BY ACETIC ACID TREATMENT | |
|--|---------------------------|---|----------|
| Weight Taken Grams | Röse-Gottlieb Extractions | Gram | Per cent |
| 4.6815 | 3 | 0.0053 | +0.11 |
| 5.2980 | 3 | 0.0030 | +0.06 |
| 5.3470 | 3 | 0.0018 | +0.03 |
| 5.0120 | 3 | 0.0025 | +0.05 |
| 4.7290 | 3 | 0.0021 | +0.04 |
| 5.4065 | 3 | 0.0032 | +0.06 |
| 5.8110 | 3 | 0.0021 | +0.03 |
| 5.4350 | 3 | 0.0038 | +0.07 |
| 4.7598 | 6 | 0.0012 | +0.02 |
| 4.0000 | 4 | 0.0017 | +0.04 |
| 5.0000 | 4 | 0.0026 | +0.05 |
| 4.3000 | 3 | 0.0021 | +0.05 |
| 4.4627 | 3 | 0.0027 | +0.06 |
| 5.4285 | 3 | 0.0021 | +0.04 |
| 10.3950(a) | 3 | 0.0018 | +0.04 |
| 10.1945(a) | 3 | 0.0007 | +0.02 |
| 9.8425(a) | 3 | 0.0019 | +0.05 |
| 9.5320(a) | 3 | 0.0021 | +0.05 |
| 9.6965(a) | 3 | 0.0021 | +0.05 |
| 9.8945(a) | 3 | 0.0022 | +0.05 |
| (a) Sweetened. Average, +0.048 | | | |

mixture of the two ethers and alcohol which will readily give a large percentage of pure fat in the first extraction. C. H. Biesterfeld found that by diluting the quantity of milk taken to 10.5 cc. with water and adding 1.5 cc. of ammonium hydroxide, as in the Röse-Gottlieb method, and increasing the alcohol to 15 cc., a mixture of equal parts of ethyl and petroleum ethers extracted fat very easily. A method was developed accordingly.

As the method was studied further it was found that in the sweetened condensed milk the extra alcohol tends to extract a small amount of impurity with the fat. Although a mixture of equal parts of the two ethers is to be preferred for the unsweetened condensed milk, the proportion of petroleum ether was increased in order to obtain a method applicable to the sweetened condensed milk as well.

Theoretically, it would appear that a mixture of ethyl and petroleum ethers should have a definite rate of solubility for the separate ethers, and hence, repeated use of a mixture of this kind should disturb the

covered with tin foil for connecting with the condensers, until approximately 4 cc. remained. The recovered ethers were returned to Bottle 1. The liquid in the tube was mixed with 3 cc. of glacial acetic acid. The tube, immersed in water at 60 to 65° by a wire so that the tip of the spigot was just above the water, was heated to 80° in about 10 min. The tube was removed and cooled in running water. It was then shaken vigorously for about 2 min. with 50 cc. of Mixture 2. After standing a few minutes the ethers were filtered through the reserved filter paper into an unweighed 100 cc. Erlenmeyer flask, distilled and returned to Bottle 2. This extraction was repeated with 50 cc. of Mixture 2 and the ethers filtered into the same unweighed flask. The tip of the spigot and filter paper were washed with Mixture 2 and the ethers distilled as before. This flask was freed from the residual liquid and acetic acid vapors and dried completely by heating on a steam bath while applying suction. The fat was then dissolved with 25 cc. of petroleum ether, using small quantities at a time, and filtered through the same filter as before

¹ Z. Nahr.-Genussm., 9 (1905), 531.

into the weighed flask containing the first extract. This petroleum ether was recovered and used again. The fat was dried at 100° to constant weight, weighing with the same counterpoise flask.

As the solvents were used repeatedly, the proportion of alcohol changed to such an extent that after a time the line of separation between the aqueous and ethereal liquids reached the spigot. When this occurred the solvent mixture in Bottle 1 or Bottle 2, as the case might be, was shaken with water in a separatory funnel. For each 50 cc. of mixed solvent, 2 cc. of water were used. A portion of the alcohol was removed in this manner.

A comparison of the results obtained by the method here described in which the solvents are recovered and the Röse-Gottlieb method is shown in Tables I and II. As may be seen from these tables the former method averages 0.4 per cent higher on both the sweetened and the unsweetened milk.

Some observations were then made on the Röse-Gottlieb method to ascertain if any residual fat remains after the third extraction, and the results obtained on different brands of milk are shown in Table III.

The residual fat was obtained by adding 3 cc. of concentrated acetic acid to the liquid remaining in the tube, heating for 10 min. near 80° and re-extracting with 15 cc. each of ethyl and petroleum ethers, as usual. The ethers were filtered through a fat-free filter paper into an unweighed flask, distilled and the flask freed from acetic acid vapors and dried completely. The fat was then dissolved out with petroleum ether and filtered into a weighed flask. This avoided the introduction of any impurity resulting from the acid treatment. The average residual fat obtained is nearly 0.05 per cent. These milks were old and some were not in good condition. In Table IV, however,

| "SOLVENTS RECOVERED" METHOD | | | | RÖSE-GOTTLIEB METHOD | | | | |
|-----------------------------|---------------|------|----------|------------------------|-----------------|--------|----------|----------|
| Weight of Sample Grams | FAT EXTRACTED | | | Weight of Sample Grams | RESIDUAL FAT | | | |
| | 1st | 2nd | Per cent | | (3 Extractions) | Weight | Per cent | Per cent |
| 4.1446 | 8.08 | 0.06 | 8.14 | 4.0207 | 8.16 | 0.0017 | 0.04 | 8.20 |
| 4.2962 | 8.13 | 0.02 | 8.15 | 4.1573 | 8.08 | 0.0025 | 0.06 | 8.14 |
| 4.2220 | 7.73 | 0.02 | 7.75 | 4.2198 | 7.71 | 0.0021 | 0.05 | 7.76 |
| 4.2188 | 7.74 | 0.03 | 7.77 | 4.1394 | 7.72 | 0.0018 | 0.04 | 7.76 |
| 4.2017 | 7.72 | 0.04 | 7.76 | 4.1977 | 7.71 | 0.0021 | 0.05 | 7.76 |
| 4.2760 | 8.19 | 0.03 | 8.22 | 4.2676 | 8.17 | 0.0010 | 0.02 | 8.19 |
| 4.1897 | 8.33 | .. | .. | 4.0924 | 8.30 | 0.0019 | 0.05 | 8.35 |
| 4.1050 | 7.73 | 0.03 | 7.76 | 4.2536 | 7.73 | 0.0014 | 0.03 | 7.76 |
| 4.1594 | 8.19 | 0.03 | 8.22 | 4.4424 | 8.18 | 0.0012 | 0.03 | 8.21 |
| 4.2054 | 8.34 | .. | .. | 4.2687 | 8.35 | 0.0010 | 0.02 | 8.37 |
| 7.9267(a) | 7.93 | 0.02 | 7.95 | 10.7370(a) | 7.90 | 0.0015 | 0.04 | 7.94 |
| 7.5570(a) | 7.93 | 0.01 | 7.94 | 10.9948(a) | 7.88 | 0.0022 | 0.05 | 7.93 |
| 7.9940(a) | 7.97 | 0.02 | 7.99 | 10.8825(a) | 7.93 | 0.0010 | 0.02 | 7.95 |
| .. | .. | .. | .. | 4.8694 | 8.10 | 0.0017 | 0.04 | .. |
| .. | .. | .. | .. | 4.2902 | 8.19 | 0.0032 | 0.08 | .. |
| .. | .. | .. | .. | 4.3810 | 6.71 | 0.0030 | 0.07 | .. |

(a) Sweetened.

Average, 0.04

is shown the residual fat obtained in like manner from milks in good condition. Here the average is 0.04 per cent. The results obtained by the method in which the solvents are recovered are also shown.

The per cent of fat recovered by the second extraction in presence of acid is here given separately to show that two extractions remove all but the last traces of fat.

The error of the Röse-Gottlieb method then, when applied to condensed milk, is small, the usual range being from 0.02 to 0.06 per cent. This residual fat may be recovered by an acid extraction in the same manner as described before.

In Table V are shown the results obtained with the two methods on different products. The powders used had been kept in the laboratory for several years. In the method in which the solvents are recovered, the weight of the powder taken was stirred with 1.5 cc.

TABLE V—RESULTS ON DIFFERENT PRODUCTS
"SOLVENTS RECOVERED" METHOD (3 Extractions) RÖSE-GOTTLIEB METHOD (3 Extractions)

| No. | SUBSTANCE | Per cent | | PER CENT FAT | | |
|-----|---------------------------------------|--------------|-------|--------------|------------|----------------|
| | | Charge Grams | Fat | Charge Grams | Reg. Meth. | Acid Extr. FAT |
| 1 | Lard..... | 0.1217 | 99.89 | 0.1329 | 96.26 | 3.68 99.94 |
| 2 | Condensed Milk + 2.3% Oleic Acid..... | 4.2041 | 10.65 | 4.1803 | 9.30 | 1.18 10.48 |
| 3 | Milk Powder*..... | 1.0000 | 11.72 | 1.0000* | 10.82 | 0.70 11.52 |
| 4 | Cereal Milk Powder..... | 1.0000 | 4.80 | 1.0000 | 4.50 | 0.26 4.76 |
| 5 | Milk Powder..... | 1.0000 | 2.56 | 1.0000 | 2.19 | 0.27 2.46 |
| 6 | Milk Powder..... | 1.0000 | 1.68 | 1.0000 | 1.53 | 0.24 1.77 |
| 7 | Cream..... | 2.1580 | 20.15 | 1.8807 | 20.08 | 0.13 20.21 |
| 8 | Cream..... | 2.2870 | 19.89 | 2.5005 | 19.76 | 0.12 19.88 |
| 9 | Cream..... | 1.8592 | 19.50 | 1.8488 | 19.31 | 0.14 19.45 |
| 10 | Cream..... | 2.9554 | 19.44 | 2.8740 | 19.30 | 0.10 19.40 |
| 11 | Cream..... | 1.4209 | 35.49 | 1.6219 | 35.20 | 0.28 35.48 |
| 12 | Cream..... | 1.4050 | 36.04 | 1.5011 | 36.00 | 0.23 36.23 |

* Four extractions.

of ammonium hydroxide and 8 cc. of water and digested on a steam bath until the casein was well softened before adding 15 cc. of alcohol and proceeding with the extraction. In the Röse-Gottlieb method the same procedure was followed, using 1.5 cc. of ammonium hydroxide, 9 cc. of water and 10 cc. of alcohol. The effect of free fatty acids is most plainly seen in Expt. 2 where oleic acid was added to condensed milk. Numbers 7 to 10, inclusive, are samples of manufactured cream made from condensed skimmed milk and butter. The results obtained on the powders as well as on the cream show that the Röse-Gottlieb method may fail to remove the fat quantitatively. The method in which the solvents are recovered appears to give higher results but a sufficiently large number of determinations have not yet been made to show that it may universally be applied to milk powder.

As a result of his work on the Harding-Parkin¹ method, Biesterfeld came to the conclusion that the higher results obtained with this method were due to the use of rubber stoppers in contact with the solvents. In Table VI data are given showing the effect of using rubber stoppers.

TABLE VI—SHOWING THE EFFECT OF USING RUBBER STOPPERS IN THE HARDING-PARKIN METHOD

| No. | Method:..... HARDING-PARKIN | | RÖSE-GOTTLIEB | |
|--------|-----------------------------|--------------|---------------|--------------|
| | Sample (g.) | Fat Per cent | Sample (g.) | Fat Per cent |
| 1..... | 2.0458 | 8.14 | 6.2530 | 7.88 |
| 2..... | 2.1077 | 8.11 | 5.0940 | 7.88 |
| 3..... | 1.6810 | 7.96 | 5.0462 | 7.89 |
| 4..... | 1.6020(a) | 7.72(a) | 5.4000 | 7.78 |
| | 1.5850(b) | 7.92 | 5.0820 | 7.78 |

(a) Without rubber stoppers.

(b) With rubber stoppers.

With the last sample the Harding-Parkin procedure was conducted with and without rubber stoppers. It is believed that the great difference in results obtained by the two methods as reported by Harding and Parkin is to be explained by the error arising from the use of rubber stoppers.

¹ Loc. cit.

SUMMARY

I—The error of the R6se-Gottlieb method as applied to condensed milk is small, the average being about 0.04 per cent; the method may also give low results when applied to milk powder or cream. This error may be corrected by an extraction in the presence of acetic acid.

II—The method in which the solvents are recovered, by its acid treatment extracts free fatty acids and more completely separates fat from protein, in this manner recovering a trace of fat not obtained by alkaline extraction. Moreover, it is economical in the use of solvents.

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A RAPID METHOD FOR THE DETERMINATION OF LIME AS CALCIUM SULFATE

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The determination of lime by weighing as sulfate possesses distinct advantages, and its accuracy is vouched for by several authentic texts. The use of a factor and the constancy of the sulfate commend the method to analysts.

Treadwell-Hall¹ state that the technic is well adapted to the determination of lime occurring as organic salts in the absence of other bases. Fresenius-Cohn² outline a method, by which lime salts are converted to the sulfate by the addition of a slight excess of sulfuric acid and then precipitated by increasing the volume fourfold with ethyl alcohol. The precipitate is then filtered and washed free of the salts of other bases, and gently ignited. Glassen-Harriman³ dissolve the salts of calcium and other bases in an ether-alcohol solution and then effect the sulfate precipitation by adding sulfuric acid. The filtered and washed precipitate is then gently ignited. Olsen⁴ prescribes a similar procedure, stipulating a strength of 35 to 40 per cent for the alcohol washing solution. All of the foregoing schemes of manipulation effect the precipitation of lime as sulfate. It is quite feasible, however, to make the usual oxalate precipitation and then convert this to the sulfate. Gooch⁵ utilizes the sulfate conversion method, using H₂SO₄, in a procedure involving the separation of strontium salts from those of calcium. Crookes⁶ recommends the use of a conversion solution made by neutralizing 1 : 1 sulfuric acid with ammonium hydrate and adding ammonium chloride. The necessity for more definite provision for a positive excess of SO₃ will be shown by the data given in this article. The necessity for evaporation of the conversion solution is also an undesirable feature of this procedure. Fresenius-Cohn⁷ state: "The calcium oxalate may also be converted into sulfate. Schr6tter ignites in a covered platinum crucible with pure

ammonium sulfate. Or one may ignite in a covered platinum dish till the precipitate is for the most part converted into oxide, add a little water, then hydrochloric acid to effect solution, then pure sulfuric acid in excess, evaporate and ignite moderately. This process is also quite accurate." Lincoln and Walton¹ give essentially the same directions as in the preceding scheme. They direct, however, that the addition of acid and the gentle ignition be repeated. An unpublished modification of the procedures given by Lincoln and Walton, as advanced by Dr. Paul Potter, has been used by the writer for a number of years. In this modification ethyl alcohol is added to the oxide-carbonate residue before the addition of hydrochloric acid, in order to eliminate spattering when the determination is carried out in a small platinum crucible. The alcohol and hydrochloric acid are then driven off. The CaCl₂ is next dissolved in water, and a few drops of sulfuric acid are then added. The excess of acid is dispelled and the containing crucible gently ignited. This method is extremely accurate if carefully carried out with absolutely pure chemicals. Both the Lincoln and Walton and the Potter procedures require an evaporation in order to remove either water or alcohol. This evaporation consumes considerable time and necessitates great care to prevent mechanical loss. In order to obviate this feature we substituted powdered ammonium chloride for hydrochloric acid, and effected the preliminary conversion to chloride by means of a dry melt.

However, in using the ordinary "C. P." sulfuric acid this modification is often uncertain, as regards the attaining of constant weight of ignited calcium sulfate. In making determinations of large amounts of lime it was found that even with careful and moderate heating, during the initial conversion to sulfate, it was generally necessary again to add sulfuric acid and repeat the ignition. The reason or reasons for the irregularities in weights were then considered.

CONCERNING LOSS OF SULFUR UPON IGNITION OF CaSO₄

It has been pointed out that heating CaSO₄ to a bright red will cause a considerable loss in weight. Treadwell-Hall² attribute this to the dissociation of the CaSO₄ and loss of SO₃. Mitscherlich³ states that no loss of SO₃ occurs at a dull red heat but fusion with loss of SO₃ ensues with ignition to bright red heat. Boussingault⁴ asserts that continued heating at white heat for a long period results in the loss of all the combined SO₃. While it is undoubtedly true that loss of SO₃ does take place, it appears that the loss of weight incurred in carrying out the sulfate ignition may also be attributed to other causes. In carrying out the conversion of the ignited lime residue by the use of concentrated H₂SO₄ it was noted that wherever a result was apparently low and where an increased weight would occur with a second addition of acid an unmistakable odor of hydrogen sulfide followed the

¹ "Elementary Quantitative Agricultural Chemical Analysis," 1907, p. 33.

² "Analytical Chemistry," 1st Ed., 2 (1904), 66.

³ J. prakt. Chem., 83, 485.

⁴ Z. anal. Chem., 7, 224.

¹ "Analytical Chemistry," 1st Ed., 2 (1904), 66.

² "Quantitative Chemical Analysis," 1 (1906), 269.

³ "Quantitative Analysis," 5th Ed., 1902, p. 102.

⁴ "Quantitative Chemical Analysis," 2nd Ed., 1905, p. 173.

⁵ "Methods in Chemical Analysis," 1st Ed., 1912, p. 166.

⁶ "Select Methods in Chemical Analysis," 1st Ed., 1886, p. 47.

⁷ "Quantitative Chemical Analysis," 1 (1903), 272.

second addition of acid. The ignited lime precipitate was of course free of organic matter prior to the first addition of H_2SO_4 as a result of the ignition as well as the second heating to remove traces of the added alcohol. The only source of organic matter for possible reduction of the sulfate would therefore be the "C. P." acid itself. This objectionable feature of the conversion to sulfate by means of H_2SO_4 led to a study of the substitution of ammonium sulfate for the acid.

PRELIMINARY OBSERVATIONS

Qualitative sulfate conversion tests were made with recrystallized ammonium sulfate without obtaining any indication of the formation of calcium sulfide upon ignition of the chloride. With heavy occurrences of lime it is essential to make the preliminary conversion to the soluble chloride, when effecting the sulfate conversion by means of sulfuric acid. The same idea was at first followed in the substitution of ammonium sulfate. The chloride and sulfate radicals were introduced simultaneously by the use of a mixture of the two ammonium salts. It was thought that the use of the mixture might make possible the use of a smaller excess of sulfate. In further tests it was found that while the use of ammonium chloride in the fusion mixture is to be desired, it is not, however, necessary chemically in that a complete conversion to the sulfate is accomplished by the ammonium sulfate melt without the preliminary conversion to the chloride. The presence of ammonium chloride is particularly justified because of its mechanical effect, more especially in determinations of heavy lime

the crucible. In effecting the conversions of the lime residues to the sulfate, there is, of course, a considerable loss of ammonium sulfate by sublimation. This necessitates the assurance of a workable excess of the ammonium salt. In using the mixture of ammonium salts, it was therefore necessary to determine the excess of sulfate which would constitute a safe working basis. The only reference found, where the use of the solid sulfate is suggested, is that of Fresenius¹ who mentions, without citation, the technic of Schrötter. We have been unable to find the original in order to ascertain whether any specific directions and amounts are given by Schrötter. As a matter of fact the modification was worked out independently and the details perfected before our knowledge of the somewhat obscure reference mentioned by Fresenius, or the indefinite directions given by Crookes.²

In addition to determining the necessary excess of sulfate, it was essential to determine the most desirable proportion of chloride to sulfate in the conversion mixture. The data presented in Tables I and II were obtained in the determination of these points.

DISCUSSION OF RESULTS

The analyses given in Table I were made upon aliquots obtained from an HCl solution of Iceland spar. The results with a constant charge of chloride show that an excess of less than 0.3 g. of sulfate over the 0.2 g. charge of $CaCO_3$ fails to afford a safe working margin for a charge of this amount. The proportion of chloride to sulfate is also shown to be immaterial, insofar as the completeness of the conversion is concerned.

The results given in Table II were secured upon charges of calcium oxalate, which was made in the laboratory from "C. P." chemicals. The salt was dried, but was not heated sufficiently high to dispel the water of crystallization. The results of determinations 1, 2 and 3, made with constant amounts of the mixture, but with increasing amounts of salt, show that the charge is sufficient for the two smaller charges, but that insufficient excess of the mixture is present for conversion of the 0.7500-g. charge. It is evident from the results given in Table II, No. 3, that approximately 0.1 g. of $(NH_4)_2SO_4$ in excess of that theoretically required to convert 0.7500 g. of $(CaCOO)_2$ to sulfate is insufficient for complete conversion. In No. 4 it is shown that the same absolute amount was found insufficient to convert 0.1500 g. $(CaCOO)_2$ entirely to the sulfate, although in the latter case there is nearly 100 per cent excess of $(NH_4)_2SO_4$, as compared with only about 15 per cent excess in the former case. The results in No. 2 show an instance where a 100 per cent excess of $(NH_4)_2SO_4$ was sufficient. It seems, therefore, that an absolute minimum excess of $(NH_4)_2SO_4$ is necessary for the successful use of the method. These and additional data have led to the adoption of the amount of the mixture designated in the procedure outlined below.

¹ "Quantitative Chemical Analysis," 1 (1906), 272.

² *Loc. cit.*

TABLE I—A STUDY OF THE CONVERSION OF THE IGNITED CALCIUM PRECIPITATE TO CALCIUM SULFATE, AS INFLUENCED BY VARYING RATIOS OF SULFATE AND CHLORIDE

| No. | FUSION MIXTURE Charge in Grams | | Reagent Blank Gram | CaCO ₃ Charge Gram | CaSO ₄ FORMATION | | Conversion Per cent |
|--------|--------------------------------|---|--------------------|-------------------------------|-----------------------------|--------------|--|
| | NH ₄ Cl | (NH ₄) ₂ SO ₄ | | | Theory Gram | Actual* Gram | |
| 1..... | 1.5 | 0.3 | 0.0002 | 0.2000 | 0.2721 | 0.2597 | 95.44(a) 96.76 |
| 2..... | 1.5 | 0.5 | 0.0003 | 0.2000 | 0.2721 | 0.2721 | 100.00 0.2720 99.96 0.2720 99.96 |
| 3..... | 1.5 | 0.7 | 0.0003 | 0.2000 | 0.2721 | 0.2719 | 99.93 0.2721 100.00 |
| 4..... | 0.25 | 0.7 | 0.0002 | 0.2000 | 0.2721 | 0.2721 | 100.00 0.2721 100.00 |
| 5..... | 0.5 | 0.7 | 0.0002 | 0.2000 | 0.2721 | 0.2721 | 100.00 |
| 6..... | 0.75 | 0.7 | 0.0002 | 0.2000 | 0.2721 | 0.2723 | 100.07 |

* Corrected for blank.

(a) Test demonstrated presence of CaCl₂.

occurrences. When using the ammonium chloride and ammonium sulfate mixture the sulfate melt goes down evenly and there is obtained a skeletal mass which in the most part is readily removed mechanically from

TABLE II—THE DETERMINATION OF THE MINIMUM EXCESS OF FUSION MIXTURE ESSENTIAL TO THE COMPLETE CONVERSION OF THE IGNITED LIME PRECIPITATE INTO CaSO₄

| No. | FUSION MIXTURE Charge in Gram | | Reagent Blank Gram | Ca(COO) ₂ Charge Gram | GRAM CaSO ₄ FORMED Charge Corrected per 0.1500 g. Ca(COO) ₂ |
|--------|-------------------------------|---|---|----------------------------------|---|
| | NH ₄ Cl | (NH ₄) ₂ SO ₄ | | | |
| 1..... | 0.75 | 0.75 | 0.0002 | 0.1500 | 0.1376 0.1376 0.1378 |
| 2..... | 0.75 | 0.75 | 0.0002 | 0.4500 | 0.4131 0.4131 0.6834 0.1377 |
| 3..... | 0.75 | 0.75 | 0.0002 | 0.7500 | 0.6631 0.1313 0.1326 0.1326 0.1376 |
| 4..... | 0.25 | 0.25 | 0.0001 | 0.1500 | 0.1338 0.1376 0.1375 0.1375 0.1378 |
| 5..... | 0.50 | 0.50 | 0.0002 | 0.1500 | 0.1375 0.0689 0.1378 |
| 6..... | 0.25 | 0.25 | 0.0001 | 0.0750 | 0.0690 0.1380 |
| | | | (a) Re-ignited after addition of H ₂ SO ₄ | 0.6893 | 0.1379 |

TECHNIC OF THE METHOD

The detail of the procedure is as follows: Carefully precipitate the lime as oxalate, reprecipitating, as is usually done, where the magnesium content is appreciable. Ignite in a small platinum dish (or platinum or porcelain crucible) over a Bunsen burner (or in a muffle) until the filter is completely incinerated. For each approximate 0.2 g. of CaCO_3 add enough of an equal part and *finely ground* and *dried* mixture of ammonium sulfate and ammonium chloride to insure an excess of approximately 0.3 g. of sulfate. Effect a thorough mixture of the fusion salts with the lime residue in the crucible by means of a small glass rod, enlarged and flattened at one end. Quantitative comparisons indicate that it is decidedly preferable that the mixing be done in the crucible, rather than by transfer to a mortar. The volatilization of the excess of salts may be efficiently carried out as follows: insert the crucible in a circular opening cut in a piece of asbestos board, placed horizontally. The upper half of the crucible should extend above the upper surface of the asbestos. Direct a nearly horizontal flame from a small Bunsen burner across the surface of the crucible in such a manner as to have the side of the crucible nearest the flame intensely heated. The conducted heat will effect volatilization without spattering.

Should duplicates fail to agree within a few tenths of a milligram, the analyst may verify the results by moistening the ignited CaSO_4 with a few drops of 1 : 10 H_2SO_4 , evaporating excess of water and again igniting.

The above procedure has been tested thoroughly against reagents of known purity and as to ease in close duplication of results in a large number of unknowns, and has given complete satisfaction. We have found the modification to be especially well adapted to high occurrences of lime and to sets containing widely varying percentages.

SUMMARY

I—Though not in general use, the determination of lime as CaSO_4 is authoritatively stated in accepted texts to be accurate.

II—The procedure generally given calls for the use of H_2SO_4 as the converting agency.

III—In addition to loss of weight as a result of the dissociation of sulfate because of high temperature, there occurs a loss due to the reduction of sulfate to sulfide, as induced by the small amount of organic matter contained in "C. P." H_2SO_4 .

IV—The use of recrystallized ammonium sulfate eliminates this objectionable feature.

V—It was found that a mixture of ammonium chloride and ammonium sulfate afforded a very satisfactory conversion mixture which gives very accurate results.

VI—The detail of the procedure, as perfected, is given.

A MODIFIED METHOD FOR THE DETERMINATION OF FLUORINE WITH SPECIAL APPLICATION TO THE ANALYSIS OF PHOSPHATES¹

By CARY R. WAGNER AND WILLIAM H. ROSS

Received September 13, 1917

In the preparation of phosphoric acid from phosphate rock by the sulfuric acid method there may be found as impurities in the acid any of the constituents of the raw materials used. In the volatilization method, however, which consists in smelting the rock with silica and coke in an electric or other furnace, the impurities may be limited to those constituents of the charge which are volatile at the temperature used in the process. The most important of these volatile constituents are the alkalis, sulfur, chlorine and fluorine. The last mentioned is usually the most abundant and is found associated with lime phosphate in all mineral deposits and in the bones of animals.

In the scrubbing tower method of recovering the phosphorus oxide fumes evolved in the heat treatment of phosphate rock no separation of hydrofluoric acid from the phosphoric acid takes place since both are absorbed in the process. In experiments made in this laboratory it has been shown² that by use of the Cottrell process of electrical precipitation in place of the scrubbing tower method much more efficient and economic recovery of the acid is possible, and in addition a separation of the hydrofluoric acid from the phosphoric acid may be brought about at the same time.

In carrying out this process the phosphorus pentoxide, as it is evolved from the furnace, quickly combines with the moisture driven off from the charge or with that present in the current of air which is passed through the furnace for the oxidation of the evolved phosphorus, and is thus precipitated in the form of a solution of phosphoric acid. If the temperature of precipitation is below 100° the strength of the solution will depend on the amount of moisture associated with the acid. When the precipitation is made at a temperature above 100°, however, the strength of the acid will be independent of the moisture with which it is associated. Under these conditions any excess moisture will remain in the gaseous state while passing through the precipitator pipes and will consequently escape without being precipitated. By use of a proper temperature for precipitation, acid may thus be recovered directly of such a concentration that it will crystallize to a solid mass on cooling.

The same conditions which bring about a recovery of the phosphoric acid in concentrated form also contribute toward its purification from such volatile constituents as hydrofluoric acid with which it is initially associated as it escapes from the furnace. At a temperature above 100° these constituents will remain in the gaseous state in passing through the treater pipes and will therefore undergo no precipitation excepting that portion represented by the solubility of the respective constituents in the phosphoric acid under the conditions of the precipitation. As referred

to in experiments which are to be described more in detail in a later publication complete removal of the hydrofluoric acid or other impurities may subsequently be effected in one of several ways, as by bubbling hot air through the acid, by recrystallization or by chemical means.

In carrying out the work thus outlined on the preparation of crystallized phosphoric acid free from hydrofluoric acid, it was found necessary to make numerous analyses for fluorine when present in phosphoric acid in widely varying amounts. No official method is available for the quantitative determination of fluorine and the methods given in the literature were found to be of limited application. Accordingly an attempt was made to devise a suitable method for the determination of fluorine in the presence of phosphates or phosphoric acid. The object of the present paper is to give an account of the results obtained.

PROPOSED METHODS FOR THE ANALYSIS OF FLUORINE

The various methods which have been proposed for the determination of fluorine may be conveniently divided into four classes as follows:

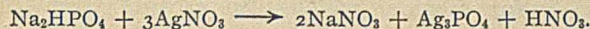
1—*Gravimetric methods*, as the Berzelius-Rose method in which the fluorine is weighed as calcium fluoride.

2—*Etching methods*, in which comparative tests are made of the action of hydrofluoric acid on glass or quartz.

3—*Colorimetric methods*.

4—*Volatilization methods*, as the Offermann method, in which the fluorine is distilled as silicon fluoride and collected in water.

I. GRAVIMETRIC METHODS—In the Berzelius¹ method as modified by Rose² and by Treadwell and Koch,³ the sample is fused with sodium and potassium carbonates, the silica precipitated with ammonium carbonate and ammoniacal zinc oxide, phosphates removed from the neutral solution by silver nitrate, the excess of silver taken out by sodium chloride, and $\text{CaF}_2 + \text{CaCO}_3$ precipitated with a large excess of calcium chloride. Calcium carbonate is dissolved after igniting the mixed precipitate in 1.5 *N* acetic acid and the calcium fluoride weighed. The method gives low results on account of the solubility of calcium fluoride in water and acetic acid. If phosphates are present the solution becomes acid when silver nitrate is added, as indicated in the equation



This acidity prevents complete precipitation of silver phosphate and, furthermore, will cause volatilization of fluorine when the solution is heated, unless the acidity is neutralized. This is a point that seems to have escaped notice in texts on the subject and could easily be overlooked by an analyst working on an unknown sample.

Ditte⁴ and Deussen and Kessler⁵ have devised methods depending upon the formation of calcium fluoride in a fusion, the remainder of the melt being removed later by solution. Dinwiddie⁶ proposed precipitation of calcium fluoride with powdered calcium sulfate and treatment of the combined precipitate with sulfuric acid. Such a mixture filters much more easily than a calcium fluoride-carbonate mixture. Starck and Thorin⁷ suggested precipitation of calcium fluoride and oxalate.

¹ *Pogg. Ann.*, 1, 69; *Schweigg. Jour.*, 16 (1816), 426.

² *Liebig's Ann.*, 72 (1849), 343; *Ibid.*, 79, 115.

³ *Z. anal. Chem.*, 43 (1904), 469.

⁴ *Compt. rend.*, 80 (1875), 561.

⁵ *Monatsh. Chem.*, 28 (1907), 163.

⁶ *Am. J. Sci.*, [4] 42 (1916), 464.

⁷ *Z. anal. Chem.*, 51 (1912), 14.

Heintz¹ precipitated calcium fluoride and phosphate, determined the weight of $\text{Ca}_3(\text{PO}_4)_2$, and got CaF_2 by difference. Kneeland² used Berzelius' method, but determined lime in the precipitate. Jannasch³ distilled hydrofluoric acid from the sample in a platinum retort and then used Berzelius' method on the neutralized distillate. Pisani⁴ claimed excellent results by precipitating $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ and igniting to thorium dioxide. Starck⁵ precipitated PbFCl with saturated lead chloride solution.

Of the various methods referred to in this class that of Berzelius-Rose is the only one commonly used when phosphates are present. The method, however, is applicable only when the percentage of fluorine with respect to the phosphate present in the sample is not below a certain limiting amount. For the determination of small amounts of fluorine in phosphoric acid, the method was found to be entirely impractical and therefore could not be used in our work.

2. ETCHING METHODS—The methods of this class are dependent upon the corrosive action of hydrofluoric acid on glass or quartz. Carles,⁶ Ost,⁷ and Woodman and Talbot⁸ compared the extent to which a glass surface is attacked with that resulting from the use of a known amount of fluorine. Westerberg⁹ and Kobell¹⁰ determined the loss in weight of a watch glass exposed to the action of the hydrofluoric acid evolved from a sample. Many other minor modifications of apparatus and procedure have been proposed but none seem to take into account the effect of silica in the sample.¹¹ When a sample containing silica is treated with acid a greater or less proportion of the fluorine, depending on the amount of silica present, will pass off as silicon fluoride. Therefore unless due precautions are taken for the initial removal of the silica a negative test may frequently be obtained even when considerable fluorine is present. Phosphoric acid prepared by the volatilization method always contains silica and to remove this constituent completely without danger of losing some of the fluorine would be very difficult if not impossible. The use of etching methods for the determination of fluorine in phosphoric acid was therefore considered impractical.

3. COLORIMETRIC METHODS—The Steiger¹²-Merwin¹³ method depends upon the fact that fluorides bleach oxidized titanium solutions. Another method proposed by Gautier and Clausmann¹⁴ depends upon the formation of lead fluoride and its transformation into lead sulfide. The turbidity caused by distilling hydrofluoric acid into a solution of a calcium salt has been recommended by Petersen¹⁵ as a means of determining fluorine.

The method of Steiger and Merwin is the best known of this class and gives good results¹⁶ for the determination of fluorine in the absence of such constituents as phosphoric acid, which have a bleaching effect on the titanium solution. All colorimetric methods, moreover, are applicable only when working with small amounts of fluorine and are therefore not of convenient application to the analysis of phosphate materials containing varying amounts of fluorine.

4. VOLATILIZATION METHODS—In this class are to be found a

¹ *Pogg. Ann.*, 77, 267.

² *Eng. and Min. Jour.*, 80 (1905), 1212.

³ *Z. anorg. Chem.*, 9 (1895), 267.

⁴ *Compt. rend.*, 162 (1916), 791.

⁵ *Z. anorg. Chem.*, 70 (1911), 173.

⁶ *Compt. rend.*, 144 (1907), 37.

⁷ *Ber.*, 26 (1893), 151.

⁸ *J. Am. Chem. Soc.*, 28 (1906), 1437.

⁹ *Chem. Ztg.*, 26 (1902), 967.

¹⁰ *J. prakt. Chem.*, [1] 92 (1864), 385.

¹¹ The same oversight is apparent in many texts on the subject, as may be noted, for example, in the etching tests given in Scott's "Standard Methods of Chemical Analysis."

¹² *J. Am. Chem. Soc.*, 30 (1908), 219. See also H. Fenton, *J. Chem. Soc.*, 93 (1900), 1064.

¹³ *Am. J. Sci.*, [4] 28 (1909), 119.

¹⁴ *Compt. rend.*, 154 (1912), 1469, 1670, 1753.

¹⁵ *Z. anal. Chem.*, 35 (1896), 585.

¹⁶ Adolph, *J. Am. Chem. Soc.*, 37 (1915), 2500.

large number of methods and modifications dependent on the volatilization of fluorine as silicon fluoride. Oettel¹ measured the volume of silicon fluoride formed. Fresenius² observed the gain in weight of a tube filled with moist pumice when silicon fluoride was passed through it. Wöhler³ recommended volatilizing the silicon fluoride and noting the loss in weight of the flask and contents. Daniel's⁴ method is a combination of the two. Penfield⁵ distilled silicon fluoride into water, added potassium chloride and alcohol, and titrated with ammonia the hydrochloric acid set free. Offermann⁶ titrated the aqueous solution with potassium hydroxide using phenolphthalein. Offermann's method has been modified somewhat in the manner of procedure by Drawe,⁷ Hileman⁸ and Adolph.⁹ Browning¹⁰ suggested decomposing silicon fluoride on moist black paper and noting the amount of silica formed. Korovaeff,¹¹ Städeler¹² and Weinland¹³ observed the loss in weight due to volatilization of silicon fluoride. Carnot¹⁴ passed silicon fluoride into a solution of potassium fluoride and weighed the precipitate of potassium silico-fluoride. Carnot's method was modified in some respects by Prost and Balthasar¹⁵ and by Burk.¹⁶ Somewhat similar methods had been proposed previously by Stolba,¹⁷ Liversidge¹⁸ and Tammann.¹⁹ Bein²⁰ collected and weighed the silica formed when silicon fluoride is decomposed by water. Lasne²¹ and Schneider²² distilled silicon fluoride into water and after removing silica precipitated $\text{CaF}_2 + \text{CaCO}_3$ and weighed the CaF_2 . Hileman²³ made use of an entirely different action of H_2SiF_6 when he titrated the iodine liberated in a solution of $\text{KI} + \text{KIO}_3$ by fluosilicic acid.²⁴

EXPERIMENTAL

The volatilization methods, unlike the methods of the preceding classes, are all applicable to the analysis of phosphates as well as other materials. The methods of this class, however, which are based on a determination of loss in weight due to the volatilization of silicon fluoride, are not suited to the analysis of material containing a low percentage of fluorine. The principle of all the remaining methods consists in passing the volatilized silicon fluoride into water and then determining, either volumetrically or gravimetrically, the amount of hydrofluosilicic acid formed. This procedure should be applicable to the determination of fluorine in amounts varying between rather wide

limits. A comparative study was accordingly undertaken to ascertain the most satisfactory details to be followed in the determination of fluorine according to this general scheme.

In carrying out these experiments use was made of a special double-trapped generating flask, designed by the Victor Chemical Co., for the volatilization of silicon fluoride. This flask (C), shown in Fig. I, was called to our attention by Dr. H. E. Patten of the Bureau of Chemistry. The remainder of the equipment and the procedure followed in the preliminary experiments were in principle the same as that used by Offermann,¹ Adolph,¹ and others. The sample to be analyzed was mixed with a small proportion of ground quartz and then treated in the generating flask with 98.5 per cent sulfuric acid. A current of carbon dioxide washed with sulfuric acid served to carry the silicon fluoride evolved in the generating flask through a U-tube filled with glass beads, to remove accompanying fumes of sulfur trioxide, and then through water in a large test-tube, where decomposition of the silicon fluoride took place as represented in the equation



The solution thus obtained was boiled to expel dissolved carbon dioxide and sulfur dioxide, and the hydrofluosilicic acid determined both volumetrically by titrating with standard sodium hydroxide, using phenolphthalein as indicator, and gravimetrically by precipitating with saturated lead chloride solution.

Satisfactory results were sometimes obtained by this procedure, but, as a rule, and particularly when working with small amounts of fluorine, the values obtained were very greatly in error. After numerous tests had been made, the principal sources of error were ascertained to be as follows:

(1) Glass beads were found to be only moderately efficient in removing the sulfur trioxide fumes carried over from the generating flask. The result is that a portion of the fumes which escape passes into solution in the absorbing tube and thus gives high results whether the hydrofluosilicic acid is determined volumetrically or gravimetrically.

(2) Sulfur dioxide, which also escapes from the generating flask, is partly taken up by the solution in the absorbing tube and a portion there undergoes oxidation to sulfuric acid. This gives high results in the same way as with sulfur trioxide.

(3) When the solution of hydrofluosilicic acid was boiled to expel carbon dioxide and sulfur dioxide preparatory to the determination of the fluorine either gravimetrically or volumetrically, loss of fluorine was found to result when using the volume of solution ordinarily specified.

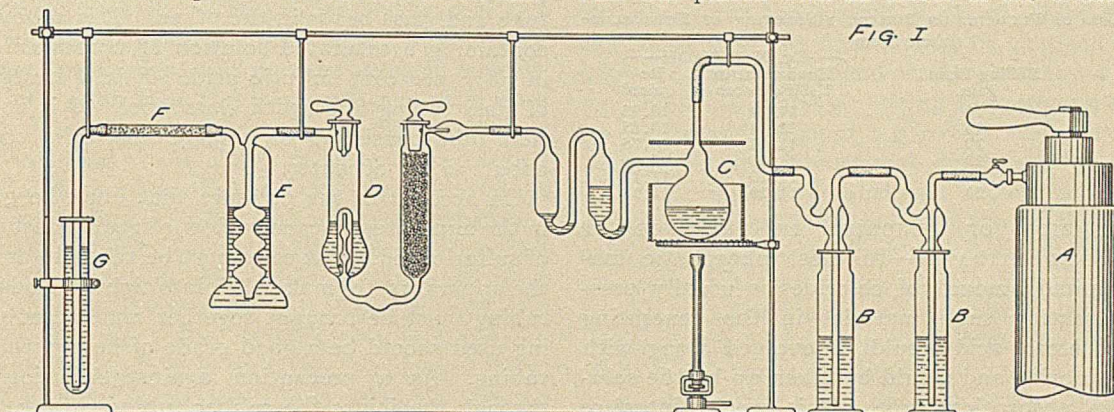
(4) Any chlorides or nitrates in the sample analyzed will result in the evolution of the corresponding acid and its absorption in the solution of hydrofluosilicic acid. This will give high results when the fluorine is determined volumetrically.

METHODS FOR THE ABSORPTION OF SULFUR TRIOXIDE IN FLUORINE ANALYSIS—When the sulfuric acid is boiled in the generating flask sulfur trioxide is carried

- ¹ *Z. anal. Chem.*, **25** (1886), 505.
² *Ibid.*, **5** (1866), 190.
³ *Pogg. Ann.*, **48** (1839), 87.
⁴ *Z. anorg. Chem.*, **38** (1904), 257.
⁵ *Am. Chem. J.*, **1** (1879), 27; *Z. anal. Chem.*, **21** (1882), 120.
⁶ *Z. angew. Chem.*, **3** (1890), 615.
⁷ *Ibid.*, **25** (1912), 1371.
⁸ *Z. anorg. Chem.*, **51** (1906), 157; *Am. J. Sci.*, [4] **22** (1906), 329.
⁹ *Loc. cit.*
¹⁰ *Am. J. Sci.*, [4] **32** (1911), 249.
¹¹ *J. prakt. Chem.*, [1] **85** (1862), 442.
¹² *Ibid.*, [1] **99** (1866), 66.
¹³ *Z. anorg. Chem.*, **21** (1899), 45.
¹⁴ *Bull. soc. chim.*, [3] **9**, 71; *Z. anal. Chem.*, **35** (1896), 580; *Compt. rend.*, **114** (1892), 750.
¹⁵ *Bull. assoc. belg. chim.*, **13** (1899), 453.
¹⁶ *J. Am. Chem. Soc.*, **23** (1901), 825.
¹⁷ *J. prakt. Chem.*, [1] **89** (1863), 129.
¹⁸ *Chem. News*, **24** (1871), 226.
¹⁹ *Z. anal. Chem.*, **24** (1885), 328; *Z. physiol. Chem.*, **12** (1888), 322.
²⁰ *Z. anal. Chem.*, **26** (1887), 733.
²¹ *Ann. chim. anal.*, **2** (1897), 182.
²² *Oesterr. Z. Berg.-Hüttenw.*, **61**, 365; *C. A.*, **7** (1913), 3582.
²³ *Am. J. Sci.*, [4] **22** (1906), 383.
²⁴ A volumetric method, belonging to none of these four classes, developed by Guyot [*Compt. rend.*, **71** (1870), 274; **73** (1871), 273] and Greef [*Ber.*, **46** (1913), 2511] depends on the precipitation of Na_2FeF_6 in neutral solution by standard FeCl_3 . As modified by Bellucci [*Ann. chim. applicata*, **1** (1914), 441], it gives good results for soluble fluorides, but is not applicable to the analysis of phosphates, since FePO_4 would be precipitated along with the fluorine compound.

over as a white fume which is difficult to condense. The proportion retained by the glass beads in the U-tube will depend on the rate at which the carbon dioxide is passed through the apparatus, but even when the flow of gas is as slow as it is expedient to use, a white fume may still be seen to issue from the end of the tube containing the glass beads. It was found, however, that complete absorption of the fumes could be effected by joining in the apparatus, in addition to the tube containing glass beads, a straight piece of glass tubing (*F*), filled with glass wool as shown in Fig. I. A perceptible coloration of the glass wool on heating to 100–130° will indicate the depth to which the fumes have permeated. Care should be taken to replace the tube before the glass wool becomes completely saturated.

METHODS FOR THE ABSORPTION OF SULFUR DIOXIDE IN FLUORINE ANALYSIS—When the fluorine treated in the generating flask is considerable, the greater part of it passes over before the acid in the flask begins to boil and before an appreciable dissociation of the sulfuric acid takes place. It was also noted that



when using pure samples of sodium fluoride in the generating flask, little or no sulfuric acid was formed in the absorbing tube when the fluorine taken amounted to 0.015 gram or more. From these observations it was thought possible that the hydrogen-ion concentration affected the oxidation of the sulfur dioxide. This would be expected if the oxidation depends on

TABLE I—RETARDATION OF THE OXIDATION OF SULFUR DIOXIDE IN ACID SOLUTIONS

| Grams NaF Taken | Cc. N/10 HCl Added to Absorption Tube | —Cc. N/10 NaOH— Equivalent of NaF + HCl | Re- quired | H ₂ SO ₄ FORMED Expressed as Cc. of N/10 Solution |
|-----------------|---------------------------------------|--|---------------|---|
| None | None | None | 0.75 | 0.75 |
| None | 1.00 | 1.00 | 1.65 | 0.65 |
| None | 3.00 | 3.00 | 3.30 | 0.30 |
| None | 5.00 | 5.00 | 5.15 | 0.15 |
| None | 10.00 | 10.00 | 10.01 | 0.01 |
| None | 10.00 | 10.00 | 10.06 | 0.06 |
| 0.0346 | 10.00 | 18.24 | 18.31 | 0.07 |
| 0.0194 | 10.00 | 14.62 | 14.40 | None |

the amount of SO₂ present, for sulfurous acid is very slightly dissociated into 2H⁺ + SO₃²⁻. The larger part of it is in the form of H⁺ + HSO₃⁻ and the presence of an acid would therefore force back the dissociation of HSO₃⁻ → H⁺ + SO₃²⁻. Several determinations were run using varying quantities of N/10 hydrochloric acid in the absorption tube. It was found that the amount of sulfuric acid formed decreased steadily with increasing amounts of acid until practically none was formed when 10 cc. of N/10

hydrochloric acid were used. Table I shows some results obtained when using the volumetric method of determining the hydrofluosilicic acid.

It was observed, however, that when organic matter to the extent of 0.1 gram or more is contained in the sample analyzed, sulfuric acid then appears in the solution after boiling out dissolved gases, even though hydrochloric acid had previously been added. So much sulfur dioxide is evolved under these conditions that the hydrochloric acid present cannot prevent the oxidation of a part of it. It is well known that solutions of sulfur dioxide are rapidly oxidized by exposure to air and some work has been done on preventive measures. Thus Saillard¹ found that a solution of sucrose exerted an inhibitive effect on this oxidation. Accordingly 30 per cent and 60 per cent sucrose solutions were made up and used in place of water in the absorption tube. The effect was very much less than that produced by hydrochloric acid.

An oxidizing solution² was then prepared consisting of chromium trioxide in 98.5 per cent sulfuric acid. This was placed with an excess of the trioxide in the

Bowen potash bulb (*E*, Fig. I). When no organic matter was used in the generating flask the quantity of sulfur dioxide that escaped was found to undergo such complete oxidation in the trioxide solution that the amount carried over was too small to give rise to any appreciable quantity of sulfuric acid in the absorption tube. When the sample analyzed contains a large proportion of organic matter, however, so much sulfur dioxide is then evolved that quick reduction of the trioxide takes place. In this case the most convenient procedure is first to remove the greater part of the organic matter by ignition at a temperature below the melting point of the material. The complete combustion of certain phosphate materials is, however, sometimes difficult and if in such cases some carbonaceous material remains unburned in the sample, the sulfur dioxide evolved may be sufficiently great to escape complete absorption in the chromium solution. In the analysis of such materials standard hydrochloric acid solution should be used in the absorption tube as an added precaution. The effectiveness of the chromium trioxide solution in the absorption of sulfur dioxide is shown by the results given in Table II.

¹ *Rev. gen. chim.*, 16 (1913), 412.

² G. Tammann, *Z. anal. Chem.*, 24 (1885), 328.

TABLE II—ABSORPTION OF SULFUR DIOXIDE IN SULFURIC ACID SOLUTION OF CHROMIUM TRIOXIDE

| SAMPLE TAKEN | Cc. N/10 HCl Added to Abs. Tube | Cc. N/10 NaOH— | | H ₂ SO ₄ FORMED | |
|--|---------------------------------|---------------------|--|---|-----------|
| | | Equiv. of NaF + HCl | REQUIRED +CrO ₃ No CrO ₃ | (Cc. N/10 Solution) +CrO ₃ No CrO ₃ | |
| None | None | None | None | 0.75 | None 0.75 |
| 0.0214 g. Na ₂ SiF ₆ | None | 16.82 | 16.80 | ... | None .. |
| 0.0050 g. NaF | None | 1.19 | ... | 2.00 | .. 0.81 |
| NaF + Starch (ignited) | 10.00 | 10.84 | 10.87 | 0.03 | .. 0.46 |
| | 10.00 | 10.84 | ... | 11.30 | .. 0.46 |

LOSS OF FLUORINE IN BOILING SOLUTIONS OF HYDROFLUOSILICIC ACID—When proper precautions were taken to prevent the formation of sulfuric acid in the absorption tube, low results for fluorine were frequently obtained, as Adolph¹ observed in his experiments with the Offermann method. This was finally traced to a loss of fluorine on boiling the hydrofluosilicic acid solution to expel dissolved carbon dioxide and sulfur dioxide. As the volume of the solution was increased, the loss of fluorine decreased, and beyond a *N*/1000 concentration of the hydrofluosilicic acid no loss of fluorine took place, as shown by the results given in Table III:

TABLE III—LOSS OF FLUORINE ON BOILING A SOLUTION OF HYDROFLUOSILICIC ACID

| Cc. Acid Solution Taken | Boiling Period Min. | Cc. N/10 NaOH— | |
|-------------------------|---------------------|---|----------|
| | | Equivalent to H ₂ SiF ₆ Taken | Required |
| 100 | 10 | 11.14 | 10.95 |
| 100 | 15 | 11.14 | 10.85 |
| 100 | 20 | 11.14 | 10.75 |
| 150 | 20 | 11.20 | 10.96 |
| 175 | 20 | 11.20 | 11.13 |
| 250 | 20 | 11.20 | 11.18 |

DETERMINATION OF FLUORINE IN PRESENCE OF CHLORIDES AND NITRATES—In most phosphatic materials a limited amount of chlorides is usually present. On treating such material in the generating flask hydrochloric acid would be evolved along with the silicon fluoride and would be taken up by the solution in the absorption tube. This would interfere with the volumetric determination of the hydrofluosilicic acid. With a view to preventing any hydrochloric acid reaching the absorption tube, the gases from the generating flask were made to pass through a Schmitz tube (*D*, Fig. 1) containing a solution of silver sulfate in 98.5 per cent sulfuric acid. Glass beads were placed in the small arm of the tube and as thus equipped it took the place of the U-tube used in the preliminary experiments. That a solution of silver sulfate in sulfuric acid is able to absorb effectively any hydrochloric acid given off from the generating flask without interfering in any way with the determination of fluorine is shown by the results given in Table IV. In carrying out these experiments the acidity of the solution in the absorption tube was determined volumetrically after the precautions already noted were taken to prevent the formation of sulfuric acid or loss of fluorine through boiling.

When nitrates are present in the sample analyzed,

TABLE IV—DETERMINATION OF FLUORIDE IN PRESENCE OF CHLORIDES AND NITRATES

| GRAMS REAGENT TAKEN | Cc. N/10 NaOH— | |
|---------------------|-------------------------|----------|
| | Equivalent to NaF Taken | Required |
| None | None | 0.05 |
| 0.0093 | 0.05 | 2.22 |
| None | None | 0.0 |
| 0.0050 | None | 1.20 |

¹ *Loc. cit.*

nitric acid will be evolved at first, but as the temperature is raised, this will decompose to give nitrogen dioxide. In either case the product evolved will be taken up by the solutions in the Schmitz and Bowen tubes and consequently no nitric acid will be formed in the absorption tube as shown by the results given in Table IV.

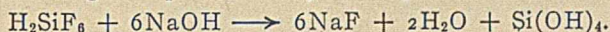
DETAILS OF PROCEDURE IN THE MODIFIED METHOD OF DETERMINING FLUORINE

APPARATUS—The equipment finally adopted in the analysis of fluorine is represented in Fig. 1. *A* is a cylinder of compressed carbon dioxide or nitrogen fitted with a reducing valve or other safety device for regulating the flow of gas. *BB* are wash bottles containing concentrated sulfuric acid for washing the gas. *C* is a generating flask of 250 cc. capacity provided with 2 traps containing 98.5 per cent sulfuric acid, that next the flask being half full while the acid in the second is just sufficient to make a seal. *D* is a Schmitz tube having a 10 per cent solution of silver sulfate in 98.5 per cent sulfuric acid in the bulbed arm of the tube and glass beads in the other. *E* is a Bowen bulb containing a saturated solution of chromium trioxide in 98.5 per cent sulfuric acid. *F* is a straight piece of glass tubing filled with glass wool. *G* is an absorption tube consisting of a large test-tube containing about 50 cc. of water.

On account of the pressure that must be generated in the apparatus to cause a flow of gas against the head of sulfuric acid, great care must be taken in assembling the apparatus to make all joints tight. Ends of glass tubing must be brought together and the rubber tubing used should be a good grade of heavy-walled gum tubing. As a precaution against diffusion of gas through the joints the rubber tubing may be covered with a good coating of shellac. Glass stopcocks should be paraffined also. An asbestos screen may be used under the flask and to minimize the danger of breaking the flask a ring of asbestos paper should be placed around it for protection against cold air currents. A mantle of asbestos over the bulb of the flask must also be used to prevent burning the rubber connection at the top of the flask. The exclusion of every trace of water from all parts of the apparatus is essential. The following additional reagents are required:

- (1) Anhydrous copper sulfate.
- (2) Ground quartz.
- (3) 98.5 per cent sulfuric acid prepared by boiling C. P. concentrated sulfuric acid for about 20 minutes in an open vessel.
- (4) A 10 per cent solution of silver sulfate in 98.5 per cent sulfuric acid. The silver sulfate should be ignited with an excess of sulfuric acid before using to drive off any volatile acids present.
- (5) A saturated solution of chromium trioxide in 98.5 per cent sulfuric acid.
- (6) *N*/10 sodium hydroxide, preferably standardized against chemically pure sodium fluosilicate.
- (7) *N*/10 hydrochloric acid, carefully standardized against the *N*/10 sodium hydroxide.

DETERMINATION—The sample to be analyzed must be carefully dried. A quantity containing between 0.001 and 0.1 g. of fluorine is weighed into the generating flask with 0.1–1.0 g. of silica and 5 g. of anhydrous copper sulfate: 100 cc. of 98.5 per cent sulfuric acid are then added, allowing the first portions to run into the traps, and the flask quickly connected to the source of carbon dioxide. The valve of the carbon dioxide cylinder is adjusted to give a flow of gas through the absorption bulbs at a rate of about 2 or 3 bubbles per sec., and this rate should be maintained the same throughout the course of the experiment. The contents of the flask are shaken until well mixed and then heated gradually to boiling. At this point a white scum indicating fluorine will appear on the inside of the flask. The flame under the flask should then be adjusted so that the condensing sulfuric acid will wash this scum freely and completely into the first trap. Care should be taken, however, to avoid heating so strongly that white fumes will be evolved in noticeable quantity, nor should the acid in the first trap be made to boil. When the second trap is half full of acid the heating is discontinued. On turning off the flame, particular pains must be taken to regulate the flow of gas so that the relatively cool acid from the traps does not flow back into the flask and thus cause it to break. The valve in the carbon dioxide cylinder must therefore be sensitive enough to admit of quick adjustment. After a minute or two of adjustment the valve may be set to give as before a uniform flow of carbon dioxide, which is continued from 25 to 30 minutes, so as to wash all silicon fluoride into the absorption tube. The latter is then removed, its contents transferred to a 350 cc. Erlenmeyer flask, the solution made up to 200–250 cc. and boiled gently for 10 to 15 minutes to expel dissolved gases. This operation should consume as little time as possible, because any prolonged exposure to the air before boiling leads to oxidation of the sulfur dioxide in solution. The solution is allowed to cool somewhat and then titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator. The end-point must be approached slowly but is fairly sharp when the fluorine present amounts to less than 0.02 g. The reaction occurring is represented by the equation



It will require about an hour to make one determination.

If an appreciable amount of organic matter is present in the sample to be analyzed, it must first be removed by burning. This is done by adding sufficient sodium carbonate to make the material alkaline and then igniting in a muffle furnace at a dull red heat until a white, or nearly white, ash remains. Care must be taken that the temperature does not get high enough at any time to melt the material or to volatilize sodium fluoride.

In the determination of fluorine in phosphoric acid the latter must first be prepared for analysis by making neutral to phenolphthalein with sodium hydroxide and then drying.

In the analysis of samples free from organic matter,

it will be found unnecessary to add standard hydrochloric acid to the water in the absorption tube, providing the fluorine in the sample is equivalent to 10 cc. or more of $N/10$ acid. If the fluorine taken is less than this, or if there is any possibility of organic matter being present, then 10 cc. of $N/10$ hydrochloric acid should be added as a precaution against oxidation of sulfur dioxide to sulfuric acid. To insure that no error has been introduced from this source, the solution, after titrating, may be concentrated to about 50 cc., acidified with hydrochloric acid and a small amount of barium chloride solution added. In case a precipitate of barium sulfate occurs, this may be filtered off, ignited and weighed, and the proper deduction made from the volume of sodium hydroxide required.

When undertaking a second determination, a portion of the acid in the trap equivalent to that which distilled over in the preceding determination must be returned to the flask. This may be done by removing the stopper in the Schmitz tube and simply lowering the flask into the proper position. Whether or not the contents of the flask should be changed with each determination will depend on the character of the sample taken for analysis. Using samples containing little carbon and weighing 2 g. or less, the same acid may be used in making several determinations. In this case the sample to be analyzed, mixed with the proper amount of silica, is placed in a thin-walled glass capsule, dropped into the flask and the latter then quickly connected with the source of carbon dioxide as before. In this way little time is lost between successive determinations. The copper sulfate may be renewed with each change of acid. Its purpose is to serve as a dehydrating agent and to prevent bumping.

The accuracy of the method described and its range of application is shown by the results given in Table V. For the sake of comparison some results obtained with the Berzelius-Rose method are also given.

TABLE V—RESULTS OBTAINED IN THE ANALYSIS OF FLUORINE COMPOUNDS

| Sample Used | Grams Taken | Cc. $N/10$ HCl Used in Absorption Tube | PER CENT FLUORINE IN SAMPLE | | Calculated |
|--|-------------|--|--------------------------------|-----------------------|------------|
| | | | Modified Volatilization Method | Berzelius-Rose Method | |
| NaF..... | 0.0346 | 10.00 | 45.63 | ... | 45.24 |
| | 0.0202 | 10.00 | 44.49 | ... | 45.24 |
| | 0.2000 | None | 45.06 | ... | 45.24 |
| | 0.2000 | ... | ... | 43.21 | 45.24 |
| | 0.2000 | ... | ... | 42.95 | 45.24 |
| NaF + $\text{Ca}_3(\text{PO}_4)_2$ | 0.4614 | 10.00 | 4.48 | ... | 4.52 |
| | 0.4220 | 10.00 | 4.52 | ... | 4.52 |
| | 0.5000 | None | 4.54 | ... | 4.52 |
| | 0.5000 | None | 4.43 | ... | 4.52 |
| | 1.0000 | ... | ... | 2.92 | 4.52 |
| | 1.0000 | ... | ... | 2.62 | 4.52 |
| | 1.1035 | 10.00 | 0.438 | ... | 0.452 |
| | 1.1610 | 10.00 | 0.434 | ... | 0.452 |
| | 1.0000 | ... | ... | 0.30 | 0.452 |
| | 1.0000 | ... | ... | 0.18 | 0.452 |
| | 5.0000 | 10.00 | 0.037 | ... | 0.045 |
| 5.0000 | 10.00 | 0.037 | ... | 0.045 | |
| 10.0000 | 10.00 | 0.015 | ... | 0.009 | |
| $\text{Na}_2\text{SiF}_6 + \text{Ca}_3(\text{PO}_4)_2$ | 0.2341 | 10.00 | 6.01 | ... | 6.05 |
| | 0.2647 | 10.00 | 6.04 | ... | 6.05 |

In Table VI are given some results obtained separately by each of us in the analysis of some commercial materials which are ordinarily supposed to offer special difficulty in the determination of fluorine.

An examination of the results given in Tables V and VI will show values obtained for the fluorine in different materials ranging from 0.01 to 45.2 per cent.

In general, the method may be expected to give results accurate to within 0.0005 g. of fluorine, and, if organic matter is carefully excluded, even greater accuracy may be secured. The lowest limit for the determination of fluorine to which the method is applicable may be taken as 0.01 per cent.

The concentration of fluorine which admits of most convenient analysis ranges from about 0.5 to 10 per cent and it is between these limits that the most accurate results are usually obtained.

In the analysis of high-grade material like sodium fluoride a slight error in weighing may produce a considerable variation in the results. The source of error may be minimized by diluting the material with a known amount of an inert substance like calcium phosphate, or by taking a sample containing a larger amount of fluorine than that ordinarily used. In

TABLE VI—MISCELLANEOUS FLUORINE ANALYSES

| SAMPLE | Cc. N/10 HCl Added to Absorption Tube | PER CENT FLUORINE FOUND | |
|------------------------------------|---|----------------------------|----------|
| | | Sample A | Sample B |
| Phosphate Rock..... | 10.00 | 1.58 | 1.47 |
| | None | 3.74 | 3.85 |
| Phosphoric Acid..... | 10.00 | 0.40 | 0.47 |
| | None | 0.67 | 0.70 |
| Monocalcium Phosphate (commercial) | 10.00 | 0.63 | 0.73 |
| | 10.00 | 0.031 | 0.032 |
| Baking Powder..... | 10.00 | 0.014 | 0.023 |
| | 10.00 | 0.043 | 0.040 |

the latter case care must be taken to use a delivery tube sufficiently flared at the point where it meets the surface of the water in the absorption tube to prevent its being stopped up by the silica that is deposited.

The sodium fluoride used in testing the accuracy of the method as represented in Table V was prepared by neutralizing C. P. sodium bicarbonate with an excess of hydrofluoric acid, igniting to drive off the excess of acid and then recrystallizing several times. The purity of the product finally obtained was verified by changing it into the sulfate and noting the increase in weight.

The sodium fluosilicate used was prepared from "Baker's analyzed" product by heating to 400° for 5 minutes, filtering off the insoluble residue, recrystallizing three times in a large platinum dish and finally drying at 130°. The purity of the product thus prepared was established by titrating with a standard solution of sodium hydroxide.

DETERMINATION OF HYDROFLUOSILICIC ACID GRAVIMETRICALLY—The results so far given in the analysis of fluorine are all based on the volumetric determination of the hydrofluosilicic acid in the absorption flask. If desired, the results thus obtained may be checked by means of a gravimetric determination of the acid. In carrying out this procedure the solution obtained after titration with standard sodium hydroxide is concentrated to about 50 cc. and the fluorine precipitated by adding 200 cc. of a saturated solution of lead chloride, as directed in Starck's method. After standing over night the precipitate is filtered through a Gooch crucible, washed with saturated lead chloride solution or, better, with saturated lead fluochloride, and finally with a few cc. of water, dried at 120° and weighed as PbFCl.

In Table VII the results obtained by this method are compared with those found volumetrically.

The values given in Table VII show that when the weight of fluorine taken is below 0.01 g. the gravimetric method gives lower results than the volumetric

TABLE VII—COMPARISON OF RESULTS OBTAINED IN THE VOLUMETRIC AND GRAVIMETRIC DETERMINATION OF HYDROFLUOSILICIC ACID

| No. | GRAMS FLUORINE | | No. | GRAMS FLUORINE | | No. | GRAMS FLUORINE | |
|-----|----------------|---------|-----|----------------|---------|-----|----------------|---------|
| | Vol. | Grav. | | Vol. | Grav. | | Vol. | Grav. |
| 1 | 0.02395 | 0.02410 | 5 | 0.00818 | 0.00798 | 9 | 0.00467 | 0.00462 |
| 2 | 0.02270 | 0.02295 | 6 | 0.00762 | 0.00758 | 10 | 0.00388 | 0.00382 |
| 3 | 0.02185 | 0.02235 | 7 | 0.00589 | 0.00498 | 11 | 0.00306 | 0.00295 |
| 4 | 0.00988 | 0.00982 | 8 | 0.00560 | 0.00457 | 12 | 0.00185 | 0.00170 |

and where the weight of fluorine is over 0.02 g. the gravimetric results are usually higher. Although not definitely proved, it seems probable that this result is due to two factors, the solubility of lead fluochloride and the adsorption of the silicic acid set free by the titration of the hydrofluosilicic acid. For small amounts of fluorine the solubility of the lead fluochloride more than offsets the adsorption of silicic acid, but for larger amounts the reverse is true. This appears reasonable from the fact that the weight of lead fluochloride remaining in solution will be practically the same whether little or much fluorine is present, but the weight of silicic acid carried down will increase with increasing concentration of fluorine. For an intermediate amount varying between 0.0075 g. and 0.0150 g. of fluorine, the two errors practically balance each other and within these limits results by the two methods closely agree.

The procedure of precipitating the fluorine with saturated lead chloride solution may thus be used as a check on the results obtained by the volumetric method, and it serves as a visible means of identifying fluorine in solution. In the case of routine analyses, however, it is apparent from the results given that there is nothing to be gained by lengthening the method beyond the volumetric determination of the hydrofluosilicic acid.

ACKNOWLEDGMENT

The possibilities of adapting a volatilization method of determining fluorine in the presence of phosphates was called to our attention by Dr. H. E. Patten, Referee for baking powders of the Association of Official Agricultural Chemists, and we wish fully to acknowledge the assistance which he and also the Victor Chemical Co. have cheerfully given in the course of this investigation.

SUMMARY

An experimental study has been made of the various processes that have been proposed for the determination of fluorine in the presence of phosphates. From the results obtained it would appear that the procedure which offers most promise for the determination of fluorine over a wide percentage range consists in volatilizing the fluorine as silicon fluoride and then collecting the latter in water to form hydrofluosilicic acid. When sulfuric acid is used to bring about the volatilization of the silicon fluoride there is evolved at the same time sulfur trioxide, sulfur dioxide and also such other products which may be present as hydrochloric and nitric acids. It was found, however, that by use of various reagents a selective removal of these products from the silicon fluoride may be effected, yielding a solution of hydrofluosilicic acid en-

tirely free from other acid constituents. By titrating this solution with standard sodium hydroxide, using phenolphthalein as indicator, closely agreeing results for the fluorine in the samples analyzed may be obtained. In the case of samples freed from water and from organic matter (by burning) a complete analysis by this procedure may be made in the course of an hour. The method is applicable to the analysis of material having a fluorine content as low as 0.01 per cent.

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A WOOL FAT (LANOLIN) SUBSTITUTE AND THE PREPARATION OF CETYLIC ALCOHOL

By SOL. AXELRAD

Received October 17, 1917

The question of substitutes for various materials has been one of prime importance during these war times, especially those substances and chemicals used in medicine and pharmacy. A year and a half ago the supply of wool fat was very limited and the price asked was four times more than that under normal conditions. A substitute called "Eucerin" imported from Germany was also scarce and the agency for this product had only four ounces left. It was claimed that "Eucerin" was made from the washings obtained in the manufacture of wool fat. The uses of lanolin are many, especially in pharmacy; as a vehicle for ointments, in the preparation of bougies, suppositories, cold creams and plasters of various kinds, etc.

This investigation on a wool fat substitute was undertaken with the idea of making a fatty composition which would have all of the desirable properties of lanolin, such as body, tenacity, power of absorbing water readily, taking up solutions of various chemicals used in pharmacy, dry powders, etc., etc.

Liebreich claimed that the absorbing power of wool fat was due to the cholesterol ethers it contained. Lifschuetz¹ isolated the cholesterol ethers of Liebreich and proved that they had very little power of absorbing water. He concluded from his experiments that the absorbing power of wool fat was due to the fatty alcohols of iso and oxycholesterols. He separated from the alkaline washings of partially saponified wool fat two saturated alcohols and one unsaturated alcohol. His experiments further proved that the more purified lanolin was, the lower was its power to absorb water, owing to the fact that during its purification the iso and oxycholesterols were partly removed.

Unna,² in his paper "Ointment Bases," states that "Eucerin" is a mixture of alcohols of the iso and oxycholesterin group with petrolatum. He does not, however, give a commercial method for the preparation of these alcohols. The absorbing power of "Eucerin" is due to these alcohols, but Roemer (see below) claims that with the employment of cholesterol for ointment bases, hydrocarbons, such as mineral oil, benzol, etc., are essential, for it is due to them in combination that the absorbing property is imparted. Roemer,³ in his

paper on "The Pharmacy of the Oxycholesterine Ointment Bases," confirms to a certain extent the work of Unna, but he also fails to give a method for the preparation of the alcohols.

Unna¹ states that "Eucerin" has been used in skin preparations in Germany, especially in pure form, for ichthyosis. According to the U. S. Dispensatory, 19th Edition, page 97, experiments have been carried on in reference to the absorption of wool fat by the skin. Patschkowski and Kaspar claim that the skin readily absorbs lanolin, but Ritter and Pfeiffer in a long series of experiments were unable to verify these results. Grimm² recommends, in his paper "Ueber die Verwendung von Aethyl in der Hautpflege," cetyl alcohol, $C_{16}H_{31}OH$, for skin preparations on account of its absorption by the skin and he further states that he has found it useful in the treatment of prurigo, weeping eczema and other skin infections.

In view of the fact that Unna and Roemer have written about the cholesterol, which are aliphatic higher alcohols, and Grimm has given a favorable report on the use of cetyl alcohol, the writer came to the conclusion that the use of this alcohol was advantageous in a substitute for wool fat.

A review of the literature failed to show any commercial method for the preparation of cetyl alcohol. There were many references as to its preparation from spermaceti by saponification with caustic potash and shaking the aqueous soap solution with petroleum ether, this being analogous to the extraction of unsaponifiable matter. Spermaceti is essentially the cetyl ester of palmitic acid. Chevreul in 1818 isolated the alcohol by the above method. Krafft³ prepared this substance by the reduction of palmitic acid to the aldehyde and heating it with barium formate. He also made the alcohol⁴ and by heating the palmitic aldehyde with zinc dust and acetic acid and hydrolyzing the acetate formed.

Levene⁵ made this alcohol by the reduction of ethyl palmitate with sodium and absolute alcohol. Schorlemmer⁶ distilled a dry mixture of barium oxide with sebamic acid. A method given in several text books for the preparation of cetyl alcohol was the saponification of spermaceti with alcoholic potash, evaporating the alcohol, taking up the residue with water, adding calcium chloride solution to form calcium soap and extracting with suitable solvents. The above methods are useful for preparing small quantities of cetyl alcohol, but for commercial quantities these methods fall down for obvious reasons.

The method of Schorlemmer was found impracticable on account of sebamic acid not being a commercial substance. The extraction process causes a considerable loss of the solvent employed and formation of troublesome emulsions.

It has been found that cetyl alcohol distills at about 340 to 350° C. without decomposition and the writer's

¹ *Proc. Roy. Soc. Med., London*, 1911-1912, p. 220.

² *Dermatologische Z.*, 6, 158.

³ *Ber.*, 13, 1416.

⁴ *Ibid.*, 16, 1721; 17, 1627.

⁵ *J. Biol. Chem.*, 20, 121.

⁶ *Ber.*, 3, 616.

¹ *Ber.*, 29, 2890.

² *J. Am. Pharm. Assoc.*, 1, 673.

³ *Ibid.*, 2, 971.

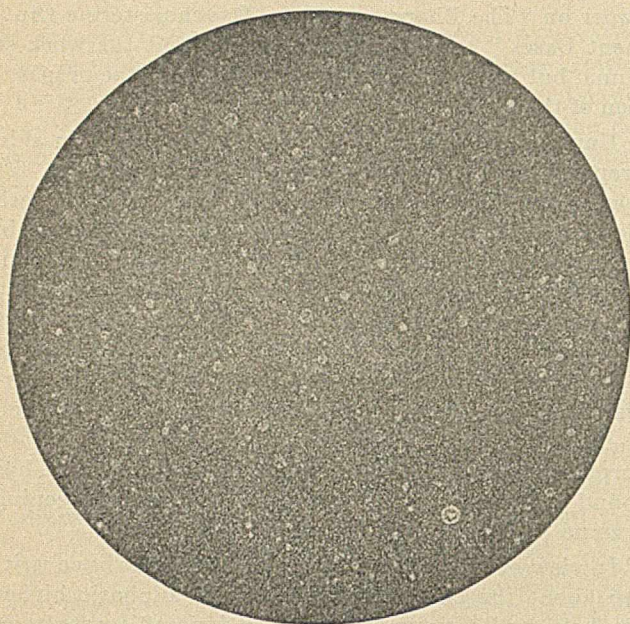


FIG. I—HYDROUS LANOLIN X 100
(WOOL FAT WITH 30 PER CENT WATER)
Average cost per pound 40 cents

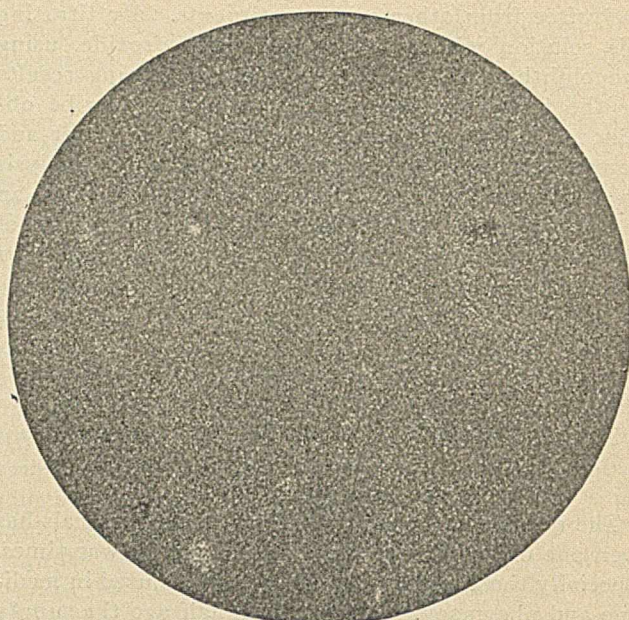


FIG. II—WOOL FAT SUBSTITUTE X 100
55 to 75 Per Cent Cheaper than Hydrous Lanolin

method is based upon the distillation of the calcium soap of spermaceti. Various experiments were performed with the following purposes in view.

- 1—Greatest yield of cetyl alcohol.
- 2—Cheapest process.
- 3—Most practical method.

EXPERIMENT I—Spermaceti (20 grams) was saponified with alcoholic potash, the alcohol evaporated and the residue heated in a distilling flask to 340° C.

EXPERIMENT II—Spermaceti (20 grams) was saponified with alcoholic potash, the alcohol evaporated and the soap dissolved in water. To the soap solution was added an excess of a 10 per cent calcium chloride solution. The calcium soap was separated and dried at 100° C. and finally distilled at 340° C.

EXPERIMENT III—The method employed was the same as in Experiment II, except that the soap solution was saturated with sodium chloride. The soap was filtered, dried at 100° and distilled. Many minor experiments were performed by this method but they did not show results of such value as to warrant their description.

EXPERIMENT IV—Twenty grams of calcium oxide containing about 5 per cent water were added to 15 grams of melted spermaceti. The mixture was heated for about 6 hours, with occasional stirring. When cooled, the mass assumed a brown-yellow color. On distilling same, frothing occurred at 100° C. due to the escape of water. When the water had all been driven off the temperature was raised to 340° when the cetyl alcohol distilled as white fumes and on cooling formed oily drops, which became pure white upon solidification, the melting point being 49.5° C. The yield obtained was over 6 grams, this being over 40 per cent of the actual spermaceti taken. The theoretical yield (calculated) was about 45 per cent.

This method gave a larger yield than the other three preceding methods, and, calculating the cost of the

alcohol obtained on a 40 per cent basis, was also cheaper than the others. The ideal temperature for the distillation of cetyl alcohol is 330 to 350°, as above this temperature a yellow liquid distills, being strongly acid and having a pungent odor; its value commercially will be investigated at a later date.

A copper still, manufactured by Sargent & Co., Chicago, for the distillation of oils, etc., at high temperatures, was found to be of most service. Glass stills are apt to crack, due to the "caking" of the residue which can readily be removed from the copper still after each distillation.

Mixtures were made having different quantities of base, cetyl alcohol, lanolin and water. The formula finally selected as being the best suitable for pharmaceutical compounding, was the following: 70 parts petrolatum, 20 parts paraffin, (m. p. about 60° C.), 10 parts cetyl alcohol, 5 parts lanolin (anhydrous), 100 parts water. This preparation stood in the laboratory for 17 months with absolutely no change in appearance or working qualities. The properties of this mixture are the same as wool fat; *viz.*, taking up solutions of salts, powders, etc., etc. The advantage over wool fat is that it will not become rancid and is considerably cheaper. The reason for using 5 parts of lanolin in the mixture was to have the "unctuous" property of wool fat. This, however, is a minor physical property.

A cold cream having very desirable properties can be made by using the above formula except for the addition of 250 parts of water instead of 100. The method of mixing the various substances is of prime importance. The petrolatum, alcohol, lanolin and paraffin are melted together. The water is warmed to the same temperature as the melted fats and added slowly with constant grinding so as to get a smooth mixture.

Microphotographs of hydrous wool fat, the substitute

and cold cream have been taken and are shown in Figs. I, II and III.

The writer believes that the wool fat substitute described in this paper will stand competition with wool fat and "Eucerin," both now and under normal conditions.

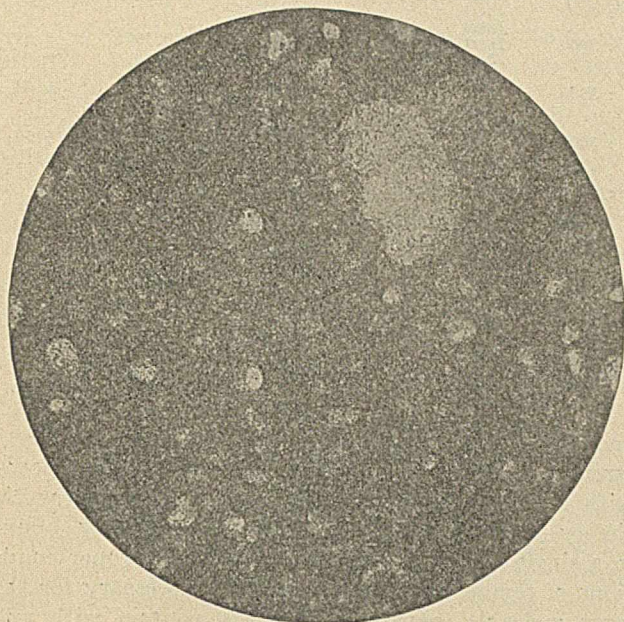


FIG. III—COLD CREAM $\times 100$
80 to 90 Per Cent Cheaper than Hydrus Lanolin

A further investigation is under way to determine the value in the preparation of a wool fat substitute, of ceryl alcohol, $C_{27}H_{56}OH$, from Chinese wax and myricyl alcohol, $C_{30}H_{61}OH$, from Carnauba wax.

In conclusion, due credit is hereby given to Mr. Sol. Bernstein, who spent considerable time in performing experiments and assisting in general to bring this paper to a successful issue.

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THE RENNETIC PROPERTIES OF PEPSIN

By HOWARD T. GRABER

Received August 29, 1917

Physiological chemistries teach us that the gastric juice consists of hydrochloric acid, inorganic chlorides and phosphates, together with mucin and the enzymes pepsin, gastric lipase and gastric rennin.

The theory as to the source of the proteolytic activity and the milk-curdling property of the juice has not been explained satisfactorily so as to be acceptable to all.

Some physiologists claim that these two properties reside in a single substance and that the milk-curdling and protein-hydrolyzing activities are present in definite and distinct side chains of a single mammoth molecule; others claim that the two properties are due to two definite and distinct enzymes secreted by separate and distinct glands.

The scarcity of the calf rennet, both in extract and powder forms, due to the foreign situation, made it imperative that a substitute be obtained if the cheese-making industry were to be perpetuated. It was natural to turn to pepsin from the hog stomach for such a substitute. The first experiments were somewhat disappointing. Our custom had been, in the assaying of the calf rennet,¹ to determine the amount of rennet necessary to curdle a definite quantity of *sweet, unpasteurized* milk in a definite period of time at a definite temperature.

When this same technique was applied to the assay of pepsin for its rennetic power, it was found that our results were not comparable. A pepsin solution which has a rennetic value of 100 per cent by our arbitrary standard did not have a strength of 50 per cent when it was diluted 50 per cent with distilled water, and in like manner a pepsin scale having a power of 100 per cent, diluted 50 per cent with milk sugar or other similar diluent, did not possess a rennetic power of 50 per cent its original strength.

This was contrary to the action of the calf rennin, which always showed an activity in proportion to its dilution.

Inasmuch as acid is an activator for the proteolytic hydrolyzing power of pepsin, it was natural to assume that our lack of uniformity in our rennetic assays was due to variations in the acid concentrations of the solutions being assayed. Experiments proved this theory correct and it was found that when the pepsin dilutions were brought back to the original acidity of the undiluted solutions our results became more concordant. The next step was to consider the reaction of the milk and to adjust it to a definite acid concentration. When this precaution was taken, the results proved to be as comparable for judging the rennetic property of pepsin as for calf rennet.

The technique observed now in judging a sample of pepsin for its milk coagulative power is the same as previously published for rennet, with the addition that the acidity of the *sweet, unpasteurized* milk is brought to 0.185 by the addition of q. s. pure lactic acid.

To illustrate the above points, I have appended the following experiments. These experiments include the determinations of the E. M. F. and P^H values, as well as the acid titrations, of the *sweet and adjusted* milk, together with the period of coagulation.

EXPERIMENT 1—The milk had developed a high state of acidity before reaching the laboratory. The acidity 0.294 developed during a thunderstorm while the milk was held in the ice box.

¹ THIS JOURNAL, 8 (1916), 909.

| SWEET (UNADJUSTED OR UNPASTEURIZED MILK) | | | | | Coag. | | MILK ADJUSTED | | |
|--|-----------|-------|------------------|----------------|------------|-----------------|---------------|------------------|-------|
| No. | Date 1916 | pH | Acidity Per cent | R _x | Strength | 1 : 30,000 Min. | in Min. | Acidity Per cent | pH |
| 1..... | 9/ 7 | 5.277 | 0.22 | 4415 No. 2 | 1 : 3000 | 3.75 | 3.75 | 0.294 | ... |
| 2..... | 9/ 8 | 6.581 | 0.16 | 4416 No. 4 | 1 : 3000 | 2.75 | 2.0 | | |
| | | | | 4893 No. 1 | 1 : 10,000 | 0.9 | 0.5 | 0.19 | 6.21 |
| | | | | 4893 No. 2 | | 2.8 | 1.5 | | |
| 3..... | 9/15 | 6.56 | 0.135 | 5532 | 1 : 3000 | Inert | 4.0 | | |
| | | | | 5528 No. 2 | 1 : 3000 | Inert | 1.75 | 0.17 | 6.34 |
| | | | | 5470 | 1 : 3000 | Inert | 2.0 | | |
| 4..... | 9/18 | 6.33 | 0.1425 | Elix. Pepsin | 1 : 3000 | Inert | 1.25 | | |
| | | | | 4468 | | Inert | 2.0 | | |
| | | | | Elix. Pepsin | | Inert | 1.5 | 0.1975 | 5.857 |
| | | | | Elix. Pepsin | | 3.61 | 1.0 | | |
| 5..... | 9/19 | 6.49 | 0.1475 | Scale, No. 1 | 1 : 3000 | 3.12 | 0.75 | | |
| | | | | Elix. 5446 | | Inert | 2.75 | 0.205 | 6.04 |
| | | | | Elix. 5447 | | Inert | 3.5 | | |
| 6..... | 9/20 | 6.41 | 0.15 | 5579 | 1 : 3000 | Inert | 1.5 | | |
| | | | | 5580 | | 30 | 8.25 | 0.2075 | 6.17 |
| 7..... | 9/22 | 5.70 | 0.1525 | 4422 No. 6 | 1 : 3000 | Inert | 6.25 | | |
| | | | | 4420 No. 3 | 1 : 3000 | Inert | 1.25 | 0.2075 | 5.784 |
| 8..... | 10/ 2 | 6.3 | 0.14 | 5520 No. 7 | 1 : 3000 | Inert | 1.0 | | |
| | | | | No. 8 | 1 : 3000 | Inert | 2.25 | 0.19 | 5.5 |
| | | | | 4420 No. 3 | 1 : 3000 | Inert | 2.5 | | |
| | | | | 4422 No. 6 | 1 : 3000 | Inert | 1.0 | | |
| 9..... | 10/ 4 | ... | ... | 5808 No. 2 | 1 : 3000 | Inert | 1.0 | | |
| | | | | 5627 | 1 : 3000 | 30 | 14.5 | 0.20 | ... |
| | | | | 5579 | 1 : 3000 | 20 | 6.5 | | |
| 10..... | 10/ 6 | ... | 0.13 | Sol. No. 1 | 1 : 3000 | 30 | 9.25 | | |
| | | | | No. 2 | | Inert | Less than 1 | 0.20 | ... |
| | | | | No. 3 | | Inert | Less than 1 | | |
| | | | | No. 4 | | Inert | Less than 1 | | |
| 11..... | 10/20 | ... | 0.145 | 4420 No. 3 | 1 : 3000 | Inert | 1.75 | 0.18 | ... |
| | | | | No. 4 | | Inert | 2.25 | | |

EXPERIMENT 2—This test illustrates the question of dilution. When the 1 : 10,000 pepsin was diluted with 7 parts milk sugar, it was apparently inert when tested on sweet milk of 0.16 per cent acidity, but when the same milk was brought to an acid concentration of 0.19 per cent lactic acid the pepsin dilution was found to test 1/8 as strong as the original.

EXPERIMENT 3—In this assay the three scales were apparently inert in milk of 0.135 per cent acidity, also one fluid drachm of the elixir failed to coagulate one quart of milk. When the acidity of the milk was brought to 0.17 per cent, coagulation readily took place.

STRENGTHS OF MIXTURES USED

- EXP. 2. Rx 4893 No. 1=1 part 4893 + 2 parts Milk Sugar
Rx 4893 No. 2=1 part 4893 + 7 parts Milk Sugar
- EXPS. 3, 4 AND 10. Elixir Pepsin=1 fluid drachm contains 2.5 grs. 1 : 3000 Pepsin.
- EXP. 6. Rx 5580=1 part 1 : 10,000 Pepsin + 7 parts Milk Sugar.
- EXP. 11. Rx 4420 No. 4=1 part 4420 No. 3 + 4 parts Milk Sugar

CONCLUSIONS

The foregoing experiments seem to indicate that the substance which gives the rennetic property to pepsin is not the same substance which gives this property to the calf rennin. It has been shown that it is necessary to activate the pepsin by means of acid before it shows its rennetic power in its proper degree. The adjustment of the milk to a definite acid concentration also aids the coagulation by calf rennet, but the great difference between pepsin and calf rennin in this respect is that calf rennin never fails to coagulate *sweet milk* or to give comparable results upon dilution, while pepsin fails more often than it produces coagulation on perfectly sweet milk. Another great difference is that pepsin acts best on very ripe milk, even to an acidity of 0.2 per cent or more, while rennin is not favored by such a high acid concentration.

Considering the above facts, together with the additional notation that in pepsin these two properties, the milk-curdling and proteid-hydrolyzing, have never been isolated, so that we have in the one case an

enzyme of high curdling power with no proteolytic strength, and in the other a high proteolytic power with no coagulative strength leads me to accept the theory that these two activities are closely bound in a single molecule, and that under the proper conditions of temperature, etc., it is only necessary for this large molecule (pepsin) to come in contact with milk and acid, or protein and acid when the respective activities of milk coagulation or protein hydrolysis takes place.

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A METHOD FOR THE DETERMINATION OF ALCOHOL

By C. J. HAINES AND J. W. MARDEN

Received June 21, 1917

The fact that so many methods have been suggested for the determination of alcohol is indicative of much to be desired in the speed and ease with which determinations can be made. The specific gravity method with which accurate results can be attained and which is most popular cannot in general be applied to liquids other than pure alcoholic solutions. This paper has been prepared suggesting a method which does not require in many cases the distillation necessary to specific gravity determinations, in the hope that the results may be of value in analytical chemistry.

Frary¹ and others have observed that potassium fluoride or potassium carbonate when added to alcoholic solutions will cause the alcohol to separate from the remainder of the solution, that is, that aqueous solutions of potassium fluoride or potassium carbonate are immiscible with alcohol. Frary has suggested a method based on these observations for the determination of ethyl alcohol by the use of potassium fluoride. The method is to add sufficient of the salt (carefully weighed out) to an alcoholic solution in a glass-stoppered cylinder to cause the alcohol to separate, add an in-

¹"Studies in Chemistry, No. I," University of Minnesota, 1912.

indicator (phenolphthalein) which colors the alcoholic solution and then gradually add water with frequent shaking till the two layers just disappear and the two liquids become completely miscible. From the weight of liquid (which is then determined) and the weight of the salt, Frary finds the percentage of alcohol from a table which he has prepared. He finds that the separation of alcohol by means of potassium fluoride is apparently quite independent of ordinary laboratory temperature conditions.

There are various objections to this method. The potassium fluoride must be perfectly dry and pure. Also, after the analyst has made such a titration as is suggested above, made the weighings and used the table he has consumed much time. It seemed at the outset of the present work that, if the salting out of the alcohol was quantitative, the entire volume of alcohol could be separated and that the process would be much simpler if the percentage by volume were read off directly.

METHOD OF DETERMINATION

The determinations were made at first in graduated tubes of 15 cc. capacity which had been prepared by cutting off 50-cc. gasometer tubes and later in centrifuge tubes of the same capacity. The tubes were all graduated to 0.1 cc. and before use were carefully calibrated with water. In every case the readings were estimated to 0.01 cc. In a determination, 10 cc. of alcoholic solution at 15.6° were used where the concentration was less than about 50 per cent, but where the concentrations of alcohol were greater than this, 5 cc. were taken and the volume made up to 10 cc. in the tube. Potassium fluoride was then added till the tube read about 13 cc. It was found by trial that this gave sufficient of the salt to saturate the solution. A small crystal of malachite green was dropped in which served to color the alcohol layer so that the volume could be easily read. Various substances could be used for this purpose such as a small piece of phenolphthalein, iodine, etc., but the malachite green proved quite satisfactory giving no color to the aqueous potassium fluoride solution. The tubes were then closed with a tight-fitting stopper and shaken vigorously for perhaps 2 minutes. If the potassium fluoride is dry the solution warms up but when placed in the centrifuge for 2 or 3 minutes, cools down to about room temperature. The alcohol separates in the upper layer while the excess of solid salt settles to the bottom of the tube. From the volume of alcohol observed and the volume of alcoholic liquid used for the determination, the percentage of alcohol by volume is readily found. Since one cc. of this alcohol changes about 0.001 cc. per degree Centigrade at room temperatures, the volume can be corrected to 15.6° if so desired. It was found by experiment that the potassium fluoride did not precipitate quite the last traces of alcohol and when the readings were made from the bottom of the meniscus it was necessary to add 0.15 cc. to observed readings to allow for this and the amount of alcohol adhering to the sides of the tube.

ANALYTICAL RESULTS

Tables I and II are given to show the results obtained by this method of analysis. The first series of determinations was made on pure aqueous alcoholic solutions, the concentrations of which had been carefully determined by the specific gravity method at 15.6°, Table I. A one per cent alcoholic solution just shows the presence of alcohol by this method.

TABLE I—ALCOHOL DETERMINATIONS IN AQUEOUS SOLUTIONS BY POTASSIUM FLUORIDE METHOD CORRECTED TO 15.6° C.

| No. | —ALCOHOL USED— | | CC. 100 PER CENT ALCOHOL | | Dif- ference | PER CENT ALCOHOL FOUND |
|---------|----------------|---------------|--------------------------|-------------|-----------------|------------------------------|
| | % by volume | Actual Cc. | In volume used | As Found | | |
| 1..... | 95.34 | 5 cc. | 4.77 | 4.71 | -0.06 | 94.2 |
| 2..... | 82.0 | 5 cc. | 4.10 | 4.11 | +0.01 | 82.2 |
| 3..... | 75.71 | 5 cc. | 3.79 | 3.87 | +0.08 | 77.4 |
| 4..... | 67.69 | .5 cc. | 3.38 | 3.40 | +0.02 | 68.0 |
| 5..... | 57.84 | 5 cc. | 2.89 | 2.84 | -0.05 | 56.8 |
| 6..... | 41.84 | 5 cc. | 2.09 | 2.07 | -0.02 | 41.4 |
| 7..... | 30.4 | 10 cc. | 3.04 | 3.09 | +0.05 | 30.9 |
| 8..... | 18.48 | 10 cc. | 1.85 | 1.88 | +0.03 | 18.8 |
| 9..... | 12.4 | 10 cc. | 1.24 | 1.28 | +0.04 | 12.8 |
| 10..... | 5.0 | 10 cc. | 0.50 | 0.53 | +0.03 | 5.3 |
| 11..... | 1.26 | 10 cc. | 0.12 | 0.15 | +0.03 | 1.5 |

Values read from bottom of meniscus and 0.15 cc. added.

Table II shows the analysis of various substances for alcohol. In nearly all cases the alcohol was determined directly, but in several analyses precipitates were formed when the fluoride was added. In such cases the alcohol was distilled and the determinations made on the distillates. Whiskey was successfully analyzed after clarifying with alumina cream.

TABLE II—ALCOHOL DETERMINATION IN DIFFERENT SUBSTANCES CORRECTED TO 15.6° C.

| No. | SUBSTANCE ANALYZED | Cc. Used | 100% ALCOHOL FOUND BY | | % Alcohol FOUND by | | Difference Per cent |
|-----|-----------------------------|-------------|--------------------------------------|-----------|--------------------------|-----|------------------------|
| | | | K ₂ F ₂ Cc. | % by vol. | Sp. Gr. Method | | |
| 1 | Alcohol (denatured)..... | 5 | 4.7 | 94.0 | ... | ... | ... |
| 2 | Beer (a)..... | 10 | 0.43 | 4.3 | 4.1 | ... | +0.2 |
| 3 | Beer (a)..... | 10 | 0.45 | 4.5 | 4.2 | ... | +0.3 |
| 4 | Cider (a)..... | 10 | 0.50 | 5.0 | 5.28 | ... | -0.28 |
| 5 | Hair tonic (a)..... | 5 | 1.45 | 2.0 | 29.4 | ... | -0.4 |
| 6 | Tincture of Iodine (a)..... | 5 | 4.55 | 91.0 | ... | ... | ... |
| 7 | " "..... | 5 | 4.73 | 94.6 | 95.0 | ... | -0.4 |
| 8 | " "..... | 10 | 4.74 | 47.4 | 47.5 | ... | -0.1 |
| 9 | " "..... | 10 | 2.35 | 23.5 | 23.75 | ... | -0.25 |
| 10 | Tincture of Iron (b)..... | 5 | 4.73 | 94.6 | 95.0 | ... | -0.4 |
| 11 | " "..... | 10 | 4.74 | 47.4 | 47.5 | ... | -0.1 |
| 12 | Vanilla Extract (a)..... | 5 | 1.35 | 27.0 | 27.65 | ... | -0.65 |
| 13 | Whiskey (b)..... | 5 | 2.50 | 50.0 | ... | ... | ... |
| 14 | Whiskey (a)..... | 5 | 2.50 | 50.0 | 50.0 | ... | ... |

(a) After distillation. (b) Before distillation.

CONCLUSIONS

I—A method has been proposed for the easy, rapid determination of ethyl alcohol which, if care is observed in reading the tubes, gives a fair degree of accuracy. The potassium fluoride used is inexpensive and need not be purified. It is best to dry this substance but small amounts of moisture in it do not affect the results.

II—The method cannot be used for solutions containing less than 1 or 2 per cent of alcohol or where other organic liquids are present such as acetone, essential oils, etc.

It might be pointed out, however, that in a solution such as the tincture of iodine the determination is very simple. The iodine solution is placed in the tube, the potassium fluoride added, the tube shaken, centrifuged, and the volume of the alcohol (which contains the iodine in solution) read. The iodine in the solution seems to have little effect on the volume of the alcohol.

ADDRESSES

"DOING OUR BIT"¹

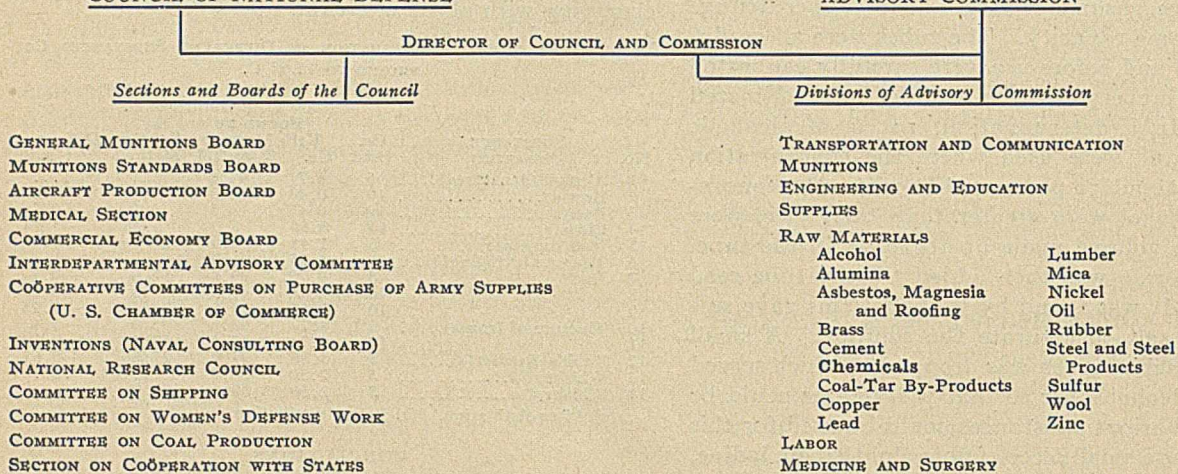
By BERNHARD C. HESSE

The American chemist, in common with all other good Americans, has his "bit" to do not only during the period of the war but also when peace returns. It is more than likely that we shall find new conditions when this war is over and to meet them we chemists will have to work along lines quite different from those to which we had theretofore been accustomed. Therefore, it can be only prudence and good policy to discuss now, in a more or less general way, just what these conditions may be and what may be the general modes of meeting them, and it is with this problem that we are now concerned.

THE PUBLIC AND SCIENCE

The general public has now realized as never before the important part that can be and in fact is played in matters of national aggression and of national defense by those who create, disseminate and apply science. There is hardly a single one of the many divisions and subdivisions of our Council of National Defense and of our National Research Council that does not call for a new application of some branch of science in one form or another. Every branch of our varied activities which pertains to the transporting, housing, feeding and equipping of our soldiers

TABLE I—ORGANIZATION OF THE NATIONAL COUNCIL OF DEFENSE AND THE ADVISORY COMMISSION



both here and abroad has to meet new and untried conditions; many of these are themselves the direct offspring of scientific knowledge, and have to make a demand upon sciences not only in their applied forms but in many cases in their pure forms; among the sciences so called upon, chemistry has been prominent.

It is inevitable that when peace does return, this new realization of the general public will not be at once laid aside. Further, it is inconceivable that, impressed as it now is with the potential and actual power of science in war, the public will not conclude that science must have equally great potential beneficial effect on peace-time pursuits and development and demand the full realization of those potentialities. This attitude of the public mind is of great importance and is something which should not be permitted to perish or to fall into decay. Unless those of us who are engaged in creating or in disseminating or in applying science make every effort to realize these fundamentally correct expectations of the public we can hardly expect their continuance, and the result will be that sooner or later and, as a nation, we shall be at a disadvantage with respect to those peoples who are not remiss in that direction.

¹ Address before the Chemical Society, Massachusetts Institute of Technology, Boston, Mass., November 22, 1917.

PUBLIC OPINION AND NATIONAL EFFORT

In our democratic government public opinion is, in general and usually, the source and fountain-head of all our governmental and national activities; whatever governmental machinery we have is here for the benefit of the public and the public is not at all here for the benefit of any of our governmental machinery. Except in times of stress we do not take orders from our government; it is our habit to give orders to our government.

We can give orders only if we have a well grounded and well founded public opinion upon which to base them and by which to give those orders force and effect.

The public is now in more sympathetic attitude towards science than ever before and it has singled out the science of chemistry as one of its especial hopes and supports, both in war and in peace. Every one of us must take hold with a will and do his level best to the end that this valuable national asset of a sympathetic public opinion and a favorable public attitude of mind be not withdrawn from us. We are the custodians of a most valuable trust and our responsibilities are co-extensive with our opportunities.

THE CHEMIST IN THE LIFE OF THE NATION

Impressed as we are with the magnitude of our task and with

the seriousness of our responsibilities let us consider the situation in some detail. Now as to the problem and its scope.

In the first place, what is our position in the general scheme of affairs of our nation? The diagram of the early organization of the Council of National Defense is probably the most complete, authoritative and effective answer we can to-day obtain. A skeleton of it is given in Table I.

In the second place, what is the general position of the chemist in the industrial activities of our nation? Broadly and fairly speaking it can be said that the chemists make up about *one tenthousandth* of our population and that in their various industrial activities they are connected with industries that employ roughly *one-sixth* of our industrial wage-earners, produce about *one-fourth* of the value of our manufactured products and about *one-fifth* of the value added by manufacture; in our foreign trade in 1913 with Germany alone in products of and for chemical industries these made up *one-twentieth* of our total international trade and provided *one-seventh* of our balance of trade.

To take only a very few from a great many striking examples of the chemist's activities it may be said that he has added between \$10 and \$12 to the value of each bale of cotton grown, has invented or discovered, made and marketed over 100 different

commercial products from corn and for these he uses as much corn as is produced in North Carolina or is produced by the nine states of Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut, New York, New Jersey and Delaware combined.

Many industries flourished for centuries before chemical knowledge and chemical treatment, as we understand them to-day, were applied to them and these are to-day brought to an efficiency, economy and diversity of production by the chemist, which without the chemist would have been impossible; such are those of leather, soap, iron, copper, textiles of all kinds, paints, varnishes, fats, paper, glass, stoneware and porcelain; there is also a large number of industries which were literally created by the chemist during the past 75 years, such as artificial fertilizers, fuel-gases, gas-lighting, photography, explosives, illuminating oils, carbide, aluminum, carborundum, dyes, medicines and in all but a very few of these the American chemist has taken a leading part and there is no reason why he should not keep right at it.

What the limits of chemical industry are, must in the very nature of things be vague but nevertheless more or less closely following that undefined thing called usage. One thing is certain, it does not include every industry making or using products of chemical change for that would include almost all human activities; it can no more be so inclusive than could every industry that employs or profits by the use of arithmetic be called a mathematical industry. Of course, there are many different accepted usages, but for present purposes the usage of the United States Census will be followed.

Coming now to more precise matters and taking the classification of the U. S. Census for 1909 as a criterion of what constitutes chemicals and allied products we find that these are nine in number, namely:

- 1—PAINT AND VARNISH
- 2—CHEMICALS
- 3—FERTILIZERS
- 4—EXPLOSIVES
- 5—DYESTUFFS AND EXTRACTS
- 6—SULFURIC, NITRIC AND MIXED ACIDS
- 7—WOOD DISTILLATION (NOT INCLUDING ROSIN AND TURPENTINE)
- 8—ESSENTIAL OILS
- 9—BONE, CARBON AND LAMPBLACK

From the 1909 census data it appears¹ that "if we compare the average chemical plant with the average plant in all domestic industries that the average chemical plant, when so contrasted, costs 330 per cent of that general average, employs 144 per cent as many persons of which the salaried employees are 264 per cent of the general average and the wage earners 134 per cent; the output value is 261 per cent of the general average and its enhancement in value is 248 per cent. Therefore, as a unit, the average domestic chemical plant costs more, produces more, enhances more, employs more salaried persons and more wage earners than the average industrial plant.

"A dollar invested in our chemical industries is not so productive as in our industries as a whole; it spends less for wages, salaries and materials and produces less product-value and less enhancement-value.

"Per \$100 of product, the general average and the average domestic chemical plant, respectively, expend \$16.58 and \$9.09 for wages, \$4.54 and \$5.65 for salaries, or \$21.12 and \$14.74 for services.

"Per individual wage earner the annual output of product is \$3,125 for the general average and \$6,035 for the average domestic chemical plant.

"Per individual salaried employee, the annual output of product is \$26,157 for the general average and \$25,733 for the average domestic chemical plant.

"The average salaries are \$1188 and \$1455, respectively, for our

industries as a whole and our domestic chemical industries; the average wages are \$518 and \$549, respectively; in the industries as a whole there are 8 wage earners to each salaried employee and in our chemical industries there are 4 wage earners to each salaried employee.

"Relatively, our chemical establishments are 0.79 per cent of all our industrial establishments and the number of persons employed is 1.15 per cent of all persons employed in manufacture.

"Hence while an average chemical plant, as such, is of greater importance to the community than the average industrial plant, yet the capital so invested is not so productive as in the average industries."

PEACE TIME GROWTH OF OUR CHEMICAL INDUSTRIES

That these nine branches of the U. S. industries of chemicals and allied products are increasing actually as well as relatively to our entire industrial activities as a whole is one of the gratifying facts shown by the U. S. Census figures for 1914 only recently available. The actual figures are given in Table II; the growth is evidenced by the percentages.

Another gratifying disclosure of the 1914 census is that the groups of chemicals and allied products have been increased in number and scope and to the nine groups above enumerated and considered the following 17 have been added:

- 1—Baking Powders and Yeast
- 2—Blackening, Stains and Dressings
- 3—Bluing
- 4—Candles
- 5—Cleansing and Polishing Preparations
- 6—Coke (not including Gas-house Coke)
- 7—Drugs (including Drug Grinding, Druggists' Preparations, Patent Medicines and Compounds, Perfumery and Cosmetics)
- 8—Gas, Illuminating and Heating
- 9—Glue, not elsewhere specified
- 10—Greases (including Grease and Tallow, Lubricating Greases and Soap Stock)
- 11—Printing Ink
- 12—Writing Ink
- 13—Cottonseed Oil and Cake, Linseed Oil, Fish Oils, Oleo and all other oils have been added to Essential Oils
- 14—Petroleum, refining
- 15—Salt
- 16—Soap
- 17—Turpentine and Rosin

This is a very gratifying state of affairs particularly if we bear in mind that the 1914 census covers the fiscal year ending with June 30, 1914, or about one month before the present war broke out. It shows that domestic capital before the war was taking more to these chemical and allied industries than to our industries in general; that the compilers of the census have become convinced that the chemical and allied industries had therefore been too narrowly defined. That can only mean that prior to this war we had obtained greater official and hence public recognition of the chemist's influence in the nation's business and that domestic capital had of its own accord increased its confidence in our business as a business.

To give an idea of what this classification-expansion of "Chemical Industries" means to the U. S., statistical position of the "Chemical Industries," Table III has been compiled.

Because of the absence of information as authentic and as carefully checked, sifted and arranged as are these figures from the U. S. Census reports no profitable effort can now be made to measure the present effect of the war on these industries; to do so we must wait until such data are available.

ONE EFFECT OF THE WAR

Since the outbreak of the war, in addition to the many departments of the Federal Government which previously were engaged in applying and developing chemistry and our chemical industries for national benefit, there have been created a number of Federal agencies of national scope whose aim is, among others, to bring out promptly and efficiently the whole of our chemical science

¹ THIS JOURNAL, 8 (1916); 1050.

TABLE II—GROWTH OF AMERICAN CHEMICAL INDUSTRIES 1909 TO 1914

| ITEM | ALL INDUSTRIES | | CHEMICAL AND ALLIED PRODUCTS | | PER CENT INCREASE 1914 OVER 1909 | | Per cent of the Whole in Chemicals & Allied Products | | Per cent Increase in 1914 over 1909 of Per cent of Whole in Chemical & Allied Products in 1909 |
|--|------------------------------------|------------------|------------------------------------|---------------|----------------------------------|----------------------------|--|------|--|
| | 1909 | 1914 | 1909 | 1914 | Indus-tries | Chemical & Allied Products | 1909 | 1914 | |
| 1 No. of Establishments..... | 268,491 | 275,791 | 2,140 | 2,461 | 3 | 15 | 0.79 | 0.89 | 13 |
| 2 No. of Wage Earners (Av.).... | 6,615,046 | 7,036,337 | 70,426 | 86,788 | 6 | 23 | 1.06 | 1.23 | 16 |
| 3 Capital..... | \$18,428,269,706 | \$22,790,979,937 | \$483,729,410 | \$722,989,000 | 24 | 49 | 2.62 | 3.17 | 21 |
| 4 Wages..... | 3,427,037,884 | 4,078,332,433 | 38,658,201 | 53,021,000 | 19 | 37 | 1.13 | 1.30 | 15 |
| 5 Materials..... | 12,142,790,878 | 14,368,088,831 | 258,115,975 | 340,218,000 | 18 | 32 | 2.13 | 2.37 | 11 |
| 6 Value of Products..... | 20,672,051,870 | 26,246,434,724 | 425,084,540 | 547,802,000 | 17 | 29 | 2.06 | 2.09 | 1 |
| 7 Value Added by Manufacture (Item 6 less Item 5)..... | 8,530,261,000 | 9,878,345,893 | 166,968,565 | 206,864,000 | 16 | 24 | 1.96 | 2.10 | 7 |
| Column..... | A | B | C | D | E | F | G | H | J |
| NOTE—Percentages given above were obtained as follows: | E = $\frac{(B - A) \times 100}{A}$ | | F = $\frac{(D - C) \times 100}{C}$ | | G = $\frac{C \times 100}{A}$ | | H = $\frac{D \times 100}{B}$ | | J = $\frac{(H - G) \times 100}{G}$ |

and industries for the good and the safety of the nation. Among these are the National Defense Council, the National Research Council, the Naval Consulting Board, the War Trade Board, the Tariff Commission and others all supplied with chemical advisers, while all the earlier Federal agencies have intensified their efforts and enlarged their scope. In addition thereto, members of the chemical faculties of almost every one of our universities, technical schools and colleges are working with governmental departments and with industrial enterprises in positions and on subjects and in a manner heretofore never known and the American chemist is to-day in better position than ever before to obtain sympathetic interest and action in any proposition he may have that looks toward national benefit. Most, if not all, of our states, and many of our cities, have similarly provided for intensified chemical aid. We have therefore, through this war, progressed along the line of coöperation between our governmental agencies, Federal, state and municipal, our universities and our industries to an extent almost inconceivable in its power for national welfare.

CHEMICAL SOCIETIES AND THE GOVERNMENT

On the other hand, all our chemical and allied associations and societies, whether business, scientific or technical in their aims and objects, have whole-heartedly placed all their resources and information at the disposal of our various governmental agencies; not the least among these societies is the AMERICAN CHEMICAL SOCIETY with a membership well beyond 10,000, meeting in 53 Local Sections throughout the country and conducting its affairs in 8 technical and similar Divisions. In order to assure as far as possible that in such a multitude of organizations there shall be a minimum of duplication of effort and lost motion the AMERICAN CHEMICAL SOCIETY has recently created a special committee to direct the participation of that Society in all matters of national scope and with this committee the expectation is that the President of the American Chemical Society will be in better position than otherwise to give prompt effect to any meritorious suggestions that may be made to him. There are therefore many avenues through which the individual American chemist can get national action on his suggestions. Other societies have made similar provision.

Thus it is clear that not only did we have in 1914 a wider public recognition and a greater confidence of capital in us than in 1909 and that both have grown greatly since the outbreak of the war but also that all our governmental and private agencies have since then immensely increased the points of contact and the avenues of communication between the chemist, the public and our governmental agencies. As individuals we also have added machinery in our hands wherethrough to direct and shape the course of events and to prevent what might ultimately become, first, a chemical bureaucracy and finally a chemical autocracy in this country. We thus have each of us our clear and well-defined duties, responsibilities and opportunities.

PROMPTNESS AND EFFICIENCY

All of our efforts are, however, bound to be vitiated if we are not at all times mindful of the fact that unless we and each of us do our share promptly and efficiently that the whole national effort cannot fully succeed; the net result can hardly be better than its poorest component nor completed faster than its slowest part. Hence, our watchword should be at all times: "Accuracy, Completeness and Despatch." The student in the classroom is no more exempt from it than is the faculty-member, the corporation head or the government official; in that respect we are each and all of us in the very same boat.

Having thus briefly summarized the position of the chemist in the public mind, in the government's view, in the view of domestic capital and in our national industrial life and having described the avenues through which the chemist can work and the agencies upon which he can draw, what is he to do? What is the problem?

"OUR BIT"

For the period of the war all our national activities will be directed toward immediate national needs largely, with only relatively small attention to after-the-war matters, and for these sufficient directing machinery exists and it is merely a question of selecting the right means.

In the period after the war and in the rush and stress of rebuilding and making up for lost opportunities in the multitudinous directions offered, the chemist is likely to be lost sight of unless he systematically and continuously plans ahead and prepares accordingly. Broadly considered, our future activities can be classified as relating to:

- 1—Matters of national defense.
- 2—Development of our natural resources.
- 3—The highest national independence possible in chemicals and allied products.

KEEPING PUBLIC INTEREST ALIVE

In order to accomplish the above-mentioned ends we must make sure that we do not lose our place in public opinion nor the confidence of capital nor the helpful attitude of our governmental agencies, legislative as well as administrative. To retain our place in public opinion we must take the public into our confidence much more than we have heretofore, and in this delinquency we are not alone; other countries and other sciences have been afflicted with the same shortsightedness. We must inform the public of such of our problems as are of public bearing in language as free from technicalities as possible and as a very valuable aid in that direction we now have through the PRESS AND PUBLICITY COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY the interested attention of a great many influential daily and other papers. Our scientific and technical societies everywhere should make an effort as does the AMERICAN CHEMICAL SOCIETY to have at least one meeting a year at which technical topics of interest to that ubiquitous and powerful person "the man-in-the-street"

TABLE III

| | 1914 RETURNS | | INCREASE | |
|-----------------------------------|---------------------------------|-----------------|----------------------------------|----------|
| | Based on Classification of 1909 | 1914 | DUE TO NEW CLASSIFICATION Actual | Per cent |
| 1 No. of Establishments..... | 2,461 | 12,374 | 9,913 | 403 |
| 2 No. of Wage Earners (Av.)..... | 86,788 | 299,569 | 212,781 | 245 |
| 3 Capital..... | \$722,989,000 | \$3,034,209,000 | \$2,311,220,000 | 320 |
| 4 Wages..... | 53,021,000 | 167,494,000 | 114,473,000 | 216 |
| 5 Cost of Materials..... | 340,218,000 | 1,289,348,000 | 949,130,000 | 279 |
| 6 Value of Products..... | 547,802,000 | 2,001,634,000 | 1,453,834,000 | 265 |
| 7 Value Added by Manufacture..... | 206,864,000 | 712,286,000 | 505,422,000 | 244 |

are presented in such a way as to receive and to hold his attention, and a readable digest of those proceedings will no doubt be very welcome in the editorial offices of most newspapers; if they are not welcome then there must be something wrong with the meeting, with the digest or with both, and the only thing to do is to go at it again.

Now, telling a technical story in non-technical language or thought is no easy matter, but all of us should endeavor so to frame our technical stories that they are free from such matter because we can none of us tell when we may be in position to render good service by such a story told in such a way. Personally, I very much suspect that we have not really mastered a technical subject unless and until we can make it understood by the willing but non-technical "average man." That ability is indispensable in creating and in holding public interest in any technical subject like ours, and since public opinion is formed wherever there is a public it behooves all of us to cultivate that ability to our utmost since we can never know when or where we can make it tell. For example, at any one of the National Expositions of the Chemical Industries, which promise to become a fixture in New York City every September, large opportunities of legitimately and helpfully adding to the public understanding and appreciation of the chemist's efforts are offered and the cumulative effect of such additions, if sound and clearly made, cannot help but be advantageous. Each of us in our ordinary routine has almost daily opportunity to aid the public thought in these matters. It should be our aim to prevent recurrence of any public apathy like that in England towards the dangers of synthetic indigo to the British indigo growing interests or in our own country when we were apprised in 1912 of foreign advances in fixing atmospheric nitrogen. This is merely preventing the chemist from crawling into his shell, *i. e.*, keeping him a human.

RETAINING THE CONFIDENCE OF CAPITAL

We shall retain the confidence of capital so long as we do not indulge in any wild schemes, so long as we keep our promises, promise no more than we can do, expose and condemn hare-brained schemes, of which there are plenty, and in general behave in a level-headed but optimistic and perhaps even enthusiastic manner. Most business ventures contain hazards but there are reasonable and unreasonable hazards, and we must exercise good judgment there; so long as we do that, capital, that is desirable capital, will not withdraw the confidence it has now given us. This is merely common-sense behavior.

OUR GOVERNMENTAL AGENCIES

Having public opinion calling for a complete and independent domestic chemical industry and capital in good standing behind us, with a fair and frank approach to them, our standing with our various governmental agencies, legislative and administrative, ought not and will not be a matter of conjecture. This is merely civic candor.

These sound trite and sophomoric, and no doubt they are. I should not have made these statements if, as a matter of fact, it had not taken this colossal nightmare of a war to shake us all awake and to bring us to our senses. We thought the public to blame and the public said we were to blame. Perhaps both were right. However, if we as a body refrain from acting along these simple general lines we need not be surprised

if sooner or later the old conditions return. It is our job to make the public take an interest in us; that, to my mind, is one of these war-lessons we should never forget; we have paid too high a price ever to let it get away. As I see it, it is of the greatest importance that, even in our college days, we should lay the foundations for these view-points and these rules of conduct.

THE NEED OF A COMPREHENSIVE PLAN

But all this will be of no avail unless we show vision, imagination, foresight, initiative, enterprise and strength of purpose on our own account. We shall have to inform ourselves very thoroughly of the country's requirements of chemicals and the like in war and in peace as to quantities and values and their uses and also their modes of manufacture and their needful raw materials; further, of our suitable natural resources, their nature, extent and location whether of vegetable, animal or mineral origin. Then we must plan wisely for the most efficient development and set about it. Sounds simple, does it not? But it is one of the tallest orders 10,000 men ever had handed to them.

A start has been made in the Norton Dyestuff Census published a year ago by the Department of Commerce. That tells us about the amounts, values and kinds of coal-tar dyes used and puts us in the way of getting at their raw materials and their uses. The reasonable expectation is that, through the initiative of the AMERICAN CHEMICAL SOCIETY, in about six months or a year from now we shall have a printed compilation giving us the names, quantities and values of every chemical other than coal-tar dyes imported into the United States from any country during the fiscal year ending with June 30, 1914, the last peace-year before the present war. Then comes the rest of it; the manufacturing methods, the needful raw materials and where they are located in this country and elsewhere, and in what industries these chemicals are used. Through the initiative of the AMERICAN CHEMICAL SOCIETY it is expected that this will also be completed within a reasonable additional time. After that, plans have to be made as to how, when and where these various things shall be made, and in deciding that there comes in the further question as to the importance of the individual chemicals to the nation's welfare, their arrangement in the order of their importance, and an efficient plan of making them at home. That is going to take some "midnight electricity."

GOVERNMENTAL HELP

Further, it is not inconceivable that some of these important things will not be made without added governmental help, as, for example, by increased tariff-protection. This will not be as difficult as heretofore for the very important reason that both principal political parties, Republican and Democratic, have by enacting the present dyestuff tariff emphatically affirmed sweeping, and let us hope lasting, changes in their heretofore views of tariff-legislation. The Republicans have in the past refused to help chemicals because they did not employ enough labor or because their products were "raw materials" for many industries that stood well in the eyes of that party largely because they did employ much labor. Now the Republicans admit that there are industries which are "key industries" because their products are "raw materials" for many industries and hence they should be made in this country and protected by tariff, if need be. The Democrats by levying for, I believe, the first time, a tariff avowedly for the purpose of creating an industry in this country

and necessarily thus potentially depriving the U. S. Treasury of a corresponding amount of revenue have also endorsed the "key industry" view-point.

But right in this comparative ease is where difficulties are going to come for us chemists. "Key-industries" is a new expression; just exactly and precisely where it begins and ends, no one yet knows. Merely because the Republicans and the Democrats have agreed that because coal-tar dyes constitute a "key-industry" and hence should be protected is a very long way from saying that they have agreed that every "key-industry" should be so protected, but it is a very tempting inference. It would be a peculiar kind of a product, chemical or otherwise, for which a more or less plausible argument of "key industry" could not be constructed. Unless we are very cautious we may find this "key-industry" notion a very unwholesome and treacherous thing. In presenting to Congress or to the Tariff Commission the "key-industry" claims of any particular thing, we shall have to be very circumspect and very frank and straightforward. I very much suspect that there may be times when this will be a severe test of our civic candor. Whenever we are sure that any such product really, or fairly so, is a "key-industry" in the sense of coal-tar dyes and in the manner that the 64th Congress viewed them then we must have sufficient strength of purpose to keep at Congress or the Tariff Commission or at both until they "see the light," for surely that is what public opinion now wants. When we believe that the country's welfare, as viewed by that public opinion, demands our industry and there is opposition to it, we must seek out that opposition and bring it down; that is not merely our privilege, it is our civic and professional duty.

THINKING IN TERMS OF THE NATION

In this same connection we shall all have to learn to think in terms of the Nation and have the map of the world in our minds as we study our chemistry and apply it to our industries. In order to do that our publications will have to make a change. None of our chemical journals systematically and in a form that lends itself to preservation, presents its readers with world-information, both detail and general, at any stated periods or in any correlated or coördinated way. In that respect we have much to learn from foreign chemical journals and particularly the German journals which, while they did it far better than others, still left a very great deal to be desired. Then, after our journals have made such a change you and I and all the rest of us will have to learn to read those statements. They are dry; but there is no help for it. It is a new language and a new job, but we have simply got to master it. Perhaps the AMERICAN CHEMICAL SOCIETY may be able to find a way to sugar-coat that pill and if it does, more of us may be induced to take it.

The Superintendent of Documents, Government Printing Office, Washington, D. C., will supply for cash or money order (stamps will not be received) any of the Government publications dealing with our domestic and foreign commerce. For domestic production the 714-page cloth-bound publication, entitled "Abstract of the Census of Manufactures—1914" (price, 65 cents); for our foreign import business, the 90-page paper-bound publication, known as "Summary Table No. 9 of the Annual Report on Commerce and Navigation" (15 cents) and for all the U. S. activities and as a whole the 749-page paper-bound publication entitled "Statistical Abstract of the United States" (50 cents) make a good starting point, not only for individual study in college or after, but for the majority of our chemical publications as well. If then we apply only a very small fraction of the industry we usually put on the statistics of our baseball players we ought very soon to show a marked increase in our knowledge and appreciation of the place chemical industry holds in the business and economic affairs of our Nation and of the world. All our publications must more systematically than heretofore help to disseminate in coördinated and more readily appreciated and preserved

form the vast amount of fundamental and valuable information collected by our Government. The Government cannot do it all; we as individuals have a share to perform.

OUR EDUCATIONAL INSTITUTIONS

But even with all this our task is not yet done. All these efforts will be of short life, from the point of view of the Nation, if we overlook or fail to encourage the science of chemistry in its purest forms as well as in its applied forms at our universities, colleges, and technical schools or if we overlook keeping them in the very forefront of educational efficiency. We must test and examine every scientific advance made anywhere as to its potential value for, or harm to, this country and act accordingly. It goes without saying that our chemical industries must each and all have their own research laboratories, whether individually or in groups, and these must be as well equipped and manned as any for it is not inconceivable that publication of research results in foreign countries hereafter may not be as unrestricted as it was before the war. Chemical fellowships like those of the Chemists' Club will, no doubt, be a welcome help in this direction.

OUR GOVERNMENT OFFICIALS

Nor would we be fully utilizing our opportunities of aid and help were we to overlook the various Federal governmental departments or committees of the AMERICAN CHEMICAL SOCIETY or other chemical societies that coöperate with them. Our Federal officials are more than ready at all times to help the Nation and if they have not in times past done all that we now think they should have done the blame for that rests squarely on our own shoulders—we simply have not told them, and perhaps have not even tried to tell them, how they could help or where and in what way we needed help in any such fashion as to make help on their part practical or practicable.

Successful chemical industry calls for dependable labor and therefore labor laws, workmen's compensation acts and the like will call for a good deal of our attention. Should we also have an eye on export business additional competent chemical members of our foreign trade and consular service will also be required.

COÖPERATION THE ONLY WAY

From this, of necessity sketchy and fragmentary outline, it is obvious that the American chemist has and will have a multitude of new things to engage his attention and that the only practicable way of handling them is through coöperation. Unless all signs fail there will be more of national coöperative effort throughout the world than ever before and we must shape our course accordingly. As a first-step student chemical societies like this one at "Tech" are to be highly commended and supported either as independent organizations or as sections of the AMERICAN CHEMICAL SOCIETY which has done so much to coördinate the efforts of American chemists in so many different ways and which is the best organized and the largest chemical society in the world. The trial now being made by the section of the AMERICAN CHEMICAL SOCIETY at Buffalo, New York, of affiliating and meeting with other local technical societies is a step forward and in the right direction. We should also seek out opportunities for coöperative effort with our educational and governmental institutions as well as with strictly commercial organizations such as Boards of Trade, Chambers of Commerce, Merchants' Associations, and the like, of local, state, national and of international scope. We must widen our horizon in every direction and we can do that only through coöperative effort, intelligent and persistent.

"THERE ARE OTHERS"

It must not be forgotten that the chemist is not the only one who was shown to be behindhand as a result of this war. A very good index of that is supplied by a recent and dependable statement that of the some 650 British enemy-owned patents under which license to operate had been granted British manufacturers under the British Trading-with-the-Enemy Act, only "some

scores' applied to the dyeing industry, while the remainder dealt with the following twenty arts, namely: leather substitutes; sewing machines for boots, etc.; wood impregnation; taximeters; turbine compressors and pumps; explosive engines; magnetic separators; treatment of waste paper and fibrous materials; reduction of ores; aluminum alloys; speed indicators; electric ignition apparatus; incandescent gas lamps; elastic bandages; embroidering machines; calculating machines; electricity meters; talking machines; internal combustion engines and printing machines. Quite a formidable list. It will be most instructive similarly to follow the course of events under our own recently enacted Trading-with-the-Enemy Law.

PATENTS AND INVENTIONS

The proper lesson for us to learn from this seems to me to be that whenever a foreigner patents anything anywhere we should really invent and make something better or just as good ourselves. It may, and no doubt will be expensive, but will it be more expensive to the Nation than our present situation has turned out to be? I say decidedly not. And this applies to others besides us chemists. It will certainly be better than tinkering with our patent laws. The proper answer to an invention is another invention and not a hamstringing or a boomeranging change in our patent laws.

CONCLUSION

This, then, presents, in rough outline, as I at present see it, our future and the work it holds for us; our work may fairly be said to be stupendous and it is made so wholly by the national complacency, not to say indifference, of our entire country's past. We must all make up for lost time and for lost opportunity. With an enlightened public opinion and a truly national spirit in our Federal legislation, the American chemist can safely and confidently be depended upon to do his full share, and more, toward making this country as independent of any other nation on earth as it is possible to be, and toward making our democratic government lastingly as efficient and as far-sighted as any autocratic government ever dreamed of being.

25 BROAD STREET
NEW YORK CITY

MERCHANDISE CONTROL LABORATORIES

By ELLWOOD HENDRICK

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An episode in the history of the Bureau of Chemistry of the U. S. Department of Agriculture may throw a little light on the progress and workings of private laboratories in the few mercantile concerns that have adopted chemical control.

The Pure Food Law was passed and it was necessary to have means to enforce it. The law and the courts were in existence but other machinery was needed. In the Bureau of Chemistry more inspectors were appointed, happily under civil service rules, for at the first examination for inspectors only 16 out of 1400 applicants passed. They then went about collecting samples and brought them into the department for analysis. They looked for breaches of the law and they found them; found them with increasing facility as they developed the art of search. Convictions were frequent. The question then arose whether increasing the number of convictions was the best and most useful work that the Bureau could do. The conclusion was reached that while this was a necessary part it was not the whole duty of the Department of Chemistry in the interest of general welfare. Various industries were studied from the standpoint of chemical control and producers of foods were informed how to avoid error and how to get the best results. Vigilant inspection makes adulteration dangerous while chemical supervision and aid improves the product. The government is not the enemy of honest producers but rather their friend. Chemical control goes far beyond police duty.

Now the introduction of chemical aid in mercantile establishments seems to develop in a similar manner as time and experience enrich their laboratory records. Foods and drugs are standardized by law; they are already under chemical control and we shall not even discuss the pharmaceutical trade for the obvious reason that it is already established in chemical technology. The same holds good in regard to the preparation and handling of meats, the great packing houses being models of efficiency in the administration of materials. The fisheries are in sore need of chemistry but the possibilities in the utilization of these products would not be within the scope of an article on merchandising.

In order to determine what advances have been made in this respect a number of large, progressive houses were visited. Of these several were entirely willing to display their laboratories and methods in the interest of science, but insisted that no special praise be accorded them for their accomplishments on the ground that it would smack of gratuitous advertising. I shall therefore make the record as impersonal as possible.

Foods, drugs and insecticides are under government supervision while most other merchandise is not, but as we proceed, I think it will be borne out that wherever efficient chemical control is instituted, there it stays, law or no law; and that those who maintain it would not do without it. A guaranty is a good thing in its way; it is a kind of free insurance policy thrown in with the goods. What is wanted of it is that it shall be passive, for, as a general rule, the better a guaranty is the less frequently is it brought into action. It is always an endorsement and therefore a liability. Chemical control on the other hand determines the status of the goods warranted; it fixes credit by the establishment of fact and it is therefore an asset.

A leading wholesale grocery house was good enough to give me the following outline of the functions of their laboratory, which speaks for itself:

1—Without a competently conducted laboratory we should not of our own knowledge know what we are selling.

2—Our laboratory is maintained for the protection of our customers, and in order to keep our qualities uniform.

3—Raw materials differ greatly in percentages of essential parts, so that to buy intelligently the make-up of each lot must be studied.

4—The greatest function of the laboratory is to safeguard purity and wholesomeness. The enforcement of Federal and State Food Laws must necessarily be based upon standards and these cannot but be of a technical nature. We must be certain that all food products meet legal requirements and thus conform with the iron-clad guaranty of the house that all its goods comply with all Food Laws. With a laboratory any contaminations are discovered.

5—The laboratory does creative work. New food products are constantly sought and many good ones are discovered. These are both simple and complex. In the latter class various food substances are mixed together. During the past three years several very successful combinations have been worked out.

6—The laboratory maintains records of all our drug supplies. The value of this is shown by a recent instance. A physician in a small town purchased of a customer several half pint bottles of Castor Oil. He complained that it was not U. S. P. From the markings on the bottle labels the lot was traced back to the identical original package for which there was complete analysis. This analysis was submitted to the physician with the suggestion that he also analyze the oil, and make a comparison. The result was a complete vindication of the product.

7—Another instance showing the value of the laboratory is the case of a customer who claimed to be able to purchase Pure Black Pepper at a considerably lower price than we were quoting. A sample was procured, and analysis showed the competing article to consist in large part of *Piper longum* instead of *Piper nigrum*. On our laboratory report the business of this customer was retained.

The creative or synthetic work calls for varying degrees of scientific application. To mix up fruits and spices until a sweetmeat is achieved that commands a successful sale may be more the job of a candy man than of a chemist, but you never can

tell. The line is hard to draw. It requires a chemist to prepare a permanent mayonnaise dressing in which the oil does not separate out, of which great quantities are now sold for salads as well as a substitute for butter for making sandwiches and the like in hotels and restaurants. Thirty-five cents worth of this mayonnaise has the spreading value of seventy cents worth of butter.

ADVANTAGES OF CHEMICAL CONTROL

Chemical control saves the day occasionally. A very large order for vanilla powder was given by a consumer who buys on specification and analyzes the product. For good measure and safety the goods were made up a little above specification in vanilla, but the whole shipment was declined on the ground that it was not up to standard. Details were not available except that analysis showed that the powder failed to reach specifications, but the refusal was very clear. A visit by the chemist to the purchaser's chemist and investigation into his methods brought out the fact that he had made the test for sucrose and let it go at that. The discovery that the vanilla content was above specification made the delivery acceptable.

Maple syrup, jams, preserves, olive oil and many other goods require constant supervision to substantiate guaranties and make them not only acceptable to the purchaser but profitable to the seller. One firm is planning to print the food value in calories on every package.

A good control laboratory is usually available for consultation to all department heads in addition to routine work in testing those classes of merchandise that may be accidentally or intentionally adulterated. To a concern that does a jobbing business, chemical control is of signal value.

Most manufacturers are conscientious and do the best they can, but the presence of the laboratory is like the policeman on the block; the occasional crook is more likely to try a house in some other locality than where the policeman is stationed.

A first-class house is very jealous of its good name and would rather spend a large sum than have its goods confiscated for deficiency in standard. The value of the laboratory comes in time and again to provide for the avoidance of this. For instance, whether an added chemical preservative is deleterious or not is not the question; if the label does not state that a parcel of goods contains it, it must not be present. In a certain state not long ago the charge was made of the presence of borax in mince meat and under the rigid control exercised it was known that none had gone in. The Commissioner held to his point. The analysis was followed up and the trace of borax proved, but the cause was found to be the raisins which were grown in an alkali soil in California, and such raisins are not taboo. The house demonstrated that borax had not been used as a preservative and avoided the penalty.

A good laboratory also works the other way. Last Spring the demand for macaroni was not only high but rampant. The market was bare. A manufacturer offered some for sale that had just the color of durum wheat, but alas, analysis showed coloring matter that does not grow in that cereal. The manufacturer knew better, and, being an emotional man, he offered to jump out of a seventh story window if the presence of foreign coloring matter could be proved to him. He was urged to spare his life while this factory was investigated. His foreman finally acknowledged that he had "just tried out a little color" on that particular batch.

Maple sugar is a stormy petrel in groceries but it has greatly improved since the Pure Food Law went into effect. The ash is characteristic, the acid is malic and the base is lime, but it can be imitated through the use of sucrose, glucose, burnt corn cobs and commercial maple flavoring extract. Grape juice calls for testing for added sucrose, glucose, preservatives and water. A few pails of water in a barrel of grape juice is easy money.

It has been found profitable to keep very complete records of analyses to meet a certain shortening of the memory from which some retailers occasionally suffer, when, under attacks of absent-mindedness, unsatisfactory goods are returned that were procured from other sources.

While the standard of 25,000,000 per cc. has been fixed as the bacterial count for tomato products by the Department of Agriculture, the ordinances stop here. It seemed wise to one organization in particular to get ahead of the game and apply laboratory cleanliness to their own manufacture of preserves, jams and jellies. Few manufacturers are clean in the laboratory sense. A good kitchen standard is as high as most of them reach, and spores multiply. The result of this forward step has been salutary. The factory staff now knows and understands moulds and ferments as it never did before; the quality of the goods has markedly improved and certain economies have been established. Figs, for instance, ferment so easily and persistently that large stocks of this raw fruit are never carried. Fruits are generally bought in season and placed in cold storage, but the demand can never be gauged with sufficient accuracy to determine whether the stock will last through the season or be used up by Christmas. It has been observed also that fruits change as the season progresses, even in cold storage, which has an important bearing on the making of jellies. A jelly that grows fluid is sure to be returned, whereas if it is too hard the housewife is very likely to refuse it on the ground that it is made with gelatin even though it does not contain gelatin. Control of this factor based on research enables jellies to be made and shipped within 24 hours and by freight at that, with all the rough handling that goes with it. The absolute control of jellies is thus an accomplished fact.

Research plays an important part in meeting legislative whimsies as well as in matters of general importance. For instance, when bone-dry laws came into force, soft drinks were suspect, being made with alcoholic flavors. In the present temper of the public mind one molecule of alcohol will almost ring the alarm. The 0.25 per cent content of alcohol in ginger ale might have been a tragedy. So the whole list from sarsaparilla to harvest-pop has had to be worked out to stand bone-dry laws.

From the foregoing it will be observed that the wholesale grocery trade is already acquainted with chemical control, though the practice is by no means general. Many large houses depend upon occasional analyses or the guaranties of manufacturers. But of those with which I am acquainted and which have established laboratories with competent men in them, not one could be induced to do without such laboratories. Let us note, then, that there is legal protection to the purchaser of foods and drugs, that the Pure Food Law makes it difficult for manufacturers to escape its searchings and that under it, dealers have recourse against manufacturers; nevertheless dealers of the first rank in foods and drugs find it profitable to maintain chemical control. Observe also, however, that other merchandise knows no law and everything goes. The manufacturer produces and "finishes" his wares, an agent sells them, a wholesaler buys them, a jobber distributes them and a retailer guarantees them. In hard, soft, wet and dry goods, trade is pretty wild and the real nature of the materials is known only when the articles are worn out or used up instead of when it should be known, at the time of purchase. Here is where chemical control comes in and it is a new thing, far from its complete development, but it bids fair to call for a large number of chemists as soon as standards are established. Until then, any chemist who overguesses his own knowledge in such an undertaking is likely to do more harm than a hundred good men can repair.

The only general trade into which chemical control appears to have entered is that of certain mail order houses and these have indeed blazed the trail in scientific merchandizing. Mail order houses claim to sell to the consumer at approximately

jobbers' prices plus transportation and the free return of unsatisfactory goods is a necessary condition of successful merchandizing by mail. If a customer returns merchandise the transaction is more expensive to a mail order house than an unsuccessful sale made over the counter is to a local retailer. If a mail order customer is dissatisfied he is likely to remain so because he is too far away to be jollied around. It is therefore of very great importance that dealers who sell by catalogue be able to make descriptions of their wares that shall be correct.

OPERATION OF MAIL ORDER LABORATORIES

The arrangement of a laboratory for general merchandise control would be hard to determine without specifications; but the following division of the work is employed in the laboratory of a house that sells nearly everything:

- I—Textiles of all kinds, Furs, Paper, Dyes.
- II—Foods, Drugs, Insecticides, Cosmetics, Detergents.
- III—Feeds, Fertilizer Materials.
- IV—Iron and Steel, Non-ferrous Metals and Alloys, Physical Testing and Metallography.
- V—Oils, Paints, Varnishes, Japans, Asphalts.
- VI—Miscellaneous Products (including Rubber, Leather, Wood, Earthenware, Glue, etc.) and Experimental.

Another arrangement that is in successful operation with staff consisting of a chief chemist and a corps of assistants is:

- I—Textiles.
- II—Foods.
- III—Drugs.
- IV—Metals.
- V—General (including paper, leather, shoes, etc.).

Physical tests are very important in determining the endurance of mechanical devices, and apparatus are required for testing the hardness, elasticity, and tensile, transverse and torsional strengths of materials. The range of materials that come under observation is very wide and extends from cotton tape to canvas belting, from thread to hemp rope and from piano wire to steel cable.

Of special value is metallographical and metallurgical control in relation to agricultural and mechanical implements and tools. Steel is chemically tested, its tensile strength and bending strain taken and its true nature determined under the microscope. Or, specifications are made for the various parts of tools and machinery to ensure the greatest measure of strength and endurance in accordance with customs in vogue among progressive manufacturers.

Food control we have already considered. Mail order houses are large distributors of foods and the operation of their laboratories in this connection is similar to that of wholesale grocers.

Rubber goods, more particularly boots and overshoes, are usually appraised as to quality by the price charged. This is not a satisfactory practice. From a chemical standpoint the problem is not simple save to the man with experience, and yet it is very important for the seller to know whether a pair of rubbers that he offers contains a sufficient quantity of good gum or is filled in, under a finished exterior, with an excess of substitutes. The buyer has an interest in this too, but usually neither of them knows. The advantage of this general control to customers is very marked.

Specifications for many kinds of goods are required of general merchandise control laboratories. An important item, for instance, is paints, because the average house owner is more particular about the enduring qualities of the dress for his house and barn than he is of almost any other purchase. His grief is said to be more poignant and his lamentations more persevering if he has any cause to complain. And no paint is everlasting—although sometimes this seems expected.

TEXTILE FABRICS NEED LABORATORY CONTROL

A subject of vast importance is that of textile fabrics. Cloth is one of those half-way things: its chemical aspect is important and so is its physical nature and again, from another standpoint, it travels on its looks. The chief chemist of a great establishment told me that the first thing he did on entering upon his engagement was to look out for weak spots as, for instance, in the men's clothing department, where goods supposed to be all wool were sometimes not. His first professional interview with a woolen goods buyer resulted in a resolution on the part of that gentleman never to travel without a microscope again. I can do no better than quote liberally from a paper on "Laboratory Control of Textile Merchandise," read by Mr. D. M. Nelson before the Chicago Section of the American Chemical Society.

"In making a selection between a number of fabrics for sale, the buyer for a distributing house is guided chiefly by appearance or price. Under appearance he considers the pattern, color, weave and finish and the clearness or brightness of the sample, as well as the firmness of the weave, the draping qualities and the softness of the feel. The determination of these characteristics can be made only by the experienced buyer, who has in mind the customer. Usually the customer buys for appearance alone, having little knowledge of the composition of the stuff and relying principally on his confidence in the retailer or manufacturer for the service he expects. The responsibility of the distributor ceases only when the customer gets the service he has a right to expect, and here the laboratory inspection may be a large factor in supplementing the buyer's off-hand examination. The buyer, through long experience, is able to judge with surprising accuracy, but it is possible to fool the most experienced in this respect."

The accuracy of the buyer is surprising because he guesses; if he were a chemist and his guess as to the content were taken as an analysis he would not be praised at all.

The situation in regard to textiles is probably less orderly and less reliable than anything else that is sold. There are no standards. A thing may be all wool and yet be mostly felted dust, or sold as wool and be 2 to 100 per cent cotton. "Manufacturing routine in the textile industry," said Mr. Nelson, "is largely carried on by rule of thumb and is conducted with the idea of giving the fabric as good an appearance and as good handle as possible, even at the expense of quality if need be." We must not blame the manufacturer for this. The trouble is with the rest of us who are so dead set after style that we will have none of his goods unless he gives them an imitation million dollar look. On the other hand, "manufacturers are able by expert finishing to disguise the cheaper fibres and make very successful imitations of more expensive fabrics that almost defy detection in an off-hand examination." How true this is!

A chemist in one of the laboratories visited observed that mercerized cotton is strengthened by the process although the primary demand for it is because of its looks, that is, because of its lustre and its smoothness. Now mercerization may be cleverly imitated by calendaring, but the first washing will destroy the lustre produced by this process whereas the true mercerized cotton will retain it. The same holds good, for instance, in regard to silk hosiery; unweighted silk has a far better lustre and sheen after washing than has weighted silk. Appearances, which are usually of primary value in textile goods, do not deceive the laboratory as they frequently do deceive the senses.

These laboratory reports on the nature and content of textile fabrics mark a distinct step in advance in merchandising. I know of no dry goods house or department store that maintains this control although I speak with very slight knowledge of their practices. In preliminary correspondence in regard to this article one firm reported that they are now organizing a laboratory

but that it was not yet in working order. Two great mail order houses at least have established themselves in advance of the times in this respect and they certainly have found it profitable. On the basis of an off-hand examination, no buyer alive can be sure of the precise content of every piece of goods. His guess is indefinite. The laboratory report is definite. On the other hand, without more experience than is available today, the laboratory report will not take the place of knowledge and experience as a complete guide to wearing qualities. The merchant with a good buyer and no laboratory control is better off than the one with a dunderhead for a buyer and a good laboratory. The two must work together, as men of successful experience, insist and repeat and then insist again. The use to which goods are to be put is another factor which must be known, and here again experience is needed until standards are established. It is doubtful if all the Nobel Prize chemists together could pass satisfactory judgment on the wearing requirements of women's dress goods.

An old established house dealing in various kinds of merchandise whether in wholesale, retail or mail order trade will naturally go right on whether there is a laboratory upstairs or not. Buyers have grown up in the business and they do not care to have somebody who is not as well informed as they are, criticize their transactions. But the expert buyer cannot go below the surface of things. Of values, of demand and selling qualities, he knows a hundredfold more than the chemist; but the chemist can impart to him information of the greatest value, and surprise him time and again.

Right here we meet a psychological turn that has nothing whatever to do with chemistry, except that it has the power to make chemical control possible or to kill it. If the buyers come to the chemist asking information all is well and good; together they will know far more than either would know alone. If the chemist criticizes the buyers and condemns their purchases against their own judgment, there will be trouble in the air and chemical control of that establishment is likely to enter into eclipse. I have yet to meet a successful chemist in a mercantile establishment who does not insist that he must work in harmony with buyers so that the wisdom of both may be available to the house.

Another point that needs emphasis is the possible development of a practice that is certain to end in failure: we refer to over-advertising or false advertising of the laboratory control of merchandise. It cannot be too strongly stated that the art of laboratory control is not far enough advanced to be exploited in the manner customary among many writers of advertisements. Its purpose is to protect the merchant, to substantiate his guaranty and to bring his customer into more intimate understanding of the wares sold, but it is of no value whatever in aiding the sale of defective merchandise.

To return to Mr. Nelson's paper, he proposes a more elaborate examination than has been reached yet for textiles, and with definite standards fixed for various purposes the ability to purchase according to quality should be greatly augmented.

I—MICROSCOPIC

- 1—IDENTITY OF FIBERS
- 2—QUALITY OF STOCK
 - a—Length of fibres
 - b—Diameter of fibres
 - c—Uniformity of fibres

II—CHEMICAL

- 1—PERCENTAGE COMPOSITION
 - a—Fibre composition
 - b—Weighting or sizing
- 2—FASTNESS OF DYESTUFF
 - a—Washing
 - b—Light
 - c—Rubbing
 - d—Special uses

III—PHYSICAL

- 1—BREAKING STRENGTH AND ELONGATION
- 2—WEIGHT PER YARD OF A SPECIFIED WIDTH
- 3—PICKS AND ENDS PER INCH
- 4—YARN STRUCTURE
 - a—Single or double
 - b—Amount and character of twist
- 5—COUNT OR SIZE OF YARN
- 6—SHRINKAGE IN SPONGING OR WASHING

In made-up goods it is sometimes difficult to distinguish exact qualities of material, as, for instance, in wool, to know quantitatively the fleece, pulled wool or shoddy in the stock. The composition of a fabric as to different kinds of fibre is in most cases easily determined. Cotton and wool are quickly separated by boiling in a 5 per cent sodium hydroxide solution. A simple way to determine silk is by ravelling out and weighing.

In fastness of dyestuffs again, the use of the fabric determines the quality of fastness needed. In millinery goods, for instance, it is especially fastness to light that is desired while rubbing and washing tests are negligible. In all goods the nature of the test is indicated by their prospective uses.

Breaking strength and elongation are factors that throw most light on the question of durability, although here again we lack standards. The results are comparative rather than absolute. But minimum breaking strengths can be established which will serve to draw the line between what is desirable and what is not. The test is of special value in checking deliveries from factories because a decrease in strength indicates a lower quality of stock or less care in manufacture. The moisture content of the sample plays a very important role, but 40 per cent increase in relative humidity will increase the tensile strength of cotton yarns 16 per cent and decrease that of woolen yarns about 18 per cent. More research on this subject is needed. Mr. Nelson noted two general methods of controlling the moisture factor: to break the sample bone dry and to break it in a standard atmosphere of constant humidity and temperature; the latter more nearly approximates usual conditions, but is more difficult to control. The type of apparatus, the speed of moving jaws and the length of test sample between jaws are all factors that affect the result of the test.

In conversation with Mr. Yundt, he noted the special value of the thread count in silk or linen dress goods in determining quality. The only method of determining shoddy content is by microscopic examination and the nearest one can conveniently come is an estimate. Dye tests are for fastness to light, wash and spotting from mud and rain. Exposure is the best with regard to light but the peroxide test will give an indication in a hurry. The mud test Mr. Yundt makes with lime water and the wash test with soap. Silks are tested for weighting as well as for quality and whether natural or artificial. The artificial fabric, generally speaking, breaks more easily than the natural product.

In this connection the value of the microscope and a trained eye is of leading importance. Indeed, although the man in the laboratory must have a sound chemical training to pass on textile goods, he must also have training as a textile microscopist. Thus he can gain rapid and wide information from a small clipping from the seam of a suit or a shirt. Recovered wool may show fraying ends, possibly indicative of brittleness due to improper carbonization or more likely to the tearing apart of the fibres in milled goods. Pulled wool will show the roots of the fibres in raw stock. In manufacturing the roots are usually torn off. Lamb's wool shows the natural end, which is easily distinguishable from the wool of a sheep that has been sheared.

It occurs with increasing frequency that jobbers take the reports of these mail order house laboratories when they have earnest and serious questions to ask of manufacturers. The case was related of a linen manufacturer who bought his yarns and guaranteed his products to be all linen. He was an honest man

and a good manufacturer, nevertheless his product was half cotton. He couldn't and wouldn't believe it until he saw the test, and even then he could hardly believe his own eyes. It proved that his yarn, that he bought for all linen, was only half of flaxen origin. The rest was cotton. He had been buying it and guaranteeing it for years.

In the extensions under way in the laboratories of the mail order houses examined, provision is made for the separation of the respective departments, with a view to greater efficiency. Under pressure of work a man from one department may be assigned to work in another but the chief chemists are unanimous in favor of this separation and are resolved upon it.

The proof of the pudding is in the eating. A question directed to any one of the establishments visited as to the value of chemical control would bring but one kind of reply. "The trouble," as one chemist says, speaking of the use of the laboratory by the many departments of the concern with which he is connected, "is to hold them back." Chemical and technical control do not come ready made. But their value is beyond measuring. It discounts the trademark premium on goods in buying. It strengthens and augments guaranties, because, as we have already intimated, if it is known that a merchant knows what he is selling, his guaranty is better than if it is merely an assurance of "your money back if dissatisfied." Usually, when one makes a purchase, he does not want his money back but he does want to be satisfied.

SUCCESS OF CONTROL LABORATORIES NOW ESTABLISHED

In proof of the value of a well-conducted laboratory by the right man, I am permitted to go behind the scenes a little and quote parts of a letter written by a general manager to another officer of the same company in regard to a proposal that their laboratory facilities be increased and extended.

"I am very much impressed with the good that has come and can come from the fact that we have a complete laboratory and our merchandise gets a thorough examination from a scientific standpoint before we make any claim in our catalogue as to its qualifications. There is no question in my mind that in time there will be legislation on textile merchandise somewhat similar to the Pure Food Laws, making it necessary that we state of every article whether it be made from cotton, wool, etc., and if made from a mixture of cotton and wool, just how much cotton and how much wool it contains. It is a known fact that the statement that an article is pure wool has been much abused, and I am sure it is only a question of time when legislation of a national nature will control this condition.

"I believe we should anticipate this; the nature of our business should compel us to do so. I positively believe we should not put any article in our catalogue, no matter what its nature, without having it go through our laboratory to be passed on scientifically; in other words, we should not take the word of salesmen or manufacturers, but should obtain an absolute knowledge of it ourselves before making any claims.

"I further believe you cannot put a dollar and cent value on the good that will result from this work; it is work along lines so good and wholesome that it cannot help but make our future assured."

ACKNOWLEDGMENT

In conclusion, and despite the stipulation of certain houses visited that this article be prepared in the interest of chemistry and that it in no wise partake of the nature of that quality of publicity which is akin to advertising, candor and chemical conscience require that I make the following acknowledgment:

I am indebted to Messrs. Austin, Nichols & Co., of New York, and Messrs. Sears, Roebuck & Co., Montgomery Ward & Co., and Sprague Warner & Co., of Chicago (in the order visited), and to their respective chief chemists, Dr. J. A. Riche, Messrs. A. V. H. Mory, C. R. Yundt, and Dr. Paul D. Potter for a great deal of the information above set forth.

139 EAST 40TH STREET
NEW YORK CITY

THE PRODUCTION OF SCIENTIFIC KNOWLEDGE¹

By C. E. KENNETH MEES

The great value of scientific research both to the industries and to the nations at large is now generally recognized throughout the world and in the last few years there has been a remarkable increase in the efforts made to stimulate the production of scientific knowledge. In 1914 the American Association for the Advancement of Science appointed a Committee of One Hundred to inquire into the steps which should be taken for the increase of scientific research in the United States and the work of this committee has been continued and expanded by the National Research Council. Among the European nations there is a great awakening to the national value of scientific research. The British government has appointed a Department of the Privy Council to deal with the subject, while it is announced that in France a new national laboratory on a very large scale has been projected. In Australia the government has appointed a special department to consider what steps should be taken for the organization and development of research work in the Commonwealth, and in Canada the matter has been the subject of government inquiry and solicitude.

The increase of scientific knowledge can be divided into three steps:

I—The production of new knowledge by means of laboratory research.

II—The publication of this knowledge in the form of papers and abstracts of papers.

III—The digestion of the new knowledge and its absorption into the general mass of information by critical comparison with other experiments on the same or similar subjects.

The whole process, in fact, may be likened to the process of thought. We have first the perception by means of the senses. The precept is then stored in the memory and in the mind is compared with other previously stored precepts, and finally forms with them a conception.

I desire in this paper to consider the methods by which these three sections of the production of knowledge may be carried on, to suggest an arrangement of laboratories to produce experimental results dealing with any branch of science, then to consider how the knowledge so obtained may best be stored and classified and finally the methods to be employed to make the results of scientific research available for application.

I—RESEARCH WORK

The agencies engaged in scientific research are of several kinds. The traditional home of research work is in the university, and the bulk of the scientific production of the world comes from institutions connected with teaching. The industries are more and more supporting research laboratories, a large number of which contribute to the general fund of scientific knowledge by publishing the results which they obtain, and some of which are engaged upon purely scientific work of no mean order. Consulting and technical laboratories engaged in industrial work make frequent contributions to science, and there are some very important laboratories engaged in pure research work which are supported by philanthropic foundations.

The classification of research laboratories is not altogether an easy task. They may obviously be classified according to the source of the funds which support them; *i. e.*, we may classify them as university laboratories, industrial laboratories, government laboratories, institution laboratories, and so on, but if we look at them simply in the light of the research undertaken, this does not seem to be altogether a logical classification since there is little distinction between the work done in some university laboratories and in some industrial laboratories, and the work of the government and institution laboratories again overlaps that of the two former classes.

The University of Pittsburgh, for instance, has an industrial

¹ Address before the Rochester Section of the Optical Society of America, October 23, 1917.

laboratory where definitely technical problems are dealt with. The research work on photometry done at Nela Park and at Cornell University would seem to be similar in kind, and work on physical chemistry or on the structure of chemical compounds is of the same type, requires the same class of workers, and produces the same results, whether it be done in a university, in a laboratory of the Carnegie Institution or in such an industrial laboratory as that of the General Electric Company. It is equally difficult to classify laboratories according to the purpose for which researches are avowedly carried on. Most university laboratories are willing to undertake work of industrial value, and, indeed, some specialize in such problems; while many industrial laboratories are quite willing to carry out a research of purely academic and theoretical interest provided the problems involved bear a relation to the general work of the laboratory.

A useful classification of laboratories can, however, be obtained if we consider whether the problems investigated in a laboratory are all connected with one common subject or whether the problems are of many kinds, having no connecting bond of interest.

problems carried on in the same laboratory are not necessarily related in any way whatever.

The greater number of university and industrial laboratories are necessarily of this type. It would be a disadvantage for a university laboratory, whose primary business is training students, to be too narrowly specialized. Specialized university laboratories are only desirable in the case of post-graduate students, and it would be very inadvisable to allow the laboratories responsible for the general training of scientific men to specialize in one branch of science, since as a result the students would acquire a proper acquaintance with only a limited portion of their subject.

Industrial laboratories, on the other hand, must necessarily be prepared to deal with any problems presented by the works, and as these will be of all kinds, covering generally the whole field of physics, chemistry and engineering, it is impossible for the usual works laboratory to specialize except in so far as it deals with the works processes themselves.

In the "convergent" laboratories, however, although the

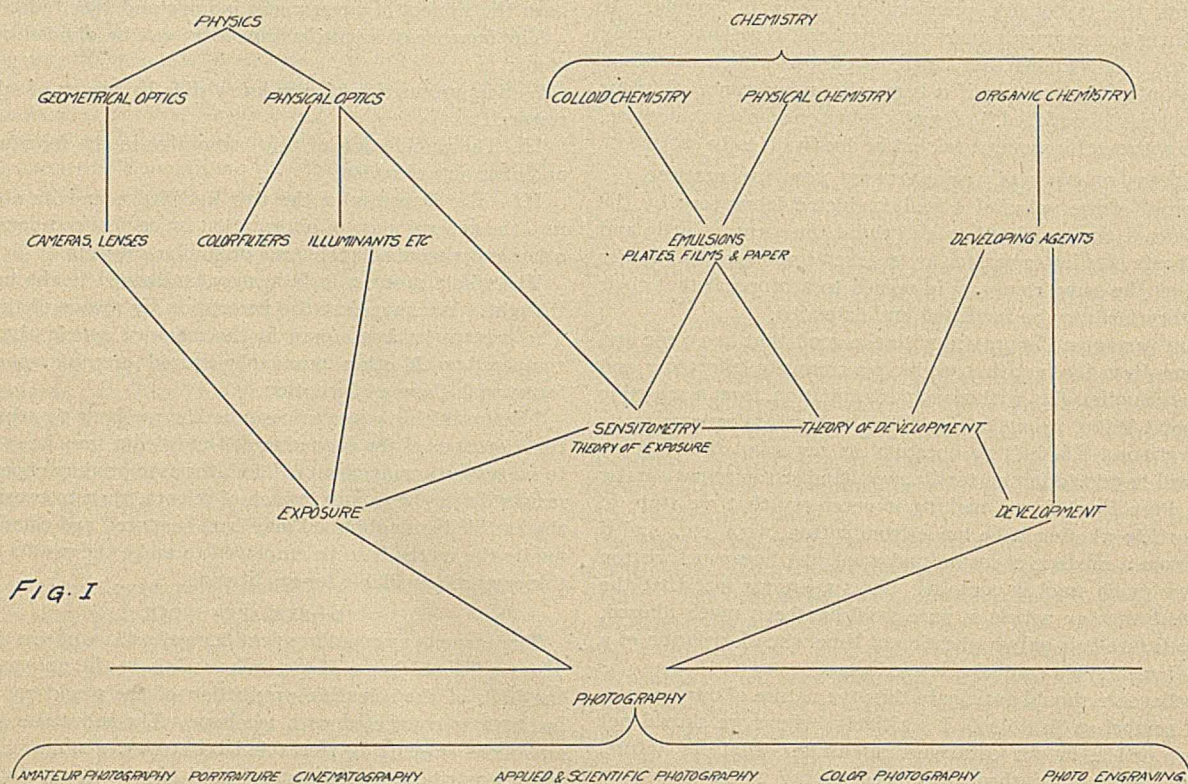


FIG. I

I would suggest that the first type of laboratory might be called "convergent" laboratories and the second "divergent."

In the "divergent" group of laboratories are included all those research institutions which are interested in science in general or in science as applied to industry and which will attack any problem which may seem to promise progress in knowledge or, in the case of an industrial laboratory, financial return. Most university laboratories are of this type. When they devote themselves to special problems it is usually because of the predilection of some professor, and as a general rule a student or instructor may choose any problem in the whole field of the science in which he is working and may carry out an investigation on that problem if he be interested in it without regard to the relation of his work to the other work which is carried on in the same laboratory.

Correspondingly, in most industrial laboratories the problems investigated are those which present themselves as a result of factory experiences or of suggestions from the men working in the laboratory and which promise financial return, and the different

actual investigations may cover as great a range of science as those undertaken in a "divergent" laboratory, yet all those investigations are directed toward a common end; that is, towards the elucidation of associated problems related to one subject. Thus, the staff of the Geophysical Laboratory, which includes physicists, geologists, crystallographers, mineralogists and chemists, works on the structure of the rocks, and although the field of the actual investigations range from high temperature photometry to the physical chemistry of the phase rule, yet the results of all the work carried out are converged on the problem of the structure and the origin of the earth's crust.

The Nela Park Laboratory, in the same way, is studying the production, distribution and measurement of illumination, and all its work, which may involve physiology, physics and chemistry, is related to that one subject. Such convergent laboratories sometimes develop in universities owing to the intense interest of a professor in a single subject and to the enthusiasm which inspires students and assistants to collaborate with him and to concentrate all their energies on the same group of problems.

There are many examples of such laboratories, such as the laboratories dealing with radioactivity, and those which are concerned chiefly with spectroscopy. Among others may be mentioned the Cavendish Laboratory at Cambridge and several of the larger university laboratories which deal with the physical chemistry of solutions.

But these university laboratories are rarely able to concentrate onto the group of problems which they are studying, specialists from such different branches of science as are available for similar laboratories outside the universities, owing to the fact that it is very difficult to obtain inter-departmental coöperation in research in a university. In a specialized laboratory, on the other hand, workers in all branches of science may well collaborate in the investigation of problems representing different points of view of one general subject.

In addition to the examples of industrial and institutional laboratories mentioned above I should like to illustrate the structure of a convergent laboratory, if I may be forgiven for doing so, by referring to the organization of the research laboratory with which I am connected—that of the Eastman Kodak Company.

The purpose of this laboratory is the investigation of the scientific foundations of photography and its applications, everything relating to photography in all its branches and applications being of interest. The branches of science which are of chief importance in photographic problems are those of optics in physics and of the colloidal, physical and organic branches of chemistry, and the relation of these sciences to photographic problems are shown in graphic form in Fig. I.

Optics deals on its geometrical side with the materials used in photography—cameras, lenses, shutters, etc.—and on its physical side with such materials as color filters and illuminants, but especially with the study of the relation of the photographic image to the light by means of which it was produced—a study which is known by the name of sensitometry. The manufacture of the sensitive material itself, which in the case of modern photographic plates, films and paper is called the emulsion, is a province of colloid and physical chemistry, colloid chemistry dealing with the precipitation and nature of the sensitive silver salts formed in their gelatine layer, while physical chemistry informs us as to the nature of the reactions which go on, both in the formation of the sensitive substance and in its subsequent development after exposure.

The organic chemist prepares the reducing agents required for development and the dyes by which color sensitiveness is given to the photographic materials and by which the art of color photography can be carried on, and while the physicist therefore deals with sensitometry and the theory of exposure, the chemist must deal at the same time with the theory of development and with the conditions relating to the development of photographic images.

A laboratory, therefore, for the study of photographic problems must be arranged with a number of sections such as are shown in Fig. II. In physics we require departments dealing with sensitometry and with illumination, reflection and absorption, colorimetry, spectroscopy and geometrical optics. We need a department of colloid chemistry, one of physical chemistry, one of organic chemistry, one of photochemistry to deal with the action of light upon the plate, and finally a number of photographic departments, dealing with photographic chemistry, with portraiture, color photography, photo-engraving, motion picture work and X-ray work, and all these departments are converged together upon first, the theory, and then upon the practice, of photography.

Each research specialist in the laboratory is given work corresponding to a limited field of science, so that while his special attention is devoted to that one department his field of activity just overlaps that of the departments on each side of him, while

his general knowledge of the subject should, of course, cover a much wider range. It is important that each man should have his own special field of work and that overlapping should not be complete since such complete overlapping will inevitably produce friction destructive of coöperation and harmony. The way in which such a subdivision is arranged may perhaps be best illustrated by Fig. III, which shows the range of the specific investigations of those who in our laboratory cover the range of research work between sensitometry and pure physical chemistry. There are five workers in this range; the first, *A*, being a pure physicist; *B*, a physicist with a considerable experience of chemistry; *C*, a physical chemist who has specialized in photography; *D*, a physical chemist who has specialized in photographic theory; and *E*, a pure physical chemist. The interest of each of these workers overlaps the field of the other workers but nevertheless each of them has his own specific problem, his own equipment and apparatus. Thus, *A* and *B* use sensitometric apparatus chiefly; *C*, both sensitometric apparatus and the thermostatic and electrical equipment of physical chemistry; *D*, microscopic apparatus and chemical apparatus dealing with the precipitation of silver salts; and *E*, the analytical and solubility apparatus of chemistry.

The whole of this range is also connected with colloid chemistry and especially the overlap of the different sections involves colloid problems, so that we can consider colloid chemistry as dealing with the inter-relations of the different sections of photographic chemistry and can represent its province in the diagram by shading the overlapping areas. The colloid division of the laboratory will therefore be interested in the work of each of the specific investigators and will be of assistance to all of them.

These charts, prepared for a photographic laboratory, are equally applicable in form for almost any other convergent laboratory, so that if we have to work out the organization of a research laboratory which is to study any inter-related group of problems, we can do it by the construction of charts similar to these. Thus, considering Fig. I, we place first at the bottom of the chart the general subject considered and its various branches and then above these the scientific problems involved, separating out on opposite sides of the chart those problems which would involve different branches of pure science. Thus, we can place on one side biological problems, then physical problems, then chemical problems, and so on, thus reconstructing a chart similar to Fig. I from the bottom up until at the top we have the various branches of pure science involved, subdividing these branches until each subdivision represents the work capable of being handled by one man in the laboratory.

It will now be possible to draw Fig. II, showing on the circumference the different sections of the laboratory for which accommodation, apparatus and men must be provided and showing the relation of these sections to the problem as a whole, and having worked this out it is easy to find the amount of space and the number of men which will be required or which the funds available will allow for each part of the work.

Specialized laboratories may originate in various ways, but it seems clear that with an increasing total amount of research and with an increasing realization of the importance of research more laboratories will be developed and no doubt laboratories which originally were of the divergent type will with their growth tend to split into a linked group of convergent laboratories. Consider, for instance, a very large industrial research laboratory covering a wide field of research and dealing with many different types of problems. There are two types of organization possible to such a laboratory. It might be divided according to the branches of science in which the workers were proficient. It might have, for instance, chemical divisions, physical divisions, and so on, but if the groups of problems dealt with were reasonably permanent in their character it would more probably develop into a group of convergent laboratories in which men from different branches of science—chemists, physicists, and so on—worked

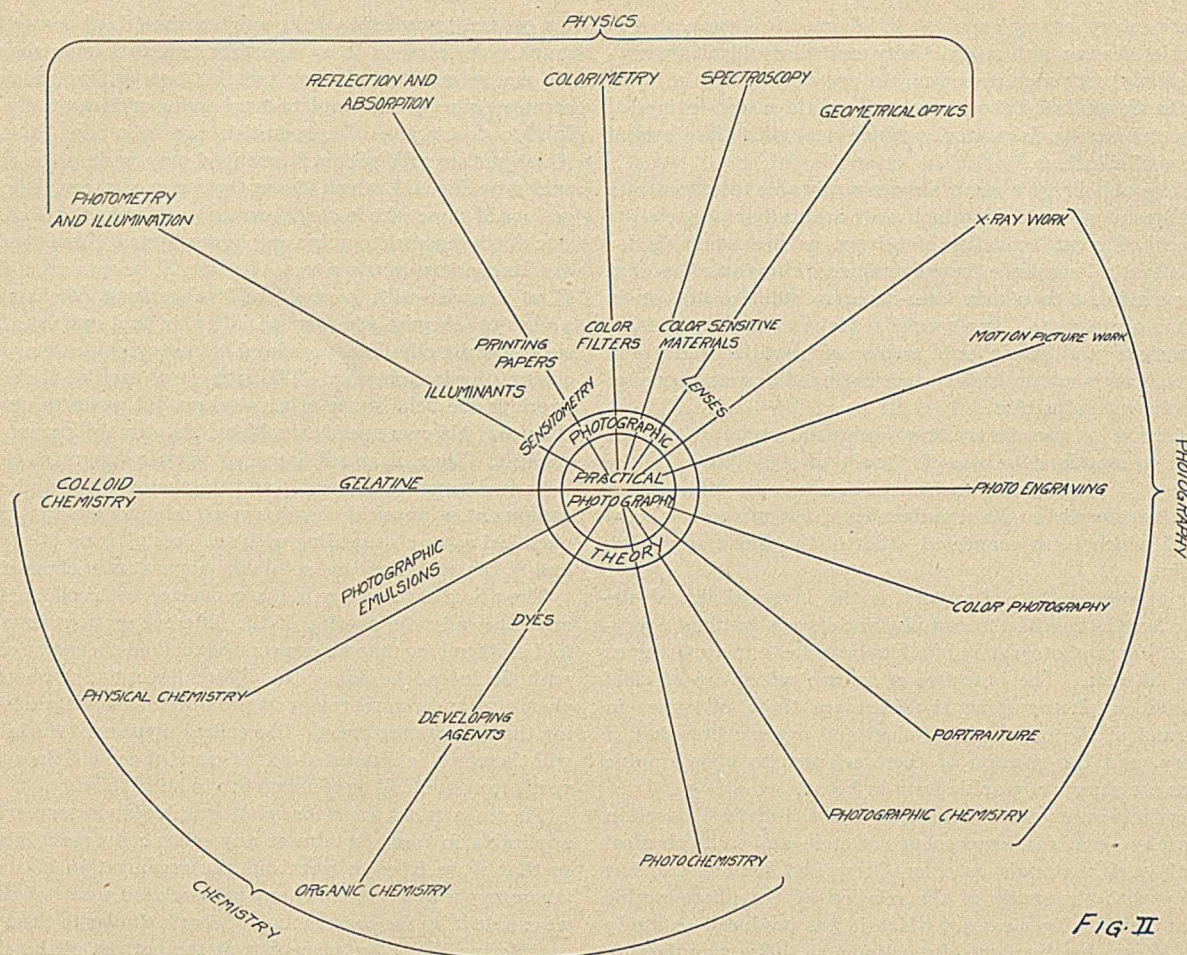


FIG. II

together (and probably even had their working places in proximity) because they were working on the same general problem. Any national laboratory which is developed for industrial research, for instance, should almost certainly be organized as a group of convergent laboratories rather than as a group of separate physical, chemical, engineering, etc., laboratories.

We may expect then that the general organization of scientific research will tend towards the production of numbers of specialized laboratories, each of which will be working on an inter-related group of problems and attacking it from various stand-points.

Some of the questions relating to the internal organization suitable for these convergent laboratories have already been discussed in a former paper¹ and I need add here only that the "conference" system described there as a method of actually carrying on the scientific work of the research laboratory has continued to prove quite satisfactory.

II—THE CLASSIFICATION OF SCIENTIFIC KNOWLEDGE

The work of the research laboratories is published by various methods in the form of scientific papers, and with the increasing amount of research done the number of technical journals is increasing steadily, so that the workers in most branches of science find it difficult to keep up adequately with the current literature and especially those who become interested in the light thrown upon their own problem by other branches of science find it a task of great magnitude to acquaint themselves adequately with the literature. In order to meet this difficulty the various scientific societies publish journals giving abstracts, in a conveniently indexed form, of all the important papers published; these abstract journals are of great value in searching for information on special subjects.

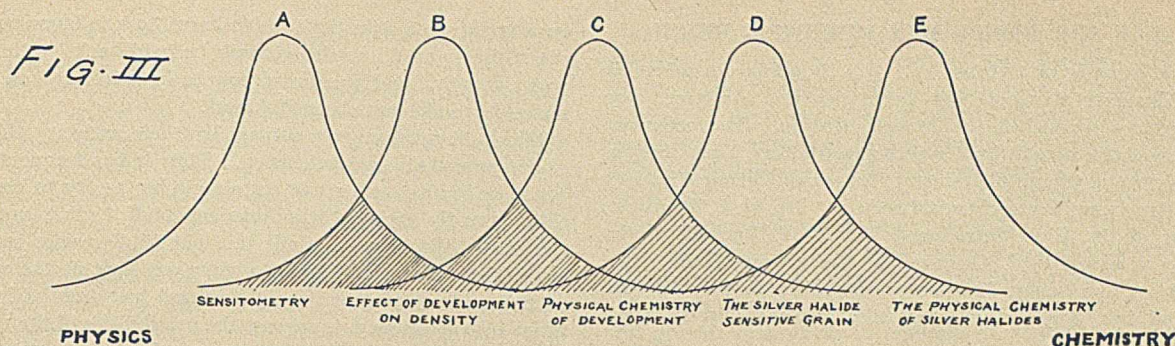
¹ "The Organization of Industrial Scientific Research," *Science*, 1916,

In spite of these abstract journals the task of obtaining all the references to the literature on a given subject is still a formidable one and might be very much simplified by the adoption of some radical changes in the organization of the abstraction and classification of scientific knowledge.

In the first place, there seems to be no reason why abstracts of scientific papers should be prepared by the national societies. At present, for instance, there are at least four complete sets of abstracts of chemical papers prepared in different countries, together with a number of less complete sets, and this represents a great overlapping and duplication of effort. On the other hand, sciences which have not so many or so wealthy workers as chemistry cannot afford to produce any complete abstract journals, so that in these sciences reference to the literature is much more difficult. There seems to be no reason why an interchange of abstracts between different countries could not be arranged and, indeed, it might be the best method of obtaining abstracts to have the author of a paper supply an abstract suitable in form and length for the abstract journal at the same time that he sends his paper in to the journal which publishes it. The editor of that journal could suggest modifications in the abstract which in his opinion were desirable and forward both the corrected and uncorrected abstract to the editor of the abstract office, where it would be re-edited for insertion in the international abstract journals and these journals would, of course, be supported by subscriptions, either through the societies or by individuals in the same way as the abstract journals which are at present published.

Whether such an ambitious scheme of international scientific abstracts is capable of realization or not, reference to the abstract journals would be made much simpler if some method of numerical classification could be adopted.

In this connection, an experiment has been made in the last



two years at the laboratory of the Eastman Kodak Company which has proved successful and which seems to be worth trying on a larger scale. The laboratory publishes each month for the use of the employees of the company an abstract bulletin of the photographic journals, including also abstracts from other scientific journals which have any relation to photographic problems or manufacture, the abstracts being made by the laboratory staff, and attached to each abstract is a reference number. These numbers refer to a numerical classification of photography based somewhat on a decimal system but adapted to the special needs of the subject. Each month as the bulletin is issued the abstracts are clipped out, pasted on cards and filed under the number printed on them in numerical order so that each recipient of the bulletin can prepare for himself a file either of all photographic literature or of any portion of it in which he may be specially interested. For example, in the classification, photographic apparatus commences with the number "2", and if any particular worker is not interested in anything but apparatus, if he has no interest in materials or in photographic processes or in applications of photography, then he need file only the cards starting with "2", while, if his interests are even more limited, if, for instance, he is interested only in photographic shutters, he can file the cards starting with "262" thus obtaining only a very limited file which is, however, complete for the subject in which his interest lies.

If the abstract journals would print such a numerical classification attached to each abstract, adopting as their basis either the numerical classifications of the international catalogue of scientific literature, which have proved themselves satisfactory after trial, or some different classification adopted after due consideration, then each recipient of the abstract journals could prepare for himself card index files of the scientific literature in which he was interested.

To prepare a card index of all science or even a complete index of one large branch of science in this way would be too formidable an undertaking either for an individual or even for a small library, but it should certainly be possible for large libraries such as those of the scientific societies or of large cities to keep such numerically indexed files to which reference could be made by correspondence from any research worker. Thus, adopting the classification of the international catalogue, a worker who became interested in questions, *e. g.*, of catalysis, could apply for a copy of the reference cards on this subject, which would include all those indexed under 7065 and could be supplied with a complete file or with a partial file covering any period of time; the copies could easily be made by photographing the cards with such a camera as the "Photostat."

III—THE UTILIZATION OF SCIENTIFIC KNOWLEDGE

The actual application of science to industry is so vast a subject that it cannot be considered here, but it is not satisfactory to leave the results of research at the point where they are published in papers and filed in the abstract journals. In order to make them available as a part of scientific knowledge the new information as it is obtained must be incorporated in books.

There are three classes of books dealing with scientific work which require separate consideration. The first class comprises the dictionaries, in which almost all the progress in some branches of science can conveniently be summarized. Beilstein's "Handbook of Organic Chemistry" is a good example of the way in which almost all the facts of a science can be absorbed in a classified form and made available for ready reference. These dictionaries, in fact, represent the critical and discriminating summary of the scientific publications on the subjects with which they deal and the preparation of such dictionaries should be ensured by international coöperation of the national societies.

Other sciences, however, do not by their nature lend themselves to the convenient preparation of dictionaries and what is wanted in this case are critical and well arranged handbooks covering the whole science and resuming impartially but critically the various additions which are made from time to time in the different branches of the subject. These handbooks, as well as the dictionaries, would, of course, require the addition of supplementary volumes from time to time and occasional complete revision.

The preparation of both dictionaries and handbooks would, of course, be greatly facilitated by the existence of a numerically classified card index to the literature concerned, and the preparation and revision of such books might well be undertaken in connection with the large libraries having in their possession the complete classified card indexes.

On the other hand, for the assistance of advanced students of science, what is required is a steady supply of monographs correlating critically and comprehensively all the literature in a special field, and these must be brought up-to-date from time to time. Such monographs are especially required in connection with rapidly developing new branches of science; it is difficult to overestimate the importance and value for progress in research of such a book as Bragg's "X-Rays and Crystal Structure" for instance, and while nothing should be done to hinder individual initiative in publishing such books, it would seem that when it was apparent that some branch of science required such a monograph a national society might very well approach well-known workers in the field and request them to write such a book, offering its assistance in the matter of bibliography and also offering to arrange for the publication of the manuscript. The initiative in indicating the need for such a book might come in the form of suggestions from members of the Society or other scientific men. It is quite true that at the present time the scientific publishers are extremely active in searching for suitable books to publish, but necessarily they must consider the probable demand rather than the actual need for a book, and this leads to an overproduction of books dealing with those fields of science which have a large following and an insufficient supply of books in those fields where the workers are few, though for progress the more sparsely worked fields would seem to require almost as much representation in literature as those which are of wider interest.

FRANCE AND AMERICA IN SCIENTIFIC UNION

On the evening of October 19, 1917, honorary membership in The Chemists' Club of New York City was conferred upon Prof. Victor Grignard of the French Mission. The ceremony took place at the regular joint meeting of the New York Sections of the Society of Chemical Industry, American Chemical Society and the American Electrochemical Society. Dr. M. C. Whitaker, president of the Club, introduced Dr. L. H. Baekeland who officially informed Prof. Grignard of the action of the Club. In accepting the honor, Prof. Grignard replied in French. Dr. Baekeland has prepared a translation of the address, which follows.—[EDITOR.]

ADDRESS

By PROF. VICTOR GRIGNARD

GENTLEMEN—I feel truly perplexed before all the marks of sympathy, all the honors, which have come to me like an avalanche since I put my feet on this beautiful land of America.

From the moment I arrived, even on the ship itself, already two of your eminent representatives, Dr. Baekeland and Professor Bogert, kindly put themselves at the disposal of Mr. Engel and myself and offered the hospitality of this House.

Since then, everywhere we present ourselves, we have encountered the same enthusiastic welcome, the same sincere desire of being of service to us.

Then again, at the beginning of the month of August, a charming and unforgettable banquet, even more touching by its intimate cordiality than any great official galas which often are more arranged for the gallery than for the participants, brought us together in this same place.

Then again, that important meeting in Boston where Professor Stieglitz announced so kindly the great honor which was conferred upon me by the American Chemical Society and which has been appreciated as much as it was unexpected.

And, to-day, gentlemen, you open to me all the big doors of your Great House, you welcome me in the intimacy of your Home, in a word, you adopt me as a member of your great family.

Let me tell you that this honor impresses me even more than the preceding ones because there is in this something which touches me more particularly in a personal way.

Undoubtedly, I am happy and proud to have been for you an occasion to manifest your sympathies, even your admiration, for France in general and for French chemistry in particular. But, believe me, I would be less impressed when bringing home from here honor certificates and diplomas, if I did not know I am taking home to my country also somewhat of your hearts.

This ceremony proves to me that I am not mistaken in this. Therefore, gentlemen, I desire to express more particularly my profound gratitude, my great happiness, to have been able, notwithstanding my lack of knowledge of the English language, to bring to you the impression that, in spite of the sorrows of the present hour, French chemistry, like all France, lives and works; and only desires to live and work still more and we look upon our big American sister as particularly qualified to help us in this work of reconstruction.

Indeed, gentlemen, you possess all that is necessary for this. Thanks to the immensity of your magnificent territory, you have natural forces and mineral riches of the most varied nature, of greatest abundance and of the most precious kind which nature has been able to give to any people.

You have the confidence and enthusiasm of youth; you have also the audacity thereof, and fortune, which loves the audacious, smiles upon you. Have you not shown excellent proof of this in the creation and the prosperity of the Chemists' Club? You

have banking organizations which know how to favor beginning enterprises; you do not let yourself be held back by timid men or by skeptics, and you know how to look forward on a large scale—large like your beautiful land.

Many of your projects surpass by their audacity the limits of our immediate comprehension. Thus it has frequently happened in France, at least in certain circles, to try to class such enterprises by saying, "It is American bluff." But, nothing of the kind. We have to admit it. The bluff resides merely in our imagination. It is not in yours; you look at the world in all the boldness of your imagination and your dream of realities which sometimes seem to surpass the possibilities of the moment. You have the vision of grandeurs of the future—that is all. But do not let us call this bluff; let us admire it.

What can your older little sister bring you to complete such a powerful ensemble? Truly, very little, but, nevertheless, something: A finer sense of truly scientific ways, due to a tradition and an education of older duration; after all, the privilege of seniority is not always enviable, but it may often render its services.

France owes it to this that in many directions, and more particularly in chemistry, she was an innovatrix, and this privilege would have been still more obvious, even to the minds of those who are less informed, if our laboratory men, if our engineers, had had behind them sufficient backing, well equipped laboratories, more elastic budgets, well informed manufacturers, daring capitalists.

Many new ideas which germinated in France might have grown up there and might have contributed to make the halo of French science still more brilliant.

For instance, to speak of a question of burning actuality, the synthesis of ammonia which at this moment preoccupies all the Allies, the so-called Haber process, is called thus because it has been studied and put in shape in the laboratory of Haber by a Frenchman, Rossignol. It is probable that if Rossignol had possessed in France a laboratory which commanded the resources of that of Haber, France would not be, at this moment, anxious to procure ammonia and Germany might, perhaps, have been short of it long ago. Furthermore, the principle of this process, that is to say, the combination of nitrogen and hydrogen under pressure at a sufficiently high temperature and in presence of a catalyzer, was discovered a long time ago in Paris by our eminent chemist Le Châtelier.

Unfortunately, the gaseous mixture at one of the tests was ill-prepared and still contained oxygen, and caused the explosion of the apparatus and the experiments did not go further. We should not think, of course, that when an apparatus blows up, it is the French scientist who retreats. No, alas, it is simply his budget which blows up!

And thus was it that the synthesis of ammonia, which ought to have been a French conquest, has taken the aspect of a German discovery.

Well! We know at present in what soil we shall have to plant the good seed; whenever the old French humus will no longer be deep nor rich enough to permit a rapid and powerful growth, do not let us lose our way among our rapacious eastern neighbors, who are always on the alert for some new plunder; let us take it to you where we shall find the confidence, the daring perseverance, with all the material and financial resources which can assure success.

In this way, long ago, the inventor of the triple effect evaporator, when he was misunderstood in his own country, brought to your sugar refiners his ingenious discovery, which since then has had a splendid development in many industries. It is necessary that a close coöperation on scientific and industrial lines should be organized more and more between our two countries.

The horrible war which has been imposed upon us, has already made a big step in that direction.

In order to save the world from Prussian hegemony, in order to stop the grasping hand of Germany over every liberal thought and generous instinct, we cannot have enough of the support of the United States alongside that of the European Allies. And this brotherhood of our armies has made indispensable, more particularly between our two countries, the scientific and industrial alliance which is necessary to conduct this war, —a war more scientific than anyone ever might have imagined.

Without citing too many examples, our metallurgists have already brought to you precious improvements in the manufacture of steel; from your side, you bring us a solution, and perhaps two solutions, to the worrying nitric acid problem.

This fecund collaboration should continue after our victory.

Yesterday we exchanged professors; to-morrow we shall exchange students. Thanks to the zeal of my devoted collaborator, Engel, thanks to the friendly efforts of some among you, quite a number of American chemists have already subscribed their names for membership in the Société de Chimie Industrielle which recently has been founded in Paris, and I hope that at our return in France, we shall be able to reciprocate and to increase the number of members of the American Chemical Society.

In this way, the field shall have been well prepared for the exchange of ideas which will precede our common efforts.

In their own turn, other elements of intimate collaboration will present themselves to reinforce all that exists already, and if I am enabled, within a few years, to visit again your beautiful land, I have the firm conviction that I shall be able to bring then the greetings of a newer France to a still greater America.

CURRENT INDUSTRIAL NEWS

ESTIMATION OF TIN IN LOW-GRADE STUFF

Mr. A. Adair contributes to a recent issue of the *South African Mining Journal* a method of estimating tin in low-grade ores, tailings and slimes. The method is stated to have been devised on account of the difficulty which the sodium peroxide and other fusion methods present, owing to the trouble experienced in separating the tin from the excessive amounts of gelatinous silica produced, for, in practice, evaporation with hydrochloric acid to render the silica insoluble results in large losses of tin as stannic chloride. The method described depends on converting the stannic oxide into its phosphide without fluxing the gangue. The metal is then dissolved and readily separated from the non-gelatinous silica. The ore is roasted or treated with nitric acid and washed free from pyrites. It is then ground to impalpability and mixed with 0.4 its weight of dry ammonium phosphate and 0.2 charcoal, both ground finely and well mixed. For 5 g. ore take an annealing cup and grind a lid to it till it closes all around. The inside is wetted and rubbed with a little black lead to get a good coating for polishing when dry. A kerosene blast lamp and jacket are used, first heating gently for 20 min. and then at a red heat for one-half hour, cooling off with the vapor of the lamp. Any charcoal remaining is blown off and the ignition transferred to a porcelain crucible and ground to the finest powder. It is transferred to a flask and wetted with alcohol. 25 cc. of boiled hydrochloric acid are added and the mixture left in a warm place over night, by which time the tin is in solution and easily filtered from the gangue and charcoal. Results on a sample of ore containing 1.5 per cent stannic oxide, from seven successive tests, gave an average value of 1.21 per cent.—A. McMILLAN.

COCONUT INDUSTRY

From a recent report it would appear that the coconut industry of Trinidad and Tobago, which has been affected by prolonged droughts in previous years, has now recovered. The export figures for 1916 show an increase of 3,000,000 nuts above the number exported in 1915. On the other hand, however, the export of copra has decreased by about 1,000,000 lbs., which works out at about 2,500,000 nuts, so that the real increase for 1916 is only 500,000 nuts. The cultivation is being rapidly extended. The following figures show the distribution of the coconuts among the various countries:

| | Nuts | Copra (lbs.) |
|--------------------------|------------|--------------|
| United States..... | 15,576,595 | 2,928,944 |
| United Kingdom..... | 1,783,364 | 410,904 |
| Canada..... | 484,800 | |
| British West Indies..... | 1,604 | |
| Other Colonies..... | 2,844 | |
| TOTAL..... | 17,849,207 | 3,339,848 |
| VALUE..... | \$484,270 | \$228,665 |

—M.

STARCH SUBSTITUTES IN GERMANY

In all countries, says the *Oil and Color Trade Journal*, 52 (1917), 985, articles which were quite common prior to the war have now had to be replaced by others, either because the importation of the necessary raw materials from foreign countries has ceased or because such raw materials are being employed for other purposes to better advantage. Some interesting data regarding starch substitutes have recently been published by Dr. R. Koenig, who has investigated several types. At the beginning of the war starch substitutes in Germany consisted chiefly of potato flour mixed with chalk ground as fine as possible. When potato flour was no longer available, admixtures of powdered gelatine, white glue and fine white chalk were used. The percentage of chalk increased very rapidly as gelatine advanced in price so that in one instance it was found that the percentage of chalk increased from 20 to 35 per cent in 14 days. Although these products, as long as the glue was not of a yellowish color, were fairly satisfactory, still their price was generally out of all proportion to their actual value. Other preparations placed on the market consisted of crystallized bitter or "cat" salts, water and burnt magnesia. The latter was afterwards sold as "fatless" washing medium. This contained 70 per cent bitter salt, 23 per cent water and 70 per cent magnesia. The salt was dissolved in water and the magnesia thoroughly stirred in till dissolved, whereupon it was allowed to stand in moulds for some hours till it stiffened through the formation of oxysulfate.—M.

SALTPETER PRODUCTION IN INDIA

From the bulletin issued by the Agricultural Institute, Pusa, it would appear that, subject to certain conditions being realized, there is a good opportunity for developing the production of saltpeter in India. The general conclusions arrived at are as follows: (1) The present sources of saltpeter are not fully utilized on account of the drawbacks at present associated with the *nuniah's* business and the low price of crude saltpeter; (2) artificial niter-beds, on account of the favorable soil and climatic conditions in Bihar would probably form a useful added source of saltpeter; (3) the present methods do not allow of recovery of all the nitrate present in the earth worked. It is to be determined whether a better method of extraction could be devised capable of being carried out and whether the efficiency of this method would necessarily depend upon some relaxation or revision of the restrictions at present imposed by the Salt Department; (4) the present conditions of trade in this commodity require examination to determine whether a great demand for Indian saltpeter would result from organized efforts to improve them such as the elimination of the middleman and the standardization of the product itself.—M.

CERAMICS

In an instructive paper on "Ceramic Objects of Pure Materials" published in *Zeitschrift für angewandte Chemie*, the author insists on the finest subdivision of the materials when it is intended to prepare "tun-walled" refractory objects. His materials are the rare earths, magnesias, alumina, carbides, silica, etc., and especially also the nitrides of boron and titanium which he has been studying. The calcined materials should be crushed to grains of 1 mm. and then ground down in steel mills to powders of particles of from 0.001 to 0.005 mm. Though this extreme subdivision seems to undo what has been gained by calcination of the briquetted materials, he considers that the uniformity obtained increases the strength of the objects and reduces the tendency to shrinkage. As binding materials, he recommends water, colophony, oils of turpentine, celloidin in amyl acetate, bakelite varnish, glycerine, and caramel. The last two he prefers, for example, for thoria, and describes how zirconia can be provided with a glazing of thoria. The preparation of boron nitride from boric anhydride and, similarly, of titanium nitride, is an elaborate process. The oxide turns into the nitride when heated at 1200° C. in an atmosphere of ammonia, but the presence of water, which is difficult to expel, interferes with the reaction and the first formed superficial coating of nitride prevents further access of ammonia; high pressure also accelerates the reaction. Mixed with paraffin, the nitride can be squirted into threads 0.1 mm. in diameter. The resulting nitride stands 2,000° C. quite well, and is used for making the tubes in which granular carbon resistances are baked. The boron nitride, density 1.92, does not melt in the arc burning in an atmosphere of nitrogen; it is, however, attacked by oxygen and also by boiling water, especially if a little boron anhydride should still be left in it.—M.

BRITISH BOARD OF TRADE

During the month of September the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

CHEMICALS:

Aluminate of soda
Chromic acid
Monochloronaphthalene
Sodium sulfide

MACHINERY AND PLANT:

Complete cork preparing plant
For making plough chains
For manufacturing fret saws
For peeling lemons
For making toy marbles
Flexible shaft-driven portable tools
Machines for cutting click gears

Articles for West African native trade

Buckle frames, metal or cardboard
Celluloid marking rings for pigeons
Chain coat-hangers

Chamois leather
Curling irons, cheap
Electric driven machinery for floor-polishing
Eucalyptus red gum
Glove makers' waste
Leather waste, *i. e.*, bucks, chamois, suede, etc.
Manioc flour
Paper knives, bone and ivory
Piercing saws for metal
Powder for making beer
Skins, kid
Soap boxes, metal
Synthetic essential oil of mustard
Thimbles, steel and silvered
Wood preservative not containing coal-tar oils
Wooden shovels for margarine factories

—M.

MANGANESE STEEL

A catalog issued by Allen & Co., of Sheffield, England, relates to their Imperial manganese steel and to its use, especially for parts of dredgers, crushing machines and conveyors where great resistance to wear and abrasion are required. This steel is so hard that it cannot be machined and must be finished by grinding and, at the same time, is so tough that it may be bent double while cold without fracture. It has a tensile strength of 55 tons per sq. in., or over, with an elongation of about 40 per cent in 4 in., and is non-magnetic. It is supplied in castings, rolled bars, sheets, forgings and patent rolled rails.—M.

HARDENING OF ALUMINUM BRONZE

According to an article in the *Giesseri Zeitung* for June 1, aluminum bronzes can be improved by thermal treatment. When they contain less than 7 per cent copper, the thermal treatment will not affect the properties much. Higher grade bronzes can be hardened, however, and by the further addition of iron, silicon and other elements, the mechanical properties of the alloys can be much varied. Thus, *e. g.*, bronzes can be prepared having a Brinnell hardness of 100 without being brittle. An aluminum bronze resembling in its mechanical properties a 0.35 carbon Swedish steel was given hardness values ranging from 100 to 260 by various thermal treatments; such bronzes of great hardness will answer as bearing metals even for high speeds. The following figures are given as to the properties of a 10 per cent aluminum bronze containing some titanium, the percentage of which is not quoted:

| | Bronze as cast | Quenched Bronze | After Thermal Treatment at Different Temperatures |
|------------------------|----------------|-----------------|---|
| Limit of Elasticity... | 9.6 | 19.8 | 27.7 to 19.2 kg. per cm ² . |
| Tensile Strength.... | 51.8 | 73.6 | 67.7 to 64 kg. per cm ² . |
| Elongation..... | 19.5 | 1.0 | 5.5 to 1.4 per cent |
| Contraction of Area. | 33.7 | 0.8 | 9 to 18.5 per cent |
| Brinnell Hardness... | 100 | 262 | 158 to 140 |

—M.

POTASH FROM FLUE DUST

A recent article by Mr. H. T. Cranfield in the *Journal of the Board of Agriculture* deals with the extraction of potash salts from blast furnace flue dust. The number of furnaces in full blast in Britain, the author reckons to be 300, and the quantity of flue dust produced per week works out at 20 tons black dust, 5 tons red and 1 ton cream colored. On the assumption that the black dust contains 2.5 per cent, the red 7 per cent, and the cream 10 per cent, each furnace would yield about 50 tons of potash per annum, giving an annual production of 15,000 tons. At least 50 per cent of this would represent soluble potash. From these figures, this may be regarded as an important source of potash and until arrangements can be made and plant erected for the extraction of the water-soluble potash salts, Mr. Cranfield suggests that the raw flue dust might be used on land deficient in potash in the past two years.—M.

A NEW TEST PAPER

A very delicate test paper has been prepared in Japan from the fruit of the Tama-tsubaki, which has a violet color and is turned to greenish blue by a mere trace of alkali and to red by an extremely dilute acid solution. The plant is also known in Japan as Nezumimochi or Teratsubaki. The inventor noticed that the color of its fruits never fades, while the color of the flowers quickly fades. He squeezed the fruit and dyed a filter paper with the juice which gave a violet shade.—M.

FERRO-CONCRETE SHIPS

During the past three months, says the *Times Engineering Supplement*, No. 515, the Committee of Lloyd's Register of Shipping have approved plans for the construction in ferro-concrete of a number of non-propelled barges, some designed to carry 500 tons dead weight, and also of a motor vessel. These vessels will be built in the United Kingdom and in Norway, under the inspection of the Society's surveyors, and are intended for the British and Scandinavian coastal trade. Plans of other ferro-concrete vessels of larger capacity for certain sea trades are at present under consideration. One of the society's principal surveyors recently made a tour of inspection in Scandinavia, where, owing to circumstances arising from the war and other causes, the use of ferro-concrete for ship construction has so far been most developed and the report of his visit has naturally placed the Committee of Lloyd's Register in possession of valuable data on the subject.—M.

RUSSIAN COTTONSEED OIL INDUSTRY

The Russian cottonseed oil industry is established for the most part in the Ferghana, Murgal and Merw districts. The cottonseed from the first-named district contains a high percentage of oil specially suitable for refining. It is stated, says the *Chemical Trade Journal*, that in the Ferghana mills there are more than thirty 16-in. hydraulic presses, seven 12-in. presses and several small ones. The total quantity of cottonseed formerly treated was about 144,000 tons per annum, the working year being 250 days. The yield of oil was approximately 21,600 tons in addition to 48,000 tons oil-cake. Just lately, two new mills have been established and the old mills have been enlarged. The output, therefore, is considerably increased and the total quantity of cottonseed dealt with is now about 192,000 tons. The export of cottonseed from Turkestan in 1913 was about 20-320 tons. It is said that 36 lbs. cottonseed of first quality yield 18 per cent unrefined cottonseed oil, 40 per cent oil-cake and 50 per cent husks, the remainder consisting of linters and other waste.—M.

JAPANESE PAPER-MAKING INDUSTRY

Among the trades in which Japan is sure to make great efforts to maintain a permanent position after the war is the manufacture of "European" paper, says the *Chamber of Commerce Journal*. Before the war a heavy import duty compelled most publishers to use Japanese-made paper although it was both dear and bad and export was hardly dreamed of. Now a large part of the Asiatic trade is in Japan's hands and the new energy put into the business may bring it up to European level. Saghalien makes important pulp contributions—a welcome sign of development of a rather neglected territory. Without the war, it is doubtful whether paper manufacture would ever have been a success, but extraordinary circumstances have justified this and various other protected industries. They have, however, a time of severe trial before them, for in many cases they are far from working as cheaply as Europe in spite of low wages.

The Japanese demand for paper in 1915 was 145,000 tons, of which 60,000 tons were ground pulp and 85,000 tons chemical pulp. The ground pulp was chiefly supplied by home producers, only a small portion being imported. Of chemical pulp about 60,000 tons came from abroad, the home production being limited to 25,000 tons of lower grade material and 7,500 tons of superior grade. The total cessation of imports to Japan since the war began and the enormous rise in prices have stimulated the Japanese pulp industry. Many producers are now exploiting the timber resources of the Saghalien forests and several chemical paper factories have been established recently in Saghalien. With a view to encouraging the pulp industry in Japan, the Japanese Investigation Committee suggests that timber for pulp-making should be supplied at the lowest possible price, and that all possible facilities, for the transport of material, timber and pulp, should be given to producers.—M.

APPLICATION OF RADIO-ACTIVE SUBSTANCES FOR BATTERIES

A recent French patent is concerned with the use of radio-active material for the purpose of facilitating the chemical action taking place in accumulators. For this purpose radium barium sulfate is used. The material is insoluble in the electrolyte and does not appear to enter into chemical action with the lead oxide or the metallic lead of the plates. Its presence is assumed to render the chemical action more complete during charge and discharge, otherwise the process is normal. About 0.2 microgram of radium per lb. of lead oxide is used, the radium compound being merely incorporated in the oxide used on the grid of the plates.—M.

LINING WHITE METAL BEARINGS

In order to ensure uniformity of composition in white metal alloys used for lining bearings the Monometer Manufacturing Company of Aston, Birmingham, has introduced a melting furnace which is provided with a device for thoroughly mixing the components of white Babbitt and similar alloys. This device takes the form of a propeller, carried on ball bearings to reduce friction, the blades of which are rotated in the melting pot by means of a handle. The alloy is drawn off from the melting pot, which is enclosed, through an outlet at the bottom controlled by a screw valve, and a thermostatic regulator, which acts on the fuel supply and can be set to suit any particular alloy, maintains the metal at the proper temperature for running into the bearings. An oven for heating the shells of the bearings before they are tinned, made by the same firm, is fitted with a similar automatic controller which keeps the temperature at the correct point for tinning, and the shells need simply to be rubbed with a stick of tin as they are withdrawn. Automatic temperature control is also provided in a die-casting machine for use in connection with small bearings.—M.

ARTIFICIAL WOOD

The Austrian paper, *Kunststoffe*, states that leaves are now being used for the production of artificial wood, which has for some time been manufactured from sawdust, subjected to high pressure either with or without a binding material. The leaves are dried and boiled in water or lye, mixed with a binding material such as glue, resin, waterglass, etc., and squeezed into blocks under a pressure of 300 to 400 atmospheres. Any desired color can be obtained by appropriate additions. It is claimed that artificial wood so produced can be worked like natural wood and can be used for the most varied purposes.—M.

PAINTS AND VARNISHES FOR SIAM

Siam is a prosperous country, says a contemporary, and the bountiful rice crop, the staple product, which has been recently gathered in, should be favorable to the import of manufactured goods. There is a growing demand among the people of Siam for paints and varnishes for the decoration of their houses. These goods are not made in the country and the trade should be noted by manufacturers of these articles. The sending of catalogues and price lists to the leading importers in Bangkok is recommended, but a better means of gaining a business connection would undoubtedly be the visit of a representative.—M.

COTTON TRADE IN JAPAN

The British Attaché at Yokohama writes, drawing attention to schemes which are being devised for the amalgamation on a large scale of the various cotton spinning interests in Japan with a view to consolidating the position of the cotton textile industry in that country and enabling the mills to retain their hold of British, American and German goods which will, no doubt, supervene at the close of the war. A firmer footing has been gained by Japanese manufacturers in many oriental markets which were considered to be the permanent markets of British or German spinners. It is, therefore, necessary to improve the financial position of the industry to retain this hold. Not only spinning mills but weaving, printing, bleaching and dyeing mills will be included in the combination. One such amalgamation, it is said, will have a total of 540,000 spindles in operation. The report also states that the cotton industry is by far the best organized in Japan and that the amalgamation of these large concerns will certainly tend to reduce expenses and obviate needless competition.—M.

NOTES AND CORRESPONDENCE

HYDROGENATION OF OIL

[The following opinion was rendered Oct. 3, 1917, by Judge Augustus N. Hand, of the U. S. District Court (Southern District of N. Y.) on the Burchenal Patent No. 1,135,351 in case of Proctor and Gamble Co. (Complainant) vs. Berlin Mills Co. (Defendant). Kerr, Page, Cooper and Hayward were Solicitors for the Complainant with Alfred N. Allen, Livingston Gifford and Thomas B. Kerr as Counsel. For the Defendant, John C. Pennie was Solicitor, with Marcus B. May and Mr. Pennie as Counsel.]

This suit is for infringement of patent No. 1,135,351, granted to the Complainant as assignee of John J. Burchenal, on April 13, 1915. The application for the patent was filed November 10, 1910. The specification states that the invention is for a food product consisting of a vegetable oil, preferably cottonseed oil, partially hydrogenated and hardened to a homogeneous white or yellowish semi-solid clearly simulating lard.

Claims 1 and 2 alone are in issue and read as follows:

1—A homogeneous lard-like food product consisting of an incompletely hydrogenated vegetable oil.

2—A homogeneous lard-like food product consisting of incompletely hydrogenated cottonseed oil.

The special object of the invention is, according to the specification:

* * * to provide a new food product for a shortening in cooking in which the liability to become rancid is minimized and in which the components of such vegetable oils which are inferior and detrimental to use as such a food product have been to a large extent converted into a higher and more wholesome form. All such vegetable oils contain glycerids of unsaturated fatty acids and among these notable quantities of fatty glycerids of lower saturation than olein. It is the presence of these glycerids of lower saturation that seriously affects the rancidity of the material. Oxidation is largely the cause of rancidity, which oxidation weakens the fat at the point of absorption at the double bonds, and these glycerids of lesser saturation readily absorb oxygen from the air at ordinary temperatures while the more highly saturated glycerids, as olein, only absorb oxygen at elevated temperatures. It is evident, therefore, that oils or fats containing notable quantities of glycerids of linolic acid or of lesser saturation are distinctly inferior as an edible product to those containing a minimum of these glycerids with a larger per cent of olein. On the other hand, while it is important to get rid of the readily oxidizable glycerids of lower saturation, it is also important not to supply too large a per cent of fully saturated glycerids.

* * * In manufacturing this product, cottonseed or other vegetable oil is caused to chemically absorb a limited amount of hydrogen by reacting on the oil with hydrogen in the presence of a catalytic agent and at an elevated temperature. The oil is preferably agitated in a closed vessel in the presence of an atmosphere of compressed hydrogen, a catalyzer of finely-divided nickel carried by kieselguhr being maintained in suspension in the oil and its temperature being raised to about 155° C.

According to the present invention, the amount of hydrogen absorbed is carefully regulated and limited. In practice, the operation is stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid more closely resembling lard than do the commercial mixtures of cottonseed oil and animal oleo-stearin while in many respects the product is superior to the best leaf lard as a shortening. It is not so liable to become rancid and the product can be heated to a considerably higher temperature than lard without smoking or burning. The high temperature to which my product can be raised without smoking or burning makes the product ideal for frying, inasmuch as a crust forms almost instantly on the food fried, which prevents any absorption of the shortening. A lard-like product thus prepared from cottonseed oil has a saponification value of about 195 and an iodine value ranging from about 55 to about 80. The product having an iodine value of 55 has a titer of about 42° and a melting point of about 40° C., that having an iodine value of 80 has a titer of about 35° and a melting point of about 33° C. While but partially hydrogenated, containing from about 1.5 per cent to 2.5 per cent of additional hydrogen more than in the non-hydrogenated material, it shows no free cottonseed oil when subjected to the Halphen test, thereby differing from all commercial lard substitutes containing this oil. It contains from twenty to twenty-five per cent of fully saturated glycerids, from five to ten per cent linolin, and from sixty-five to seventy-five per cent olein; and an average of a number of samples gives twenty-three per cent of saturated fats, seven and five-tenths per cent linolin and sixty-nine and five-tenths per cent olein, while the cottonseed oil before treatment contained seventeen per cent saturated fats, thirty-seven per cent linolin and forty-six per cent olein. It will thus be seen that I have produced an ideal food

product which is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures.

The complainant urges that Burchenal first taught the art that a partially hydrogenated vegetable oil, preferably cottonseed oil, was edible and was a useful lard substitute. It contends that prior to Burchenal's conception it was not known that hydrogenated cottonseed oil was edible and that the only processes then in use aimed at complete saturation and produced a hard non-edible product. Before discussing the prior art, I would say in general that Normann, whose patent will later be referred to, had already disclosed a method of hydrogenating oils, and had set forth in his specification that the process was progressive and involved "no secondary reaction." The method of adding cottonseed oil to beef stearin for use as a lard compound was well known and much used, as it still is. The hydrogenation of cottonseed oil resulted in a reduction of the fluid and substitution of the solid fats. Normann's patent, as well as various experiments of scientists, indicated that the addition of hydrogen to cottonseed oil would result in the reduction or elimination of the fluid and substitution of solid or partially solid fats. No one has shown that the product resulting from such hydrogenation was ever non-edible or unsanitary in any respect.

The British patent No. 0, 83 (1887), to Joseph Sears, was for a lard substitute composed of refined unbleached cottonseed oil and a fat adapted to give a stiffness to the compound corresponding substantially to that of refined lard. The specification provided that the temperature should be raised sufficiently to melt the fat or stearin, the heated ingredients mixed and then chilled rapidly so as to prevent crystallization and separation. This general process was well known in the art before the date claimed for the invention of Burchenal and indeed is referred to in the patent in suit. A very large market for such lard-like compounds exists at the present time and has existed many years past.

The British patent No. 1515 of 1903, to Normann, discloses a process for the reduction of glycerines resembling that of the patent to Burchenal. Normann's patent says that:

The property of finely divided platinum to exercise a catalytic action with hydrogen * * * is already known. * * * Recently Sabatier and Senderens of Paris have discovered that other finely divided metals will also exercise a catalytic effect on hydrogen; viz., iron, cobalt, copper and especially nickel.

By causing acetylene, ethylene or benzene vapor in mixture with hydrogen gas to pass over one of the said metals (which had just been reduced in a current of hydrogen) the said investigators obtained from the unsaturated hydrocarbons, saturated hydrocarbons, partly with simultaneous condensation.

I have found that by this catalytic method it is easy to convert unsaturated fatty acids into saturated acids.

This may be effected by causing fatty acid vapors, together with hydrogen, to pass over the catalytic metal, which is preferably distributed over a suitable support such as pumice stone. It is sufficient, however, to expose the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance.

For instance, if fine nickel powder, obtained by reduction in a hydrogen current, is added to chemically pure oleic acid, the latter heated over an oil bath and a strong current of hydrogen is caused to pass through it for a considerable time, the oleic acid may be completely converted into stearic acid.

The quantity of the nickel thus added and the temperature are immaterial and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids, the reaction passes off without any secondary reaction. The same nickel may be used repeatedly. Instead of pure oleic acid, commercial fatty acids may be treated in the same manner. The fatty acid of tallow which melts between 44 and 48° C. has an iodine number 35.1 and a yellow color will after hydrogenation melt between 56.5 and 59°, while its iodine number is 98 and its color slightly lighter than before, and it will be very hard.

The same method is applicable not only to free fatty acids, but also to the glycerines occurring in nature, that is to say, the fats and oils. Olive oil will yield a hard tallow-like mass; linseed oil and fish oil will give similar results.

By the new method all kinds of unsaturated fatty acids and their glycerides may be easily hydrogenated.

The Normann patent clearly discloses that oils may be completely hydrogenated, that the process is progressive and that it

involves "no secondary reaction," in other words, that cottonseed oil which starts edible remains so. The experiments and articles of Paul and Roth, which were alluded to at the trial, show that hydrogenization of oils including cottonseed oil was understood in the prior art.

Such being the state of the art, Edwin Cuno Kayser wrote Procter & Gamble from England that he had a process of considerable value and would like to talk to them about it; thereafter he came to America, about November, 1907, bringing samples of hydrogenized cottonseed oil. He showed these to Burchenal, the superintendent of Procter & Gamble. As a result of his visit, he made an arrangement under a preliminary contract of January, 1908, to experiment upon the hydrogenized cottonseed oil as a substitute for lard. The first project was apparently to use hydrogenated cottonseed oil as a compound to be added to a percentage of beef stearin and cottonseed oil. Burchenal says he had done no work in connection with hydrogenizing cottonseed oil before he saw Kayser. He testified that:

"Mr. Kayser went out to our factory and made sketches as to the apparatus that would be necessary to carry on this work, and the apparatus was ordered at once; a little plant was installed for experimental purposes and I think it was ready to operate sometime in January or February, 1908" (Deposition of Burchenal, page 11).

The defendant succeeded in obtaining contemporaneous memoranda as to some of Kayser's experiments from the records of Procter & Gamble. The first experiment was as follows:

FAT HARDENING PROCESS BY E. C. KAYSER

First experimental lot was completed January 17, 1908. Fat treated—Summer Yellow Cottonseed Oil. Used Nickel Sulfate and Kieselguhr as described. Experiment was conducted by Mr. Kayser alone. He claims to have used about 1 per cent Nickel Metal and 2 per cent Kieselguhr.

M. p. of fat after 3 hrs., 55½° C.
M. p. of fat after 6½ hrs., 60.3° C.
Dr. Bender reports as follows:
Melting point of fat, 60.3° C.
Hydrocarbons, 0.33 per cent.
Iodine value of fat, 7.14 per cent.

The fat does not contain free fatty acids. This material is much superior to the samples from J. Crossfield & Sons, which showed an iodine value of 52.26 and a melting point of 39.3° C. (The laboratory sample melted at 49.9° C.). Their samples contained 5.12 per cent free fatty acids and 2 per cent hydrocarbons.

Mr. Kayser reports as follows: "The melting point of fatty acid, prepared from first lot hardened cottonseed oil, is 62° C. This is several points higher than I ever got before. Presumably the composition of your oil differs somewhat from that of the oil I handled formerly."

Another experiment by Kayser of the date of March 5, 1908, was also obtained from the Procter & Gamble records, in which the following melting points appeared:

5 hrs. at ordinary pressure, 42° C.
1½ hrs. at 60 lb. pressure, 43° C.

Von Phul testified that Kayser told him in 1907 that he was getting up a patent for a food product and even Burchenal's own testimony shows that Kayser supposed that the product he was making was edible. If Kayser at first told him it was not edible, he did so when they were negotiating and he wished to keep his process in the dark until he had arranged his terms. That Kayser's statement that it was not edible was not taken seriously by either party is shown by the following testimony:

Q. 887. But you did not know as a matter of fact whether it would be edible or not? A. I did not. Mr. Kayser stated that it would not be, but that was his method of talking.

Both of these men were proceeding soon after Kayser's arrival in this country to develop hydrogenated cottonseed oil as a food product. Even if the thought first occurred to Burchenal I cannot see that he did anything to carry it out in practice. Kayser's patent No. 1,004,035, application for which was filed March 20, 1908, disclosed the process which was employed to make the product covered by the patent in suit, and the specification for this Kayser patent contains the statement that, "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." It is to be remembered that Burchenal distinctly disclaimed in his testimony that he had anything to do with the invention of the process covered by the Kayser patents and we thus have a situation where Kayser invented the process and developed the product to the point where it was applicable to use as a food product. He came to America with a sample which, as appears from the written record taken from the files of the complainant, had a melting point of

only 3° and developed other samples with melting points of but 42° and 43° in his March 5, 1908, experiments.

Moreover, it is to be remembered that Crossfield had employed Kayser to experiment in hydrogenating oil, that the former had been in close communication with Normann, who had patented only four years before the process I have mentioned and that Crossfield had so strenuously objected to the use by Procter & Gamble of the processes of Kayser that they were obliged to purchase their rights to them. It is also noteworthy that Kayser refused to testify in this case and that the witnesses, as to the work of Kayser in America are officers or employees of the complainant. Under such circumstances the meagerness of the evidence which has been adduced to show that Burchenal had anything to do with the development of the lard-like food product which is the subject of the patent in suit, coupled with his admission that the entire process under which it was made was the work of Kayser, is most significant and makes it impossible to find that Burchenal invented anything. The defendant has been embarrassed in its defense by many difficulties and has been obliged to go into the enemy's camp to secure almost all its ammunition. In spite of this, it has been established that Kayser at the very beginning had developed not only a process but a product little differing from Crisco. Kayser remained with Procter & Gamble until well into 1910, and did not leave America until about July of that year. While there is some general evidence of what Burchenal and others did, or directed, I can find no real proof that anyone but Kayser did anything of substantial moment. No step was taken by Burchenal that could possibly amount to invention.

Complainant urges that the experiments of Kayser and the patents of Normann and Kayser aimed at complete saturation and that neither realized the importance of a partially hydrogenized product. But the process under which their products were made involved in its progress partial hydrogenation, and Kayser's patent, No. 1,004,035, distinctly stated that "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." Kayser, as far as I can see, did everything that was done to develop Crisco, and if his work fell short of this, he achieved enough so that the final step was inevitable to one skilled in the art. Kayser's process was the complainant's process and his product involved a progressive reaction fitted for any purpose. The broad discovery as between him and Burchenal certainly belongs to him.

Furthermore, under any fair interpretation of the patent, there is no infringement. The file wrapper indicates that the examiner rejected the claims as originally filed, saying:

* * * If the problem of simulating lard from cottonseed oil were presented to an oil chemist, an incomplete hydrogenization of the cottonseed oil would at once suggest itself to him as a solution of the problem. All the claims are accordingly rejected on the * * * ground of lack of invention.

Thereafter new claims were rejected upon the Kayser patents for the reason that his process could be arrested at any time to produce an incompletely hydrogenized product. Then, and for the first time, Burchenal filed an amendment setting forth certain percentages of linolin, olein and stearin which his product should contain. It seems quite evident, therefore, that Claims 1 and 2 of his patent would, under such circumstances, if valid at all, be limited to substantially the chemical composition described in the amended specification. Indeed, the specification closes with the statement that the inventor has produced a product which 'is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures.'

Under such circumstances it is impossible to treat the melting point as practically the determining actor, and if this is not done the defendants' product Kream Krisp does not infringe. After the examiner had held that an incomplete hydrogenation would suggest itself to any chemist seeking to simulate lard and rejected the claims on Kayser, the patentee, as I have shown amended by specifying a particular product and dwelling upon the advantages of a small percentage of linolin to avoid rancidity. If, therefore, the inventor contributed anything to the art it was this special chemical composition which his patent discloses. Claims 1 and 2 should consequently be construed in the light of the proceedings of Burchenal before the Patent Office and not given a scope which would monopolize an art in which Normann, Kayser and others had been the real pioneers.

Kream Krisp has a chemical composition extremely remote from that described in the specification of Burchenal. The following are the relative percentages:

| PER CENT | BURCHENAL | KREAM KRISP |
|---------------------|-----------|-------------|
| Saturated fats..... | 20 to 25 | 28.0 |
| Olein..... | 65 to 75 | 34.3 |
| Linolin..... | 5 to 10 | 37.7 |

Thus it appears that Kream Krisp, instead of being low in linolin, is extremely high, and that instead of being high in olein as specified in the Burchenal patent, it has a percentage of olein which differs but little from that existing in refined cottonseed oil unhydrogenated. In fact, Kream Krisp seems to present many of the objections referred to in Burchenal's specification and to lack the very things upon which the latter based his right to receive a patent. Indeed, the composition is much closer to the lard compound Jewel made out of stearin and cottonseed oil than to Crisco.

The bill should be dismissed with costs because the patent is void for lack of invention and for the further reason that Claims 1 and 2, if properly construed, are not infringed by the defendant.

THE AMERICAN COAL-TAR PRODUCTS INDUSTRY PRODUCTION TO BE ASCERTAINED BY THE UNITED STATES TARIFF COMMISSION

The United States Tariff Commission is planning to ascertain the production within the United States during 1917 of all substances treated in Title V of the Special Tariff Act of September 8, 1916. The substances there enumerated may be classed under the general name Coal-Tar Products and are divided into three groups.

Group I includes "all products that are found naturally in coal tar, whether produced or obtained from coal tar or other source" except phenol. These substances are admitted free of duty.

Group II includes the so-called Intermediates and are made dutiable at 15 per cent plus 2½ cents per pound.

Group III includes "all colors, dyes, or stains, whether soluble or not in water, color acids, color bases, color lakes, photographic chemicals, medicinals, flavors, synthetic phenolic resins or explosives, not otherwise specially provided for in this title, when obtained, derived or manufactured, in whole or in part from any of the products provided for in Groups I and II." These articles are dutiable at 30 per cent plus 5 cents per pound with certain exceptions which are dutiable at 30 per cent.

Under the law the duties are made dependent on the growth of the industry within the United States. It is therefore the intention of the Commission to follow this growth from year to year in order to report the facts to Congress.

The Tariff Commission is planning to send to each manufacturer a questionnaire calling for information in regard to his production during 1917 of each separate commodity, as well as for certain other data. This information will be published in such a form that the operations of individual firms will not be disclosed. A preliminary questionnaire has recently been sent out, designed to aid in perfecting the mailing list. Any individual or firm engaged in the manufacture of any of these articles which did not receive a copy of the preliminary questionnaire is requested to write to the United States Tariff Commission, Washington, D. C., to insure being placed on the mailing list.

U. S. TARIFF COMMISSION F. W. TAUSSIG, *Chairman*
WASHINGTON, November 5, 1917

SAMPLING FATS AND OILS—CORRECTION

In the "Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils other than those of the Coconut, Butter and Linseed Groups" as published in THIS JOURNAL, 9 (1917), 1066, the strength acid for acidifying under determination of TITER, page 1068 (1st column, 4th line above foot-notes), should read "30 per cent" instead of "50 per cent."

November 17, 1917

W. D. RICHARDSON

CONCERNING THE MANUFACTURE OF PHTHALIC ACID AND PHTHALIC ANHYDRIDE

The Department of Agriculture announced on June 16, 1917, that the Color Investigation Laboratory of the Bureau of Chemistry of this Department had perfected on a laboratory scale a new process for the manufacture of phthalic acid and phthalic anhydride, and invited coöperation with the manufacturers for the purpose of testing this laboratory process upon a commercial scale. It was also stated in the announcement that the offer of assistance would not be held open by the Department for an indefinite period.

Arrangements have been made with several concerns to test this process on a commercial scale and the Color Investigation Laboratory is not in a position to receive or handle any additional offers of coöperation. The offer made on June 16, 1917, therefore, is withdrawn and no additional offers of coöperation can be considered.

DEPARTMENT OF AGRICULTURE D. F. HOUSTON, *Secretary*
WASHINGTON, November 1, 1917

CHICAGO CHEMICAL EXPOSITION PLANS ABANDONED

After serious consideration and correspondence with all exhibitors, the managers of the Chemical Exposition have decided to abandon plans to hold a Chemical Exposition in Chicago in the Spring. This action was taken because of insufficient support secured to make a large and representative exposition, all the exhibitors wishing to confine their efforts toward making the Fourth National Exposition of Chemical Industries in New York, week of September 23, 1918, the greatest event in the history of American Chemical Industry, it being their intention to show there the many advances they are making as a result of their researches.

NITRIC ACID SOPHISTICATION—CORRECTION

The following corrections should be made in my article printed in THIS JOURNAL, 9 (1917), 771:

Page 775, 2nd col., line 44,

"at 7¼c.....7.28" should read "at 7¾c.....7.25"

P. 776, 1st col., line 18,

"127 lbs.....\$10.16" should read "127.77 lbs.....\$10.22"

line 19, "1.82" should read "\$1.88"

line 21, "1.51" should read "\$1.54"

line 23, "0.51" should read "\$0.53"

October 29, 1917

JAMES R. WITHROW

THE DETERMINATION OF SULFUR DIOXIDE— CORRECTION

The following corrections should be made in my article printed in THIS JOURNAL, 9 (1917), 949:

Page 949, 2nd col., line 34, omit "Both Dymond and Hughes and the Selby Smelter Commission used sodium sulfate for their standard."

Page 950, 1st col., first line under heading APPARATUS should read "One extra heavy 24-liter, or larger, bottle such as a carboy, carefully housed to avoid serious trouble from collapse and, etc."

Page 950, first line under heading METHOD OF PROCEDURE should read "Large sample bottle is evacuated to about 380 mm. and the pressure, etc."

November 8, 1917

JAMES R. WITHROW

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

DEMAND FOR CHEMICALS NOW GREATER THAN SUPPLY

Despite the concerted action of many of the nation's most capable chemists the demand for many essential articles is outstripping the supply. Most of the men in Washington who are working on chemical problems are willing to admit that the shortage of many chemicals threatens to become exceedingly serious. Much has been accomplished in speeding up the production of chemicals, but the point is being reached where the spur is less effective. Many plants are reaching the maximum of their production while requirements are exceeding even the highest estimates.

NEW WAR POLICY NECESSARY TOWARD CHEMISTS OF MILITARY AGE

The situation has reached a degree of seriousness which at last is arousing the military authorities to the need of a more practicable policy with regard to the disposition of chemists of military age. Plans are now practically ready for announcement of a new policy with regard to chemists. A sweeping order such as that which gave a blanket exemption to all men engaged in the shipbuilding industry hardly is expected at this time, but it is believed that certain classes of chemists will be hurried back from military camps and again placed at their regular work.

Requirements of sulfuric acid for 1918 bid fair to exceed those of the current year by 1,500,000 tons. Unmistakable signs have come from Chile that that country intends to take advantage of the world situation to squeeze the greatest possible profit from her nitrates. Apparently importers of manganese and those who are pinning more faith on increasing the domestic production are in deadlock. After much pulling and hauling on the part of each faction in an effort to influence the Shipping Board, Chairman Hurley apparently has shunted the responsibility to the War Industries Board. The result is an uncertainty which is retarding domestic production and is causing much concern to the steel makers. The iron pyrite situation is substantially in the same position. Visible supplies of platinum, so imperatively needed as a catalyzer, are entirely inadequate for war uses. The situation has become more complicated by the attitude of Colombian producers whose tendency to hold back shipments to this country is believed to be meeting with official favor in that country. Regardless of the seriousness of this situation, heavy articles of jewelry made of this metal continue to appear for sale. Those who are charged with responsibilities in connection with the ammonia situation are working day and night in their efforts to keep the supply in advance of the demand. Arsenic is becoming harder and harder to obtain, while the Explosives Act has added to the difficulties of those handling its ingredients. These are just a few of the problems which are confronting the government's chemical specialists and those who have come here to aid in coördinating the country's industries looking to the most effective conduct of the war.

Some one high in authority seems to have fallen under the spell of the Alabama Senators and there no longer is a question that the most ambitious plans of the Muscle Shoals promoters have begun to be carried out. Members of the Senate and of the House of Representatives who favor the manufacture of nitrates, in accordance with the recommendations of the nitrate board, are marshalling their facts and a battle royal between the two camps is certain to be staged at the approaching session of Congress. In the meantime, the uncertainty is pushing further into the future the day when the United States will be able to contribute to the amount of nitrates it is consuming, and plans for the Chilean monopoly are reported to be progressing rapidly toward consummation.

COMMITTEE ON CHEMICALS DISBANDED

Further impediment of the efforts being made to secure the maximum production of chemicals and in the general work being done in the handling of the chemical problems which the war has thrust to the fore has come with the reorganization of the Council of National Defense. The Committee on Chemicals, of which Dr. W. H. Nichols is the head, has been instructed to terminate its work as an official division of the Council of National Defense. No conclusions as to the future plans of the committee have been announced. It is very evident, however, that the War Industries Board expects to take a leading part in the handling of the entire chemical situation. The naming of a director of chemicals by this body is expected to be one of the developments of the near future. The director of chemicals will be incorporated in the raw materials division of the War Industries Board. I. L. Summers and M. F. Chase already have the chemical work of the War Industries Board well started. The Board, however, is not yet prepared to outline officially the plans of its chemical division. Mr. Summers, who demonstrated unusual ability in the handling of munitions purchases for J. P. Morgan and Co., when that concern was doing the purchasing for the Allies, has been connected with Bernard Baruch's committee on raw materials since the formation of the Council of National Defense. Mr. Chase comes from the staff of the Commercial Acid Company, of St. Louis. He is well known among eastern chemists, due to his long connection with the New Jersey Zinc Company.

ADVISORY BOARD FOR BUREAU OF MINES

Because of the great amount of war work being done by the Bureau of Mines, Secretary of the Interior Lane has asked six of the prominent chemists of the country to act as an advisory board to the bureau.

The members of this board are: Dr. Wm. H. Nichols, General Chemical Company, New York, *Chairman* of the board; Prof. H. P. Talbot, head of the chemical department of Massachusetts Institute of Technology, Boston, Mass.; William Hoskins, consulting chemist, Chicago, Ill.; Prof. F. P. Venable, head of the chemistry department, North Carolina University, Chapel Hill, N. C.; E. C. Franklin, professor of chemistry, Leland Stanford University, Stanford, Cal.; and Dr. Charles L. Parsons, chief chemist of the Bureau of Mines.

The board will discuss and advise upon gas warfare research, the minerals especially needed for munitions, and the recently enacted law for the regulation of explosives.

An important expansion in the exports of chemicals was registered in September, as compared with September of 1916. The increases, however, were confined to shipments to the countries associated with the United States in the war. As the export licensing plan was in effect throughout the month of September, shipments to neutral countries were curtailed. To France, however, shipments of chemicals increased from \$32,076 worth to \$251,059 worth. To the United Kingdom, the increase was from \$131,474 worth to \$233,026 worth. Exports to Italy increased from \$62,794 to \$98,316. The exports of acids did not greatly increase, as 4,961,925 lbs. were forwarded in September of this year, while the shipments of the corresponding month of last year were 4,424,395 lbs. Notable increases were made in the exports of calcium carbide. In September of 1916, exports were 2,269,649 lbs. In September of this year they were 5,478,198 lbs. Exports of copper sulfate increased from 96,802 lbs. to 226,491 lbs. Exports of sulfur showed a falling off, as 10,052 tons were shipped abroad this year in September,

whereas the record for last year shows forwardings of 19,424 tons. The first exports of chemical glassware in years are now being made. In September, the value of such ware exported was \$5,650.

That full advantage may be taken of America's petroleum in war operations, steps are being considered by the government which will place more tank ships in the transatlantic service. It is regarded as probable that the vessels now engaged in transporting crude oil from Tampico will be drawn upon. An effort now is being made to ascertain just how many of these ships can be diverted to transatlantic service without crippling any essential domestic petroleum activity. One of the suggestions made in this connection is that imports of Mexican oil all be made through Galveston for delivery in tank cars, instead of using ships to carry crude oil from Tampico to practically every important port as far north as Portland, Maine. It is believed that sufficient tank cars can be secured to take care of the distribution within the United States, thereby releasing a number of ships. As the situation stands at present, it is tank ship space, rather than production, which is limiting the forwardings of petroleum products destined for use in Europe. It is probable that the use of ships

to bring asphalt to the United States from Trinidad and Venezuela will be curtailed entirely, as it is believed that domestically produced asphaltic materials, while inferior to the imported article, can be made to suffice very well.

SHORTAGE OF CYANIDE IN MEXICO

A serious situation has been precipitated in Mexico by the curtailment of exports of cyanide. Numerous large plants have been forced to suspend operation, on account of its shortage. The trouble has been remedied in part by the War Trade Board, which is allowing some cyanide to go to Mexico. Until this step was taken, serious disorders were threatened by the large numbers of workmen whose enforced idleness was caused by the lack of cyanide. It is probable that the policy of the War Trade Board in regard to the amount of cyanide exports will not be defined formally until more definite information is available as to the possibility of meeting all domestic requirements. It is probable that one of the conditions under which exports of cyanide will be permitted will be the formation of an association of all consumers which will guarantee complete equity in its distribution.

PERSONAL NOTES

The United States Department of Labor recently created, as a part of its employment service, a Division whose function it is to aid the employer in obtaining suitable help, and professional persons in securing suitable employment. This is known as the Teachers and Professional Service Division. While intended to embrace all professions, attention has thus far been confined to the teaching and engineering professions. The services of the Division are absolutely free to both employer and employee, all expenses being borne by the United States Government. Its methods are quite thorough, and no service is rendered the applicant until the Division has learned, from persons familiar with the applicant, that he is qualified as to training, experience, and personal qualities for the position he seeks. When an applicant is recommended for a reported vacancy, the employer is given an opportunity to examine the data gathered in the course of this investigation, thus effectually preparing for the final and most important step, the personal interview, and for this ample facilities are provided in the offices of the Division where employers may meet with prospects on appointment.

Employers and professional engineers everywhere are invited to avail themselves of the services of this Division which, as stated above, are entirely free. Employers in reporting positions are asked to state the nature of the position, its duties, requirements, etc., the probable salary, and probable duration of employment. Applicants for registration should indicate in the first letter the nature of the position desired so that the proper blank may be furnished. All communications should be addressed: Teachers and Professional Service Division, U. S. Employment Service, 845 South Wabash Avenue, Chicago, Illinois.

Dr. Andrew Bender, chief chemist of the Carnegie Plant of the Aetna Explosives Company, has been transferred to the Company's New York office as technical assistant to the General Manager of the Company.

Prof. E. Bartow of the University of Illinois has been commissioned as a Major in the Army Reserve Corps. He will go to France to take charge of the sanitary condition of our army camps.

Dr. W. L. Lewis, associate professor of chemistry at Northwestern University, has been commissioned a Captain in the Officers Reserve Corps. He is to be engaged in research work.

Dr. L. M. Henderson, instructor in chemistry at the University of Minnesota, is located at the American University at Washington. He is in the instruction department of the Government service.

Dr. Chas. S. Palmer, fellow in the Mellon Institute of Industrial Research, Pittsburgh, Pa., has disposed of his patent petroleum cracking process to the Standard Oil Company of Indiana, which also owns the Burton process.

Mr. Oscar Charles Sumner Carter, for 37 years professor of chemistry, geology and mineralogy at Central High School, Philadelphia, died November 8th, at his home.

Dr. Charles L. Reese, chemical director of the du Pont Powder Company, has been elected a member of the board of directors of that company.

Miss Leola E. Marrs, for the past six years Assistant Editor of THIS JOURNAL, has accepted the position of Managing Editor of the *Color Trade Journal*. Miss Marrs takes up her new duties on December 3rd at 200 Fifth Avenue, New York City.

Professor H. Lewis Jackson, state chemist of Idaho for four and a half years, has accepted the position of professor of industrial chemistry at North Dakota Agricultural College, Fargo, N. D. He will also be in charge of the paint and oil laboratory and paint investigational work.

The chemists of Duluth, Minn., Superior, Wis., and the range towns have organized a Chemists' Club, for the purpose of promoting the interests of chemistry, and stimulating friendship and sociability among its members. The organization has been perfected, and meetings will be held monthly at the Duluth Commercial Club or at various plants in the city. The officers for the ensuing year are: *President*, Walter H. Benson, *Vice-President*, A. D. Whealdon; *Secretary-Treasurer*, Max Latshaw.

Mr. Lawrence Addicks, consulting metallurgical engineer of New York City, has sailed for Burma to make a metallurgical investigation of the ores of the Baldwin Mines.

Dr. James J. Johnson, Newark, N. J., formerly connected with the Maas and Waldstein Company in the capacity of chief chemist, has been commissioned a Captain in the Ordnance Department, to serve in the gun division. Dr. Johnson is an expert on high explosives, having been formerly associated with the du Pont plants and also at the Picatinny Arsenal.

Messrs. Philip A. Singer and Harris Perlstein, formerly of the Industrial Chemical Institute of Milwaukee, have associated as Singer-Perlstein Company, chemical and industrial engineers, with offices in the Railway Exchange, Milwaukee. Mr. Singer was for many years with the Corn Products Refining Company as member of the Manufacturing Committee and superintendent of various departments of that corporation's plants. He has also made contribution to the technique of the ethyl alcohol from wood waste and other chemical industries. Mr. Perlstein has been connected with Mr. Singer in a number of recent enterprises.

The Pfaudler Co. announces the establishment of a branch sales office at 440 Pierce Building, St. Louis, Mo., with Mr. George E. Gray, formerly of their Chicago offices, in charge. The Atlanta agency has been granted to C. M. Jackson Co. of that city.

Mr. W. G. Gaessler has been appointed acting chief of the Chemical Section of the Iowa State College Agricultural Experiment Station, filling the position left vacant by Dr. A. W. Dox, who has been appointed Captain of the Sanitary Corps.

Mr. G. P. Plaisance, formerly of the Iowa State College Agricultural Experiment Station, has been appointed chief chemist of the Oklahoma Experiment Station at Stillwater, Okla.

Dr. J. M. Crafts, formerly president of the Massachusetts Institute of Technology, was elected honorary member of La Société Chimique de France on July 13, 1917.

Dr. John Charles Hessler, professor of chemistry in the James Millikin University at Decatur, Illinois, has been elected to the presidency of the Illinois State Academy of Science.

Mr. Victor K. LaMer, formerly chemist at the Carnegie Institution, Cold Spring Harbor, Long Island, has received a commission of First Lieutenant in the Sanitary Corps.

Professor Clarence A. Morrow, formerly professor of chemistry in the Nebraska Wesleyan University, has been elected assistant professor of agricultural biochemistry in the University of Minnesota.

Mr. E. J. Barth, formerly with the Texas Company, has accepted the position of chief chemist with the Freepport Mexican Fuel Oil Corporation at Meraux, La.

Mr. O. W. Palmenberg, 50 Church St., New York City, reports the following platinum ware to have been stolen from his laboratory: 4 crucibles (marked E. & A.) weighing about 22 g. each; 3 covers weighing about 7 g. each; lipped dish (marked E. & A.) weighing about 48.9 g.; gauze cylindrical anode weighing 8 $\frac{1}{2}$ g., for electrolytic deposits; and spiral wire weighing 7.10 g.

Mr. L. Drew Betz, formerly chemist with the Animal Oil Company, has recently been appointed chemical director of the Philadelphia Plant of E. F. Drew and Company.

The U. S. Civil Service Commission announces an open competitive examination for junior chemical engineer, for men only, on December 5, 1917. Applicants should at once apply for Form 1312, stating the title of the examination desired, to the Civil Service Commission, Washington, D. C. The salary ranges from \$1200 to \$1500 a year.

Mr. F. L. White has resigned from the laboratory staff of the National Carbon Company, Inc., to accept the position of chief chemist in the K-W Ignition Laboratory, Cleveland, Ohio.

Dr. Benjamin T. Brooks formerly with the Bayway Chemical Co. is now connected with the Commercial Research Co., Flushing, L. I.

Mr. R. P. Noble, of Indianapolis, is now with the Government and is located in Washington. H. E. Cory and J. R. Keubler, both of Indianapolis, are now in training with the National Army.

Mr. Geo. G. Schmidt, formerly engineer for the Metropolitan Street Railway Company, piping engineer for the Pennsylvania Railroad Co., Belmont Tunnels and the Ashokan Dam, is now with the Carrier Engineering Company as piping engineer. Mr. Schmidt's department has its headquarters at the main offices of the company, 39 Cortlandt Street, New York, and will have charge of all work connected with the layout and installation of piping on installations of Carrier Air Conditioning Apparatus.

Mr. Edwin G. Pierce, Youngstown, Ohio, has been named consulting chemist for the Republic Motor Truck Co. of Alma, Mich. He has equipped a laboratory at that city for general chemical work and testing materials. The laboratory is under the immediate charge of Mr. Clyde S. Morgan, a graduate of the University of Wisconsin.

Dr. R. B. Owens, secretary of the Franklin Institute, now in France on leave of absence, acting as head of the Army Intelligence Bureau, has been elevated to the rank of Major. He is serving under General Pershing.

Dr. B. A. Stagner has resigned his position as head of the chemistry department of the Fresno, California, Junior College, to accept a position in the Mellon Institute of Industrial Research.

Mr. W. R. Gildard has resigned from the research staff of the Pittsburgh Plate Glass Co. to become Director of Research for the Lancaster Lens Co.

Dr. F. B. Kingsbury, assistant professor of physiological chemistry in the University of Minnesota, has been granted leave of absence for the duration of the war. He has been commissioned First Lieutenant in the sanitary corps of the Army and will be directly under Major John R. Murlin, of the Food Division.

Mr. Richard K. Meade, Consulting Chemical and Industrial Engineer, Law Building, Baltimore, Md., announces that he has formed a partnership with Mr. Howard C. Tompkins, one of his associates, under the name of Richard K. Meade & Co.

Prof. Alexander Silverman, of the University of Pittsburgh, gave a lecture to the chemists and engineers of Delaware on Thursday evening, November 15, in Wilmington. The subject was "The Chemistry and the Manufacture of Glass."

W. H. Doran, of the Alcan Hirsch Laboratories, is leaving for Japan on December 7, to act as construction engineer of the Japan Dyestuff Manufacturing Company.

INDUSTRIAL NOTES

We learn from *Oil, Paint and Drug Reporter* that plans are under way for the establishment of a casinghead gasoline plant in the Viking field of Northern Alberta, where a considerable gas production has been developed by the Northern Alberta Natural Gas and Development Company. The casinghead proposition is backed by Montreal capitalists, who are planning to commence actual development work next spring.

Experiments have recently been conducted in Sweden in the production of potash, iodine and bromine from seaweed. It is said that the experiments have been attended by good results, and that two factories are to be erected for the purpose of extracting the materials mentioned.

Work has been started on the new potash recovery plant of the Clinchfield Portland Cement Corporation at Kingsport, Tenn. This plant will employ the Cottrell or electrical precipitation system in its latest form and will include a wet treater by means of which potash salts will be obtained.

Under the provisions of a new federal law which became effective November 15th, all persons manufacturing, distributing or using explosives must be licensed.

The largest plant in the world for the manufacture of nitrous oxide is to be established in France under the direction of chemists from Cleveland, O. The Ohio Chemical and Manufacturing Company had a \$50,000 contract from the Red Cross for this gas, which Dr. George W. Crile, of Cleveland, has taught French physicians to use as an anesthetic.

The British Commercial Gas Association has been carefully investigating the question of driving motor vehicles with coal gas as a substitute for gasoline, and in its report declares that coal gas in the present emergency may be advantageously used as a gasoline substitute by providing a large flexible holder in which the gas is stored approximately under atmospheric pressure. Experiments led to the conclusion that the equivalent of one gallon of gasoline is about 300 cu. ft. of gas, but other experiments have given only 250 cu. ft. or less, depending on the quality of the gas. In practice it seems that coal gas will show appreciable economy compared with gasoline, as at normal prices gas worth 16 cents would do the work of a gallon of gasoline. The one ground for complaint with reference to the new fuel is that it is inconvenient because of the large amount of space required for the bulky containers.

The Paris Academy of Sciences is to establish a national physical and mechanical laboratory, for scientific industrial research.

The Canadian Advisory Council for Scientific and Industrial Research has appointed a committee of twenty members to assist the development of the Canadian chemical industries and a committee of the same number to promote the metallurgical and mining industries. The Council has also taken over the exhibit of natural resources started by the Arthur D. Little Company of Montreal.

A process of electrolytic printing on both sides of paper by means of electrode plates has been patented in Germany.

It is reported that the United States Government has struck a deposit of potash in the exploration well which it has been boring near Cliffside, Texas, during the past two years. The exploration work will be extended to the territory lying 85 to 100 miles south of the present well and bordering New Mexico, where brackish water is found in many wells, and there are salt lakes which show strong indications of the near presence of potash.

The entire stock of dyestuffs, colors and chemicals of the Badische Company of New York has been taken over by a recently organized company known as Kuttroff, Pickhardt & Co., Inc., which will continue the business of the Badische Company, with offices at 128 Duane Street, New York City. The new concern was recently incorporated under the laws of the State of New York and has taken over the staff of employees and the laboratories of the old concern.

As soap is not obtainable in Germany there are many substitutes consisting of earths, chalk, alkali carbonates, sodium sulfate, sodium silicate, etc., bound together with some binding material such as gelatine. Salicylic acid or some other preservative is required also. In some of the washing powders sodium peroxide and sodium perborate are used and as accidents have resulted from their use a warning has been issued to the public.

The National Oil Products Company of Chicago has been incorporated under the laws of Illinois with a capital stock of \$100,000.

The United States Potash Products Company has been incorporated under the laws of Delaware, with a capital stock of \$5,500,000. Incorporators, D. T. Connet, White Plains, N. Y.; J. F. Roach and E. C. Bahn, of New York.

The Standard Asphalt and Refining Company of Chicago has purchased the plants and trade marks of the Sarco Petroleum Products Company. The Cities Service Co., of New York City, is the new interest back of the company, although the management will remain practically the same as in the old company.

The Aircraft Fireproofing Corporation has been incorporated at Portland, Me., to manufacture chemicals and paints. Capital \$600,000.

A coke plant that will cost \$10,000,000 will be erected in East St. Louis by the American Coke and Chemical Company of Chicago. The secretary of the company says his company will undertake an innovation in the way of coking Illinois coal. The erection of the plant will require a year under favorable circumstances.

Virginia sulfides will be mined by the American Sulfides Corporation, Charlottesville, Va., incorporated with \$400,000 capital.

A Norwegian electrical company has, after successful experiments, erected a plant for preparing aluminum sulfate from labradorite, a mineral which occurs in Western Norway. The plant is expected to supply the entire Norwegian demand for alum for the paper industry, which has hitherto been obtained from other countries.

Statistics compiled under the supervision of the U. S. Geological Survey, Department of the Interior, show that the volume of natural gas commercially utilized in the United States in 1916 was greater than that so utilized in any other year in the history of the natural-gas industry. The general increase in the production of natural gas in the United States is attributed principally to an enormous expansion of the casinghead gasoline industry in all natural gas producing States and to a greatly augmented demand for natural gas as fuel by industries engaged in the manufacture of the munitions of war.

The Lenz Apparatus Co., Inc., of New York City, announces that their capital stock has been increased to \$50,000, of which increased capital stock \$35,000 have been subscribed and actually paid for in cash, thus giving the company ample working capital to conduct its business profitably.

It is reported that Swift and Company of Chicago are to erect a sulfuric acid plant at New Orleans costing \$250,000 and having a daily capacity of 60 tons.

Vice-Consul Arthur E. J. Reilly reports from Stockholm that a company has been formed to finance a Swedish dyestuff establishment to compete with the German manufacture at home and abroad. The founding of the Company follows about two years of experimenting and the movement is supported by the country's scientific and technical experts.

The fuel oil stringency on the West Coast has pressed the Southern Pacific Railroad into a driving campaign for the development of its California producing properties with the hope of covering its needs.

The Fuelite Corporation of Manhattan, to handle compounds and chemicals for the treatment of coke, has been incorporated under the laws of New York by A. R. Bremer and E. A. and C. Alexander of Yonkers.

Mr. W. H. Thurston, connected with Clarence Whitman & Co., of New York, has answered a call from the Government to go to Washington to serve under Major Tilt in the Department of Aircraft development. Mr. Thurston is to take charge of balloon and airplane fabrics.

The E. Virgil Neal Chemical Works, 110 West 40th Street, New York, has plans prepared for the construction of a new addition to their chemical manufacturing plant at Van Dam Street and Borden Avenue, Long Island City.

Imports of colors and dyes for the eight months ending August 31 aggregate in value \$1,825,434 as against \$3,071,213 during the same period last year. Included in these imports were 2240 pounds of alizarines, valued at \$10,545.

The United States Industrial Chemical Company has been incorporated under the laws of Maryland with a capitalization of \$24,000,000. It will manufacture fertilizers and chemicals at Curtis Bay, a suburb of Baltimore.

A new fertilizer plant at Greenville, Mich., owned by the Michigan Fertilizer Company, was destroyed last Wednesday by fire.

The Color Service Corporation, Inc., has been incorporated with a capital of \$50,000, to manufacture chemicals, dyes and kindred products. The incorporators are M. M. Clancy, Wilmington, and C. M. Egner, Elkton, Md.

The manufacture of soap from sewer fat in Sweden has been taken up by the Happach Soap Company of Stockholm, which has worked out a new method for the purpose. There are also plans for using native vegetable fats, such as beechmast, horse chestnuts, etc. All this is due to the shortage in raw materials for the soap and soft soap industry.

Negotiations have been completed through the Tulsa, Okla., office of the Tidal Oil Company, whereby the Company is to purchase the Maple Oil Company in the Irvine Field of Kentucky.

One of the most prominent of the Japanese industries that have developed since the outbreak of the war is the manufacture of chlorate of potash. The Japan *Chronicle* refers to the fact that in the early stages of the war the suspension of imports sent prices up greatly, and states that established manufacturers of chlorate of potash extended their equipment, while numerous new manufacturing plants came into existence. The output was so great that prices fell considerably. Efforts were then made to ship the product abroad, and it is said that the quantity shipped to this country since the beginning of the war exceeds 10,000 barrels.

Manganese properties in Virginia will be developed by the Virginia Manganese Mining Corporation of Attaway, Va. This company has been chartered with a capitalization of \$50,000,000 and the following officers: *President*, J. W. Ruff, of Bluefield, W. Va.; *Secretary*, J. L. Phillips, of Attaway.

A fire of mysterious origin destroyed the large potash plant of the Mineral Products Corporation at Alunite, Utah, on Thursday night, causing \$250,000 loss. The fire originated in the coal dryer and was preceded by an explosion.

The Superior Oil Corporation has been incorporated under the laws of Delaware, capital \$10,000,000, by Arthur W. Britten, S. B. Howard and G. C. Reilly, all of New York.

Lyster Bros., Inc., dealing in drugs, chemicals, etc., has been incorporated under the laws of New York with a capital stock of \$50,000. Incorporators, H. W., M. J. and B. R. Lyster, New Rochelle.

The Compound Specialty Co., of Queens, makers of chemical compounds, has been incorporated with a capital stock of \$50,000 by S. Baer, M. L. Schalleck, J. R. Roth, 104 St. Nicholas Avenue.

The Illinois Platinum Corporation, of Eddyville, has been incorporated under the laws of New York; 3,500 shares common stock, no par value, active capital \$17,500.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

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. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

GEOLOGICAL SURVEY

Geology of Massachusetts and Rhode Island. B. K. EMERSON. Bulletin 597, 289 pp. This report includes a general discussion of the geologic conditions, and is accompanied by a large map giving full information.

The Enrichment of Ore Deposits. W. H. EMMONS. Bulletin 625, 530 pp. This report is an amplification of an earlier Survey Bulletin on the enrichment of sulfide ores (Bulletin 529). Fifteen elements and their compounds not considered in the earlier report are discussed with reference to their reactions in the zone of oxidation. All recent important advances in the subject have been incorporated and the general treatment has been considerably broadened.

The geologic conditions favorable and unfavorable to the formation of enriched mineral deposits are described and the criteria by which such deposits may be recognized are outlined. The natural chemical processes by which enrichment is produced are fully discussed and the behavior of each metal is considered separately and is illustrated by descriptions of many of its known valuable enriched ore bodies.

The Bull Mountain Coal Field, Musselshell and Yellowstone Counties, Montana. L. H. WOOLSEY, R. W. RICHARDS AND C. T. LUPRON. Bulletin 647, 218 pp. Paper, 50 cents.

Notes on the Greensand Deposits of the Eastern United States. G. H. ASHLEY. Bulletin 660-B, from Contributions to Economic Geology, 1917, Part I. 30 pp. Issued August 28. No attempt was made at a detailed survey of the greensands but samples were collected from the most accessible of the deposits and analyzed to determine their percentage of potash. The results of the study show that the richest and largest deposits of greensand occur in New Jersey, extending down into Delaware. Lower grade greensands occur abundantly in Maryland and less abundantly in Virginia, North Carolina, Arkansas, Texas, and doubtless the other Southern States.

The richest deposits show a potash content around 7 per cent, which is close to the percentage of potash in glauconite, of which the best greensands are almost entirely made up. These greensands occur in the basal part of the Cretaceous formation of New Jersey and Delaware and in the upper part of the Eocene. Those of New Jersey are entirely in the Cretaceous, while those of Maryland are in both Cretaceous and Eocene.

The paper also contains a contribution on "Methods of Analysis of Greensands" by WILLIAM B. HICKS AND R. K. BAILEY, discussing the methods used in making these analyses, which differ somewhat from methods previously used.

Manganese Deposits of the Caddo Gap and De Queen Quadrangles, Arkansas. H. D. MISER. Bulletin 660-C, 63 pp. From Contributions to Economic Geology, 1917, Part I. Published September 12, 1917.

The Irvine Oil Field, Estill County, Kentucky. E. W. SHAW. Bulletin 661-D, from Contributions to Economic Geology, 1917, Part II. 50 pp. Published September 5, 1917. The

Irvine oil field is by far the most productive yet developed in Kentucky. In fact, its output in 1917 will be more than twice as great as that of the dozens of other oil fields in the State, some of them long productive; and it will probably produce much more in 1918. The field is in a region where oil showings have long been known and oil has long been sought, and yet somehow this great pool 10 miles long and 2 miles wide was missed. The west side of the Irvine field is within a mile of outcrops of the oil-bearing bed, which may be seen at several places in and around Irvine. Some of the wells are less than 100 ft. deep and yet furnish good yields, even the oldest showing a relatively low rate of decline.

The Corsicana Oil and Gas Field, Texas. G. C. MATSON AND O. B. HOPKINS. Bulletin 661-F, from Contributions to Economic Geology, 1917, Part II. 41 pp. Published August 30, 1917.

The Bowdoin Dome, Montana. A Possible Reservoir of Oil or Gas. A. J. COLLIER. Bulletin 661-E, from Contributions to Economic Geology, 1917, Part II. 16 pp. Published July 27. The dome is a broadly arched portion of the earth's crust from which the strata dip away on all sides, its structure being a type known to be favorable for the accumulation of oil or gas in many fields. A well drilled here for water several years ago has been yielding a small flow of gas, sufficient probably for domestic use in one family, ever since, and it is thought that the region offers a chance of success to the driller of deeper wells. In 1915 a large gas well was drilled at Havre.

Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico, and Utah. H. E. GREGORY. Professional Paper 93. 161 pp. Paper, 40 cents.

The Geology and Ore Deposits of Ely, Nevada. A. C. SPENCER. Professional Paper 96. 189 pp. Paper, 40 cents.

Shorter Contributions to General Geology, 1916. D. WHITE. Professional Paper 98. 395 pp. This includes about twenty short papers which have been issued separately in advance.

Hydraulic-Mining Debris in the Sierra Nevada. G. K. GLBERT. Professional Paper 105. 142 pp.

Mineral Resources of the Kantishna Region, Alaska. S. R. CAPPS. Bulletin 662-E, from Contributions to Mineral Resources of Alaska, 1916-E. 53 pp.

Secondary Metals in 1916. J. P. DUNLOP. Pages 39 to 52 of Mineral Resources of the United States, 1916, Part II. Published October 6. The much higher prices for all metal products and for manufactured articles made wholly or in part from waste material has made a deep impression as to the importance of the waste-trade industry. The collection of old metals, paper bags, foil, rags, felt, and other things has been stimulated by appeals from many sources. Collections of metal have been so large that it has been difficult to obtain labor properly to break, segregate, and ship the varied classes of material. In fact, the public has been educated sufficiently to appreciate the importance of waste; even the farmers in remote regions are being asked to collect and ship scrap iron, steel, and other metals. Efforts are now being made to have the housekeepers and small dealers properly segregate the different wastes, for by so doing better prices can be obtained and an immense amount of labor can be saved. The large manufacturing plants, foundries, and smelters have increased their facilities for saving and segregating scrap metals and have also adopted methods for decreasing melting losses. They have realized that more scrap metals can be used if greater care is taken in removing deleterious substances and in better smelting practice.

Dealers in and refiners and smelters of waste metals did a large and profitable business in 1916. Stocks of many new metals were small, and spot shipments frequently were not available. The scarcity and the high prices demanded for new pig metals stimulated the sale of scrap metal. Frequently higher prices were paid for prompt shipments of scrap metals than were obtained for new metals sold under contract. There was also a large increase in the sale of guaranteed composition ingots made from scrap.

The value of the secondary metals, exclusive of gold, silver, platinum, iron, steel, and ferro-alloys, recovered in the United States, increased from \$114,304,930 in 1915 to \$265,377,856 in 1916. The increase was partly due to larger use and partly to much higher average prices.

The value of the secondary platinum, iridium, and palladium recovered in 1916 amounted to about \$4,000,000, and the value of old jewelry, dental waste, silver spoons, ornaments, and other material containing gold or silver, remelted and refined, was probably more than \$20,000,000. It is difficult to estimate the value of ferrous scrap remelted in 1916. Some of the scrap ferrous metal contained nickel, tungsten, manganese, or other alloys, which made it many times more valuable than the more ordinary commercial products. Old rails, car wheels, pipe, and other iron and steel shapes, were often sold at prices in excess of the original cost. Iron and steel scrap is used by all foundries and rolling mills, and hundreds of thousands of tons are collected, sorted, and shipped. Prices of iron and steel scrap have increased to record figures. The value of all other waste materials has increased so greatly that the total value of waste metals and other junk was 100 per cent more in 1916 than in 1915.

SECONDARY METALS RECOVERED IN THE UNITED STATES IN 1915 AND 1916

| | 1915 | | 1916 | |
|--|--------------------------|---------------|--------------------------|---------------|
| | Quantity (Short tons) | Value | Quantity (Short tons) | Value |
| Secondary copper, including that in alloys other than brass..... | 99,937 | \$33,498,882 | 140,000 | \$68,880,000 |
| Remelted brass..... | 137,500 | 40,788,000 | 300,000 | 127,440,000 |
| Secondary lead..... | 36,400 | 7,416,600 | 56,700 | 13,289,400 |
| Recovered lead in alloys | 42,500 | | 39,600 | |
| Secondary spelter..... | 52,900 | 14,433,600 | 50,700 | 14,284,400 |
| Recovered zinc in alloys other than brass..... | 5,300 | | 2,600 | |
| Secondary tin..... | 5,250 | 10,554,180 | 7,600 | 15,131,040 |
| Recovered tin in alloys. | 8,400 | | 9,800 | |
| Secondary antimony..... | 2 | 1,811,568 | 80 | 2,270,016 |
| Recovered antimony in alloys..... | 3,100 | | 4,400 | |
| Secondary aluminum..... | 5,700 | 5,802,100 | 12,900 | 23,430,200 |
| Recovered aluminum in alloys..... | 2,800 | | 6,400 | |
| Secondary nickel (1)..... | | | 16 | 652,800 |
| Recovered nickel in alloys(1)..... | | | 800 | |
| | | \$114,304,930 | | \$265,377,856 |

(1) Recoveries made by International Nickel Company from scrap nickel or alloys and from nickel in scrap ferrous alloys from any source are not included.

A reprint of the classification standards for old metal as adopted by the National Association of Waste Material Dealers for the year beginning July 1, 1917, is included; and there are detailed statistics for each of the several classes of metals summarized in the preceding table.

BUREAU OF FISHERIES

Fish Isinglass and Glue. G. F. WHITE. Document 852. 15 pp. Paper, 5 cents.

BUREAU OF MINES

Bibliography of Recent Literature on Flotation of Ores. July to December, 1916. D. A. LYON, O. C. RALSTON, F. B. LANEY AND R. S. LEWIS. Technical Paper 176. 27 pp. Paper, 5 cents. This bibliography is a continuation of that given in Technical Paper 135 of the Bureau of Mines, which covered the first half of 1916. The present paper includes references to articles that appeared from July 1 to December 31, 1916.

Abstracts of Current Decisions on Mines and Mining. Reported from January to April, 1917. J. W. THOMPSON. Bulletin 152. 77 pp. Paper, 10 cents.

Coking of Illinois Coals. F. K. OVITZ. Bulletin 138. 71 pp. Paper, 20 cents. In its endeavor to promote a more efficient use of coal the Bureau of Mines, in cooperation with the Illinois State Geological Survey and the University of Illinois, has undertaken an investigation of the coking of Illinois coals. The investigation was started by collecting from various sources the data regarding experiments already made by others; these data have been compiled and are presented herein.

The first part of this report outlines the present factors in the problem of coking Illinois coals and points out the future prospects. The quality of coke from Illinois coals alone, and from mixtures of Illinois coals with low-volatile coals is described, and the uses for which the coke is suitable are discussed. The gas-making properties and the value of the coals for making by-products are noted. Desirable methods of preparation of the coals, the impurities in them, and the effect of the impurities on the value of the coals for coke and gas making are considered.

The second part of the report deals with the character of Illinois coals, their nature, physical properties, and chemical composition. The nonhomogenous structure of the coal, the variation in composition of different beds, and even of the same bed in different localities are pointed out. Those districts in which the coals contain the smaller amounts of impurities and are more favorable for coking are grouped together.

The last part describes the tests made and gives detailed results. The tests are considered under three classes—those with beehive ovens, those with by-product ovens, and those with gas retorts. The details are as complete as the material available permits. The results of a few tests of the coke for furnace or other use are given.

Extraction of Gasoline from Natural Gas by Absorption Methods. G. A. BURRELL, P. M. BIDDISON AND G. G. OBERFELL. Bulletin 120. 71 pp. 10 cents. The Bureau of Mines is conducting a series of investigations, with a view to ascertaining the most efficient methods of obtaining gasoline from petroleum and natural gas. This report deals with a method of extracting gasoline from natural gas by absorbing the gasoline in oil and subsequently separating it from the oil by distillation. The process is quite different from those of compression and condensation which have been used for a number of years for extracting gasoline from casing-head natural gas, and has not heretofore been described in the literature.

A description of the methods employed in the manufacture of casing-head gasoline and a discussion of tests to determine whether a natural gas contains enough gasoline to warrant the installation of an extracting plant is contained in Bulletin 88 and Technical Paper 87.

Deterioration in the Heating Value of Coal during Storage. H. C. PORTER AND F. K. OVITZ. Bulletin 136. 28 pp. Paper, 10 cents.

Absorption of Methane and Other Gases by Coal. S. H. KATZ. Technical Paper 147. 16 pp. Paper, 5 cents.

Laboratory Determination of the Explosibility of Coal Dust and Air Mixtures. J. K. CLEMENT AND J. N. LAWRENCE. Technical Paper 141. 27 pp. Paper, 10 cents. "The laboratory method described in this paper is capable of measuring the inflammability of the least inflammable dusts that will propagate an explosion in the mine. A relation has been established between the results of tests on a large scale at the experimental mine and the results of laboratory tests, so that it is now possible to determine from laboratory tests alone whether or not a given dust may give rise to or propagate explosions."

BUREAU OF STANDARDS

Rules and Regulations Promulgated under Authority of the Federal Standard-Barrel Law. Circular 71. Issued September 18, 1917. 7 pp.

Some Unusual Features in the Microstructure of Wrought Iron. H. S. RAWDON. Technologic Paper 97. 25 pp. Paper, 5 cents. Issued September 20, 1917.

An Aneroid Calorimeter for Specific and Latent Heats. N. S. OSBORNE. Scientific Paper 301. 24 pp. Issued September 13, 1917. Paper, 10 cents. The calorimeter here described has been designed primarily for the measurement of the specific heats and latent heats of a certain class of materials adapted for use in the production of artificial refrigeration. These materials include ammonia, carbon dioxide, sulfur dioxide, methyl chloride, and ethyl chloride. At temperatures where the thermal properties are of importance to the engineer the vapor pressures of these materials range from less than 1 atmosphere to over 70 atmospheres.

Effects of Heat on Celluloid and Similar Materials. H. N. STOKES AND H. C. P. WEBER. Technologic Paper 98. 37 pp. "In 1907, at the request of the Steamboat-Inspection Service, the Bureau of Standards made a careful study of the literature of celluloid and other pyroxylin plastics and afterwards carried out an investigation of their properties with special reference to the hazard connected with their use and transportation. The results of the work are given in detail in this paper. In view of the present widespread interest in nitrocellulose products it seemed desirable to publish this paper, even though no account is taken in it of any advances that may have been made since 1908."

DEPARTMENT OF AGRICULTURE

The Presence of Arsenic in Hops. W. W. STOCKBERGER AND W. D. COLLINS. Department Bulletin 568. 7 pp. Issued August 8, 1917. Paper, 5 cents.

The By-Products of Rice Milling. J. B. REED AND F. W. LIEPSNER. Department Bulletin 570. 16 pp. Issued August 11, 1917. Paper, 5 cents.

Articles from the Journal of Agricultural Research

Effect of Three Annual Applications of Boron on Wheat. F. C. COOK AND J. B. WILSON. 10, 591-597 (September 17).

Energy Values of Hominy Feed and Maize Meal for Cattle. H. P. ARMSBY AND J. A. FRIES. 10, 599-613 (September 17).

Study of the Proteins of Certain Insects with Reference to Their Value as Food for Poultry. J. S. MCHARGUE. 10, 633-637 (September 17).

Formation of "Black Alkali" (Sodium Carbonate) in Calcareous oils. J. F. BREAZEALE. 10, 541-590 (September 10).

Quassia Extract as a Contact Insecticide. N. E. MCINDOO AND A. F. SIEVERS. 10, 497-531 (September 3).

Some Factors Affecting Nitrate-Nitrogen Accumulation in Soil. P. L. GAINNEY AND L. F. METZIER. 11, 43-63 (October 8).

Occurrence of Manganese in Insect Flowers and Insect Flower Stems. C. C. McDONNELL AND R. C. ROARK. 11, 77-81 (October 15).

Effect of Sulfur on Different Crops and Soils. O. M. SHEDD. 11, 91-103 (October 22).

Some Notes on the Direct Determination of the Hygroscopic Coefficient. F. J. ALWAY, M. A. KLINE AND G. R. MCDOLE. 11, 147-165 (October 22).

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Report on Cost of Production of Glass in United States. Miscellaneous Series Publication No. 60. 430 pp. Paper, 35 cents. A report on conditions in glass industry and cost of production in its various branches. Ninth of series of reports issued by Bureau regarding cost of production in different industries. Contains principal cost of production data. In addition, information is given concerning labor and industrial conditions, factory equipment, selling methods, and suggestions regarding better general accounting and more accurate cost-finding methods. A comprehensive bibliography, prepared in the Library of Congress, is appended.

BOOK REVIEWS

Elements of Mineralogy, Crystallography and Blowpipe Analysis.

By ALFRED J. MOSES AND CHARLES LATHROP PARSONS. D. Van Nostrand Co., New York. Price, \$3.00.

This fifth edition is considerably enlarged, and contains several new changes from the preceding editions, which make the volume more valuable to the student and mineralogist. The general arrangement of the volume from a determinative mineralogical standpoint is excellent, and the illustrations, which are most satisfactory, show in nearly all instances very strikingly the points that the authors have wished to emphasize. The volume is not only an excellent textbook for use in colleges and universities, but it makes a very good general book on determinative mineralogy that can be used to advantage in the laboratory and in the field.

While more particular attention is given in this volume to the physical properties of minerals, yet that part of the volume relating to the chemical properties of minerals has been very carefully worked out.

In considering this volume in more detail, Part I, relating to Crystallography, gives a very comprehensive idea of crystallography, and is arranged in such a way that the student should readily obtain a knowledge of this subject that will enable him to use the crystallographic properties of minerals to a considerable extent in their identification. The method of presenting this subject, which is always a rather difficult one, has been done in such an understandable and simple manner that it can be comprehended even without an instructor. A very valuable addi-

tion to the part on crystallography is the chapter relating to crystallo-optics; this is a very much needed side of determinative mineralogy that has too often been eliminated in textbooks on this subject. This chapter shows very careful thought and discrimination in bringing together such material as is necessary to give the student a sufficient knowledge of this subject to aid him in determining minerals, without at the same time burdening him with the more complex phases of optical mineralogy.

Part II on Blowpipe Analysis has also been developed in such a manner that the student can readily get a very clear idea of the various reactions and tests that can be made with the blowpipe in testing the various elements and compounds of which minerals are composed. The use of the spectroscope is not described in any great detail, but sufficient information is given regarding its use to enable the student to identify by a flame test many of the simpler elements that occur in minerals. This method of identification is coming more and more in use, and in the future our determinative mineralogies will include this subject to a still greater extent. Chapters 13 and 14 of Part II are in their arrangement of very great assistance in familiarizing the student with the various reactions that may be expected when certain elements are present in a mineral.

Part III on Mineralogy has been arranged in as comprehensive, complete and instructive manner as one could conceive possible in presenting this subject. The discussions of formations and occurrences add a great deal to the value of this part, and will make the student realize how closely geology and

mineralogy are connected with each other. The grouping of the minerals from an economic standpoint brings out more clearly than any other grouping the relation of mineralogy to our industrial development.

Part IV, on Determinative Mineralogy, gives tables for the determination of the common minerals, which are efficient for the identification of minerals, but are rather complicated in use.

Taking the volume as a whole it is in its present form one that should find very wide use by all who are interested in determinative mineralogy.

JOSEPH HYDE PRATT

Portland Cement Industry. By WILLIAM ALDEN BROWN, Works Manager, Aberthaw and Bristol Channel Portland Cement Co., South Wales. Pp. 153. New York: D. Van Nostrand Co., 1917. Price, \$3.00.

Probably no other industry has had so little written about its practices, in book form, as the Portland cement industry. Numerous articles appear from time to time in the various trade journals upon its many phases, but those who have the knowledge to write a general treatise have either not had the inclination nor the time to write on the subject as a whole.

Ranking with the first eight extractive industries and during the past twenty-five years showing a development quite as spectacular as that of iron and steel, it is peculiar that more books have not been written; the few that have appeared may be counted upon one's fingers.

As a textbook on Portland cement, Meade's "Portland Cement" has been the only one available, although students of the industry were able to find additional data in several other less known treatises. There now appears a book which gives a most comprehensive review of the entire process of cement manufacture and its contents indicate that its author has a thorough knowledge whereof he writes.

It is unfortunate that, in a book of this kind, the author confines himself so strictly to the English view-point and practices, as his former experience in an American plant would permit his making it more general. As his purpose seems to be to spur on his home industry to the adoption and adaptation of more modern practices, this omission may be excused.

In the different chapters the author has brought together many data which have been published in various media from time to time but never before collected. His chapter on "Power Plants" is most thorough and comprehensive.

One feature which should be of interest to American manufacturers is that all operation data are figured on a $5\frac{1}{2}$ -day week excepting, of course, that pertaining to the burning department. This is a goal towards which our manufacturers have been striving for several years.

In his chapter on the design and construction of plants, the author utters these words of wisdom, to the truth of which many American investors will subscribe from unpleasant past experiences: "Business men building a cement plant should see that the engineers engaged to design, construct and equip a plant are those who have gained their knowledge after years of practical experience in cement making, and not those who have visited a few cement plants, gleaming information from owners and managers that often proves very expensive to those who have speculated in cement, causing them disappointment and regret at having interested themselves in the industry. Many estimates of engineers have come very wide of the mark, and plants have been turned over to the owners by engineers erecting them, only for the former to find £10,000 to £50,000 must be spent in order to make the changes necessary to a successful, economical operation of the plant."

The book is a welcome addition to the bibliography of the Portland cement industry.

C. N. WILEY

Fats and Fatty Degeneration. By MARTIN H. FISCHER AND MARIAN O. HOOKER. 23 x 16 cm. ix + 155 pp. New York: John Wiley and Sons, 1917. Price, \$2.00.

The chapters are entitled: the argument; on the making of emulsions; on the breaking of emulsions; on the normal fat content of cells; on fatty change (fatty infiltration and fatty degeneration); the adhesive tissues and the fatty secretions; on the natural and artificial production of milk; on the mimicry of mucoid secretion; on the mimicry of some anatomical structures; concluding paragraphs.

From the text the unsophisticated reader will get the impression that the senior author has made valuable contributions to the theory of emulsions. As a matter of fact he has made one contribution which is not sound and he has put forward again a statement which everybody should know is wrong. When oil is emulsified in water by means of a third substance, one has drops of oil each coated by a gelatinous film and, outside of that, water containing some of the emulsifying agent. If we cut down the water sufficiently we shall get a limiting case where we have merely drops of oil surrounded by gelatinous films which then coalesce more or less completely. The authors consider that the emulsifying agent, gum acacia, soap, or something like that, forms a compound with water and that the oil is emulsified in hydrated acacia, hydrated soap, etc. (pp. 21, 29, 38). In so far as an emulsion of oil in water is stabilized by a hydrophilic colloid, there is nothing new about this. The author's contribution is that we are dealing with colloid hydrates and he considers that the colloid must bind all the water. The author offers no evidence for the existence of these alleged compounds for the very simple reason that there are no criteria which these alleged compounds could satisfy.

The author also puts forward the statement that a change in the relative amounts of the water and oil causes an emulsion to change from the oil-in-water to the water-in-oil type (pp. 12, 41, 80, 94). Pickering showed a number of years ago that with kerosene, water, and soap, only one type of emulsion can be obtained, that of oil in water, no matter what the relative amounts of kerosene and water. Pickering's results have been confirmed and generalized since then. It is also interesting to note that the author does not cite Pickering's first paper though he must be familiar with it. It is a little difficult to characterize the author's methods and yet keep within parliamentary limits. It is certainly being over-charitable to say that the author has the unhappy gift of remembering what he has read but of forgetting that he has read it.

The second part of the book on the biological emulsification of fats is interesting but suffers from the double defect that the underlying conception is wrong and that it is impossible to tell from the text just what the author has worked out for himself and what he has appropriated in an absent-minded fashion. The author's books are all interesting reading and this one is no exception; but they should be considered as advertising matter in the guise of scientific fiction.

WILDER D. BANCROFT

Annual Chemical Directory of the United States. By B. F. LOVELACE, Editor. Williams & Wilkins Company, Publishers. Price, \$5.00.

There is a very big need for a book of the kind this title indicates, and the one before us is a start in the right direction.

The essential part of the book consists of two complete lists, one being a list of American manufacturers of chemicals and dealers in chemicals, and the second a list of American manufacturers of and dealers in apparatus and equipment for laboratories and industrial plants. Following this there are: (1) a list of professional chemical firms; (2) a list of Federal, State, Municipal, industrial and professional laboratories; (3) a list of colleges, American and Foreign, offering courses in chemistry; (4)

a list of Experiment Stations; and other lists that might be interesting to the man interested in chemicals, chemistry, or chemical equipment.

This book will no doubt be of great value to anyone who is interested in having these various classified lists, and as the publishers have determined to make the Directory an annual affair, and invite criticism, there is no doubt it will improve greatly from year to year. It is a good start.

The two chief criticisms at present would probably be its lack of completeness, and, to a certain extent, a lack of proportion. It is questionable whether such headings as "Acids, all kinds," "Chemicals, all kinds," "Chemicals, technical," "Chemicals, industrial," have sufficient value to warrant the amount of space devoted to them, particularly as these lists are very far from complete. In the matter of proportion and need of technical supervision, two or three instances will indicate what is meant. If one wants, for example, methylanthranilate, there is a list of five names from which to choose, but if he wants acetate of lime he finds only two names out of the scores making and marketing this product, listed under "Calcium Acetate," and one of these is repeated under "Lime Acetate." Nitre cake is another product that is certainly very generally and widely manufactured in this country, but one finds only one name listed under that heading, and four more under the heading "Cake, Nitre" out of the scores of manufacturers and dealers. On the other hand, if one is interested in chlorine he finds four under that heading, one under the heading "Chlorine, Electrolytic" and twelve under the heading "Chlorine, Liquid," to represent the three or four manufacturers in the United States. It is not quite obvious why these three headings are needed for the one material, "Chlorine," or two headings for "Nitrate Cake," or why the headings "Chlorobenzene" and "Monochlorobenzol" are both necessary to indicate one product, all without any cross-references.

It is also interesting to see that there are only five Consulting Chemists listed in New York City. One sometimes gathers the impression that the town is full of them, and it is difficult to see just what basis of selection has been used.

These few samples indicate the direction of criticism that should be carefully considered in preparing succeeding issues. It would be well, also, to have the lists distinguish clearly between manufacturers and dealers.

The book is valuable as it exists, and no doubt will improve yearly.

J. E. TEEPLE

Technical Chemists' Handbook. By GEORGE LUNGE, Ph.D. 2nd Ed. Published by D. Van Nostrand Co., New York City. Price, \$3.50 net.

This second edition of the 'Technical Chemists' Handbook follows the fifth German edition which appeared in 1914, under the title "Taschenbuch fuer die anorganisch-chemischen Gross-industrie." Originally known as the "Taschenbuch fuer die Sodaindustrie," the subsequent German editions, as in the fourth and fifth, were revised and extended to a wider range of subject.

As set forth in the prefaces, the German work and the English edition, the second of which is the subject of this notice, have retained throughout, as a cardinal feature, such selection of methods of analysis for works control and the testing of market products that acceptable reliability and uniformity may be attained, particularly by the analyst in discussions between buyer and seller. To this end a single analytical process, with few exceptions, is presented. The new methods described in current literature as the result of recent investigations are permitted to replace those tried by long experience only after critical examination with evidence of advantage. This treatment of the

subject matter has developed in the minds of the older practitioners concerned, in the course of the 34 years since the first German edition, a sense of keen regard, almost of indispensability.

The new edition maintains in all respects the high standards set in the older issues and the same principle in the choice of material. Its chief purpose has been to revise the numerical data of the work on the basis of the report for 1916 of the International Committee on Atomic Weights. This has been felt a necessity by the author in view of the significance of such revision in some instances, even for practical purposes. In the matter of contents, as concerns detail and range of subject, the present is identical with the first edition. The general tables led off by the 1916 table of atomic weights contain a compilation covering mainly physico-chemical data, but include also mathematical features and abstracts from the patent laws of all nations. This collection is emphatically of value to the technical chemist and chemical engineer whatever his activities. The special part comprehends a selective analytical method digest for nearly every branch of the alkali, acid and related chemical industries.

The publishers present the work as before in distinctive manual form, in excellent typography and bound in flexible covers.

E. S. JOHNSON

Talks to Platers. By F. C. STANLEY. 16mo. 82 pp. Published by the Bridgeport Branch of the American Electroplaters' Society. Price, 50 cents.

The electroplating industry of to-day is in the midst of a transition from the stage of empiricism and secrecy, to that of scientific research and dissemination of knowledge. Foremost among the agencies in this movement is the American Electroplaters' Society, an educational society with numerous branches, many of which are conducting classes and laboratories. In the conduct of such classes, the importance of a study of the fundamental principles of chemistry cannot be too strongly emphasized.

The first portion of this booklet is therefore very properly devoted to an explanation of the principles of chemistry and the use of chemical formulae, equations, etc. This section of the book contains in clear, condensed form a large amount of useful information. It is difficult to understand, however, why the author uses (though not consistently) such archaic terms as sodic, calcic, ammoniac, etc.

The major portion of the book is devoted to a description of methods for the analysis of various plating solutions, in which in general the chemical principles are so simply and clearly stated that with some practice the platers should have no difficulty in obtaining approximate results.

The unpardonable fault of the book is the heterogenous mixture of metric and English units, *e. g.*, "Dissolve 1 oz. of cyanide in a liter of water," etc. Apparently the author has assumed that although platers are willing and able to learn the principles of chemistry, they are unable to use the metric system. Surely the advantages of the metric system warrant its use throughout, at least up to the point where the composition is determined in grams per liter. If then, as will probably be the case for a long time to come, the plater desires to convert this result to ounces per gallon, it is much easier to use the factor 0.134, than, as recommended by the author, to titrate 38 cc. (1/100 gallon) and to divide the result (in grams) by 0.2835 to obtain ounces per gallon. (Incidentally the author has no conception of significant figures, when, *e. g.*, he refers to 0.226568 g. of zinc, or 0.969792 g. nickel.) There is no hope for the general adoption of the metric system when its advocates (or those familiar with it, who should be its advocates) dodge its use on every possible occasion.

WILLIAM BLUM

Examination of Water: Chemical and Bacteriological. By WILLIAM P. MASON. Revised. 5th Ed. vi + 186 pp. 5 × 7¹/₄ in. John Wiley & Sons, Inc., New York, N. Y. Cloth, \$1.25 net.

This new edition (fifth) of Professor Mason's excellent little laboratory textbook has been printed from entirely new plates with a heavier, blacker, and therefore more distinct type; this change will be welcomed by all readers since a more readable page has resulted.

In general the new edition follows closely the former editions in arrangement, matter presented and actual text. The book consists of three chapters and two appendices as follows:

CHAPTER I—Introduction, Misconception as to the Character of Water Analysis, Knowledge of the Source of the Sample Necessary (7 pp.).

CHAPTER II—Chemical Examination of Water (112 pp.). Sampling, Sanitary Surveys, Keeping Samples, Reports, Equipment of the Laboratory, Turbidity, Odor, Taste, Temperature, Reaction, Color, Solids, "Comparates," Hardness, Chlorine, Nitrites, Nitrates, Free and Albuminoid Ammonia, Required Oxygen, Lead, Copper, Iron, Zinc, Arsenic, Chromium, Phosphates; Analysis Mineral Residue, Manganese, Dissolved Oxygen, Carbon Dioxide, "Putrescibility," "Relative Stability." Lime Value. Soda Value. Free Chlorine, Hypochlorite. Table Conversion parts per million into Grains per U. S. Gallon.

CHAPTER III—Bacteriological Examination of Water (33 pp.). Preparation of Media; Nutrient Broth; Nutrient Gelatine; Sugar Media; Nutrient Agar; Sampling, Sowing Media, etc., Counting Colonies. Gas Forming Bacteria. Tests for *Bacillus coli*. *Bacillus typhosus*. Diagnostic Value of the "Colon Group." Enumeration of Organisms not Bacterial.

APPENDIX A—(12 pp.). Interpretation of a Water Examination.

APPENDIX B—(2 pp.). Method of Treating Oysters for *Bacillus coli*.

INDEX.

The typography, including plates and cuts, is excellent and remarkably free from errors. The text is clearly and forcefully written and the directions easily followed and understood by students. In only one instance has the reviewer found the text confusing: on page 77 are found the directions, "Add 50 cc. of normal NaOH solution carbonate and proceed as usual."

A full index with cross references adds greatly to the usefulness of the book.

The variations from the last edition consist in the suppression of a few unimportant paragraphs here and there and the insertion of short sentences under various methods, either making them conform more closely to the A. P. H. A. Standard Methods or rendering the methods more easily followed by the student. In the latter respect the fifth edition is a decided improvement over former editions. The methods described are, in most instances, those proposed by the Committee of the American Public Health Association (3rd Ed.). Where the author has deviated from the "Standard" most water analysts will agree that the changes are well advised.

In the chapter devoted to the bacteriological examination of water, it is a pity that Professor Mason has substituted the A. P. H. A. culture media instead of retaining those described in earlier editions of his textbook. The old media are far more reliable and have been repeatedly shown to be superior. Media made from beef extract with the addition of only 0.5 per cent peptone are unreliable for general diagnostic purposes and are not adapted to the study of many waters.

It is also to be regretted that the author, who is one of the most experienced American water experts and is thoroughly conversant with the vagaries of water bacteriology, has not given the beginner a more comprehensive discussion of the

problems confronting the analyst in the interpretation of his bacteriological findings. At the present time, when there is danger of water analysts drifting back to strictly rule-of-thumb methods, a brief outline of the broad field of bacterial water examination and the importance of a knowledge of the characteristics and habitats of the great groups of the misnamed "water bacteria" could have accomplished untold good.

The pages devoted to "hardness" have been materially changed and with the exception of the questionable expediency of determining "alkalinity" with tenth normal HCl, the methods as described are better than before. Especially to be commended is the change in the preparation of the standard calcium chloride solution without the addition of ammonium hydroxide.

Other revisions of importance are to be found under the determination of nitrates, the discussion of the interpretation of results, and in the insertion of new matter such as the estimation of "relative stability" and "putrescibility" by methylene blue, the detection of "free" chlorine by ortho-tolidine and the tabulation of the analytical results of a larger number of typical waters.

There appears in this little manual one of the oversights so frequently encountered in American texts devoted to sanitary problems—the comparison of results obtained by one method of analysis with those obtained by an entirely different one. In this new edition, for example, the author has changed from Ammonia (NH₃) as Free and as Albuminoid Ammonia to Nitrogen (N) as Free and as Albuminoid Ammonia. Yet in the tables of "Comparates" the results are the same as in the fourth edition. Again, we find that the time for boiling with permanganate in "Oxygen consumed" has been raised from fifteen minutes to a full thirty minutes' boiling in a casserole. Yet here also the "comparates" which are supposed to serve as guides in the interpretation of results have not been recalculated but remain the same as before. One cannot avoid asking oneself the question: "If the results obtained by ten, fifteen and thirty minutes' boiling with permanganate can all be compared, why continue the boiling for the full half hour?" It is true that the author states very definitely that the figures given under "Comparates" are to serve as a guide in a very broad way only. Water experts will doubtless find no ground for criticism, for in their diagnosis they consider the analysis as a whole. It must be remembered, however, that beginners and laymen read into these discrepancies evidence of a carelessness in our work, and a laxity in our view-points always difficult to explain.

E. M. CHAMOT

The Aniline Color, Dyestuff and Chemical Conditions from 1914 to 1917. By I. F. STONE.

This volume consists of a series of addresses and articles compiled by Mr. Stone. While a large part of the book consists of Mr. Stone's own addresses on various subjects related to the dyestuff industry, the author has also included other important articles from various sources relating to the same subject. The volume, in fact, is a very welcome and successful attempt to put into permanent form the literature relating to the development of the American Dyestuff Industry, being collated from numerous journals, addresses before societies and organizations and tariff committees. Mr. Stone has done a good piece of work in collecting all this matter together in one volume for the benefit of chemists and all others interested in dyestuffs, and he deserves the thanks of his fellow chemists for his generosity in publishing this book for free distribution among those interested in the subject. This volume will prove a valuable and useful reference book for those connected with the dyestuff industry and for those interested in tariff matters related to this subject.

J. MERRITT MATTHEWS

NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Agriculture: *Cyclopedia of Agriculture*. L. H. BAILEY. 4 Vol. New Ed. 4to. Price, \$20.00. The Macmillan Co., New York.

Analysis: *An Advanced Course in Quantitative Analysis*. H. FAY. 8vo. 111 pp. Price, \$1.25. John Wiley & Sons, New York.

Anthocyanin Pigments. M. WHELDALE. 8vo. 318 pp. Price, \$4.50. G. P. Putnam's Sons, New York.

Brass: *The Technical Analysis of Brass and the Non-Ferrous Alloys*. W. B. PRICE AND R. K. MEADE. 12mo. 376 pp. Price, \$3.00. John Wiley & Sons, New York.

Business Law for Engineers. C. F. ALLEN. 8vo. 456 pp. Price, \$3.00. McGraw-Hill Book Co., New York.

Chemistry: *Laboratory Exercises in Chemistry*. W. A. NOYES AND B. S. HOPKINS. 12mo. 91 pp. Price, \$0.60. Henry Holt & Co., New York.

Chemistry in the Service of Man. ALEXANDER FINDLAY. 2nd Ed. 8vo. 272 pp. Price, \$2.00. Longmans, Green & Co., New York.

Coal: *The Elements of Coal Mining*. DANIEL BURNS. 12mo. 236 pp. Price, \$1.10. Longmans, Green & Co., New York.

Commerce: *History of Commerce and Industry*. C. A. HERRICK. 12mo. 562 pp. Price, \$1.60. The Macmillan Co., New York.

Correction Tables for Thermodynamic Efficiency. C. H. NAYLOR. 8vo. Price, 5s. Edward Arnold, London.

Dyestuffs: *The Chemistry of Dyestuffs*. M. FORT AND L. L. LLOYD. 8vo. 311 pp. Price, \$2.50. G. P. Putnam's Sons, New York.

Dynamos: *The Management of Dynamos*. G. W. LUMMIS-PATERSON. 8vo. 292 pp. Price, 5s. Crosby Lockwood & Son, London.

Earthenware: *Notes on the Manufacture of Earthenware*. E. A. SANDEMAN. 8vo. 390 pp. Price, 7s. 6d. Crosby Lockwood & Son, London.

Feeds and Feeding Abridged. W. A. HENRY AND F. B. MORRISON. 8vo. 440 pp. Price, \$1.75. Henry Morrison Co., Madison, Wis.

Hydrology: *The Elements of Hydrology*. A. F. MEYER. 8vo. 374 pp. Price, \$4.00. John Wiley & Sons, New York.

Inorganic Chemistry. H. G. BYERS. 8vo. 651 pp. Price, \$2.25. Charles Scribner's Sons, New York.

Lubricating Engineer's Handbook. J. R. BATTLE. 8vo. 333 pp. Price, 15s. Charles Griffin & Co., London.

Machine Design: *Elements of Machine Design*. O. A. LEUTWILER. 8vo. 607 pp. Price, \$4.00. McGraw-Hill Book Co., New York.

Materials: *Textbook of the Materials of Engineering*. H. F. MOORE. 8vo. 204 pp. Price, \$2.00. McGraw-Hill Book Co., New York.

Mechanical Science Methods. F. H. SELDEN. 16mo. 76 pp. Price, \$0.60. Maudslay Press, Valley City, N. D.

Mineral Foote-Notes. Vol. I, No. 11. Published by Foote Mineral Company, 107 No. 19th St., Philadelphia, Pa.

Mineral Industry during 1916. Ed. by G. A. ROUSH. 8vo. 937 pp. Price, \$10.00. McGraw-Hill Book Co., New York.

Mining: *Scientific Mining; Modern Ideas*. M. T. McDONOUGH. 8vo. 109 pp. Price, \$3.50. News Publishing Co., Wheeling, W. Va.

Oils, Fats and Waxes: *Technical Handbook of Oils, Fats and Waxes*. Vol. 1. P. F. FRYER AND F. E. WESTON. 8vo. 279 pp. Price, 9s. Cambridge University Press.

Organic Chemistry. H. D. HASKINS. 12mo. 472 pp. Price, \$2.00. John Wiley & Sons, New York.

Oxy-Acetylene Welding Practice. R. J. KEHL. 8vo. 110 pp. Price, \$1.00. Acetylene Journal Publishing Co., Chicago.

Paper: *Handmade Paper and Its Watermarks*. DARD HUNTER. 8vo. 22 pp. Technical Association of the Pulp and Paper Industry, New York.

Smoke Abatement: *Scientific Treatise on Smoke Abatement*. H. HAMILTON. 8vo. 168 pp. Price, 5s. Sherratt & Hughes, London.

Soils and Fertilizers. L. J. LYTTLETON. 12mo. 255 pp. Price, \$1.10. The Macmillan Co., New York.

Trade Catalogs: *Manual of Instructions for Trade Catalog Compilation*. O. A. MORONER. 4to. 87 pp. Price, \$5.00. Wynkoop Hallenbeck Crawford Co., New York.

Water: *Examination of Water; Chemical and Bacteriological*. W. P. MASON. 5th Ed. 12mo. 186 pp. Price, \$1.25. John Wiley & Sons, New York.

Watt and the Steam Age. J. W. GRANT. 8vo. 212 pp. Price, 7s. 6d. St. Brides Press, London.

Wood and Other Organic Structural Materials. C. H. SNOW. 8vo. 478 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

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Bleaching: *Comparison of Lime and Electrolytic Bleaching*. ALLEN ABRAMS. *Textile World Journal*, Vol. 13 (1917), No. 17, pp. 23-25.

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Cast Iron—Its Rust Resisting Power. E. A. AND L. T. RICHARDSON. *The Iron Trade Review*, Vol. 61 (1917), No. 16, pp. 834-835.

Coal-Tar Pitch. J. M. WEISS. *The Chemical News*, Vol. 116 (1917), No. 3017, pp. 139-142.

Color and Color Photography. C. D. HODGMAN. *Journal of the Cleveland Engineering Society*, Vol. 10 (1917), No. 2, pp. 127-136.

Copper: *Development of Copper Converting*. M. W. KREJCI. *Engineering and Mining Journal*, Vol. 104 (1917), No. 16, pp. 669-674.

Corrosion in Refrigerating Plants. M. A. SALLER. *Power*, Vol. 46 (1917), No. 17, pp. 553-554.

Electric Melting in the Foundry. DOUGLAS WALKER. *The Iron Trade Review*, Vol. 61 (1917), No. 19, pp. 994-995.

Electric Pig Iron in War Times. ROBERT TURNBULL. *The Iron Trade Review*, Vol. 61 (1917), No. 16, pp. 828-829.

Elements: *The Complexity of the Chemical Elements*. FREDERICK SODDY. *The Scientific Monthly*, Vol. 5 (1917), No. 4, pp. 451-462.

Heat Calculation for Baking and Drying Ovens. W. S. SCOTT. *The Electric Journal*, Vol. 19 (1917), No. 11, pp. 456-458.

Hot-Water Heating under Forced Circulation. C. D. ALLAN. *Power*, Vol. 46 (1917), No. 16, pp. 520-523.

Iron Atom: *The Experiences of an Iron Atom*. C. R. STURDEVANT. *Journal of the Cleveland Engineering Society*, Vol. 10 (1917), No. 2, pp. 93-112.

Leather Belting Maker's Association. L. W. ARNY. *The Iron Age*, Vol. 100 (1917), pp. 928-929.

Mechanical Ventilation for Metal Mines. GEORGE RICE. *Mining and Scientific Press*, Vol. 115 (1917), No. 16, pp. 579-581.

Metallurgical Smoke: *The Treatment of Metallurgical Smoke in Japan*. TETSUROW KOMAKINE. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 8, pp. 484-486.

Nitrogen: *How Do the Warring Nations Obtain Their Nitrogen Supply?* S. NAUCKOFF. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 9, pp. 525-536.

Preferential Flotation. W. SHELLSHEAR. *Mining and Scientific Press*, Vol. 115 (1917), No. 17, pp. 613-617.

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Radioactivity and Some Advances in Physical Science. H. H. BARKER. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 8, pp. 486-488.

Sodium Cyanide: *The Synthetic Making of Sodium Cyanide*. G. H. CLEVINGER. *Mining and Scientific Press*, Vol. 115 (1917), No. 15, pp. 537-542.

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Water: *A Sanitary Interpretation of Water Analysis*. E. C. RICHARDSON. *Journal of the Cleveland Engineering Society*, Vol. 10 (1917), No. 2, pp. 137-141.

Water Gages on Marine Boilers. W. M. McROBERT. *Power*, Vol. 46 (1917), No. 19, pp. 622-624.

White Pigments: *The Future of White Pigments in Great Britain*. A. S. JENNINGS. *The American Paint Journal*, Vol. 1 (1917), No. 52, pp. 1 and 7.

Zinc Ore: *Principles Governing Zinc-Ore Deposits*. F. L. NASON. *Mining and Scientific Press*, Vol. 115 (1917), No. 18, pp. 647-651.

Zinc Oxide Furnaces. J. F. CREGAN. *Engineering and Mining Journal*, Vol. 104 (1917), No. 16, pp. 675-680.

NEW JOURNALS

Journal of the Society of Glass Technology. Edited by W. E. S. TURNER. Quarterly. Price, 22s. 6d. per annum. The Society of Glass Technology, The University, Sheffield.

MARKET REPORT—NOVEMBER, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON NOV. 20

INORGANIC CHEMICALS

| | | | |
|--|----------|----------|--------|
| Acetate of Lime..... | 100 Lbs. | 6.00 @ | 6.05 |
| Alum. Ammonia, lump..... | 100 Lbs. | 4.75 @ | 5.00 |
| Aluminum Sulfate, high-grade..... | Ton | 70.00 @ | 75.00 |
| Ammonium Carbonate, domestic..... | Lb. | 11 @ | 11 1/4 |
| Ammonium Chloride, white..... | Lb. | 14 1/3 @ | 15 |
| Aqua Ammonia, 26°, drums..... | Lb. | 18 1/3 @ | 19 |
| Arsenic, white..... | Lb. | 16 @ | 16 1/2 |
| Barium Chloride..... | Ton | 75.00 @ | 85.00 |
| Barium Nitrate..... | Lb. | 8 1/2 @ | 11 |
| Barytes, prime white, foreign..... | Ton | 28.00 @ | 30.00 |
| Bleaching Powder, 35 per cent..... | 100 Lbs. | 1.00 @ | 1.50 |
| Blue Vitriol..... | Lb. | 9 1/2 @ | 10 |
| Borax, crystals, in bags..... | Lb. | 7 1/4 @ | 8 1/2 |
| Boric Acid, powdered crystals..... | Lb. | 13 1/2 @ | 13 3/4 |
| Brimstone, crude, domestic..... | Long Ton | nominal | |
| Bromine, technical, bulk..... | Lb. | 60 @ | 65 |
| Calcium Chloride, lump, 70 to 75% fused..... | Ton | 30.00 @ | 35.00 |
| Caustic Soda, 76 per cent..... | 100 Lbs. | 8.00 @ | 8.10 |
| Chalk, light precipitated..... | Lb. | 4 1/2 @ | 4 1/4 |
| China Clay, imported..... | Ton | 18.00 @ | 30.00 |
| Feldspar..... | Ton | 8.00 @ | 15.00 |
| Fuller's Earth, foreign, powdered..... | Ton | 35.00 @ | |
| Fuller's Earth, domestic..... | Ton | 8.50 @ | 15.00 |
| Glauber's Salt, in bbls..... | 100 Lbs. | 1.00 @ | 1.50 |
| Green Vitriol, bulk..... | 100 Lbs. | 1.00 @ | 1.05 |
| Hydrochloric Acid, commercial, 20°..... | Lb. | 2 @ | 2 1/2 |
| Hydrochloric Acid, C. P., conc., 22°..... | Lb. | 2 1/2 @ | 2 1/4 |
| Iodine, resublimed..... | Lb. | 3.50 @ | 3.55 |
| Lead Acetate, white crystals..... | Lb. | 17 @ | 19 |
| Lead Nitrate..... | Lb. | nominal | |
| Litharge, American..... | Lb. | 9 1/2 @ | 10 |
| Lithium Carbonate..... | Lb. | 1.50 @ | |
| Magnesium Carbonate, U. S. P..... | Lb. | 18 @ | 20 |
| Magnesite, "Calcined"..... | Ton | 60.00 @ | 65.00 |
| Nitric Acid, 40°..... | Lb. | 9 @ | 9 1/4 |
| Nitric Acid, 42°..... | Lb. | 9 1/4 @ | 9 1/2 |
| Phosphoric Acid, sp. gr. 1.710..... | Lb. | 33 @ | 37 |
| Phosphorus, yellow..... | Lb. | 2.05 @ | 2.10 |
| Plaster of Paris..... | Bbl. | 1.50 @ | 1.70 |
| Potassium Bichromate, casks..... | Lb. | 45 @ | 46 |
| Potassium Bromide, granular..... | Lb. | 1.35 @ | 1.36 |
| Potassium Carbonate, calcined, 80 @ 85%..... | Lb. | 65 @ | 70 |
| Potassium Chlorate, crystals, spot..... | Lb. | 47 @ | 48 |
| Potassium Cyanide, bulk, 98-99 per cent..... | Lb. | nominal | |
| Potassium Hydroxide, 88 @ 92%..... | Lb. | 82 1/2 @ | 83 1/2 |
| Potassium Iodide, bulk..... | Lb. | 2.90 @ | |
| Potassium Nitrate..... | Lb. | 28 @ | 30 |
| Potassium Permanganate, bulk..... | Lb. | 3.85 @ | 3.90 |
| Quicksilver, flask..... | 75 Lbs. | 100.00 @ | |
| Red Lead, American, dry..... | Lb. | 10 @ | 10 1/2 |
| Salt Cake, glass makers'..... | Ton | 28.00 @ | 30.00 |
| Silver Nitrate..... | Oz. | 57 @ | 60 |
| Soapstone, in bags..... | Ton | 10.00 @ | 12.50 |
| Soda Ash, 58%, in bags..... | 100 Lbs. | 3.05 @ | 3.10 |
| Sodium Acetate..... | Lb. | 13 1/4 @ | 13 1/2 |
| Sodium Bicarbonate, domestic..... | 100 Lbs. | 2.50 @ | 2.60 |
| Sodium Bichromate..... | Lb. | 18 1/2 @ | 19 |
| Sodium Chlorate..... | Lb. | 23 1/2 @ | 24 1/2 |
| Sodium Fluoride, commercial..... | Lb. | 18 @ | 19 |
| Sodium Hyposulfite..... | 100 Lbs. | 1.75 @ | 1.85 |
| Sodium Nitrate, 95 per cent, spot..... | 100 Lbs. | 4.70 @ | 4.75 |
| Sodium Silicate, liquid, 40° BÉ..... | 100 Lbs. | 2.00 @ | 2.10 |
| Sodium Sulfide, 60%, crystals, in bbls..... | Lb. | 3 1/4 @ | 4 |
| Sodium Bisulfite, powdered..... | Lb. | 6 1/4 @ | 7 |
| Strontium Nitrate..... | Lb. | 28 @ | 30 |
| Sulfur, flowers, sublimed..... | 100 Lbs. | 4.05 @ | 4.06 |
| Sulfur, roll..... | 100 Lbs. | 3.70 @ | 4.15 |
| Sulfuric Acid, chamber, 66° BÉ..... | Ton | 35.00 @ | 38.00 |
| Sulfuric Acid, oleum (fuming)..... | Ton | 55.00 @ | 60.00 |
| Talc, American white..... | Ton | 15.00 @ | 18.00 |
| Terra Alba, American, No. 1..... | 100 Lbs. | 85 @ | 90 |
| Tin Bichloride, 50°..... | 100 Lbs. | 20.25 @ | 20.75 |
| Tin Oxide..... | Lb. | 68 @ | 68 1/2 |
| White Lead, American, dry..... | Lb. | 9 @ | 9 1/2 |
| Zinc Carbonate..... | Lb. | 35 @ | 36 |
| Zinc Chloride, commercial..... | Lb. | 10 1/2 @ | 11 |
| Zinc Oxide, American process XX..... | Lb. | 14 @ | 15 |

ORGANIC CHEMICALS

| | | | |
|---|------|------|--------|
| Acetanilid, C. P., in bbls..... | Lb. | 70 @ | 75 |
| Acetic Acid, 56 per cent, in bbls..... | Lb. | 11 @ | 11 1/2 |
| Acetic Acid, glae 1, 99 1/2%, in carboys..... | Lb. | 35 @ | 36 |
| Acetone, drums..... | Lb. | 35 @ | 36 |
| Alcohol, denatured, 180 proof..... | Gal. | 82 @ | 84 |

| | | | |
|---|----------|----------|--------|
| Alcohol, sugar cane, 188 proof..... | Gal. | 5.25 @ | 5.40 |
| Alcohol, wood, 95 per cent, refined..... | Gal. | 1.30 @ | 1.35 |
| Amyl Acetate..... | Gal. | 5.25 @ | 5.50 |
| Aniline Oil, drums extra..... | Lb. | 26 @ | 27 |
| Benzoin Acid, ex-toluol..... | Lb. | 2.50 @ | 2.75 |
| Benzol, Pure..... | Gal. | 45 @ | 46 |
| Camphor, refined in bulk, bbls..... | Lb. | 74 1/2 @ | 75 |
| Carbolic Acid, U. S. P., crystals, drums..... | Lb. | 53 @ | 54 |
| Carbon Bisulfide..... | Lb. | 7 1/2 @ | 8 |
| Carbon Tetrachloride, drums, 100 gals..... | Lb. | 16 @ | 16 1/2 |
| Chloroform..... | Lb. | 63 @ | 65 |
| Citric Acid, domestic, crystals..... | Lb. | 72 @ | 75 |
| Cresosol, beechwood..... | Lb. | 1.90 @ | 2.00 |
| Dextrin, U. S. P..... | Lb. | 18 @ | 20 |
| Dextrine, corn (carloads, bags)..... | Lb. | 7 @ | 7 1/8 |
| Dextrine, imported potato..... | Lb. | 18 @ | 20 |
| Ether, U. S. P. 1900..... | Lb. | 31 @ | 39 |
| Formaldehyde, 40 per cent..... | Lb. | 18 1/2 @ | 19 |
| Glycerine, dynamite, drums included..... | Lb. | 69 @ | 70 |
| Oxalic Acid, in casks..... | Lb. | 45 @ | 46 |
| Pyrogallic Acid, resublimed, bulk..... | Lb. | 3.25 @ | 3.50 |
| Salicylic Acid..... | Lb. | 1.30 @ | 1.35 |
| Starch, cassava..... | Lb. | — | |
| Starch, corn (carloads, bags) pearl..... | 100 Lbs. | 6.30 @ | 6.40 |
| Starch, potato..... | Lb. | 13 @ | 14 |
| Starch, rice..... | Lb. | 10 @ | 12 |
| Starch : sago flour..... | Lb. | 6 @ | 6 1/2 |
| Starch, wheat..... | Lb. | 5 3/4 @ | 6 1/2 |
| Tannic Acid, commercial..... | Lb. | 80 @ | 95 |
| Tartaric Acid, crystals..... | Lb. | 78 1/2 @ | 79 |

OILS, WAXES, ETC.

| | | | |
|---|------|----------|-------|
| Beeswax, pure, white..... | Lb. | 54 @ | 60 |
| Black Mineral Oil, 29 gravity..... | Gal. | 13 1/2 @ | 14 |
| Castor Oil, No. 3..... | Lb. | 25 1/2 @ | 26 |
| Ceresin, yellow..... | Lb. | 16 @ | 17 |
| Corn Oil, crude..... | Lb. | — @ | — |
| Cottonseed Oil, crude, f. o. b. mill..... | Gal. | 1.30 @ | 1.35 |
| Cottonseed Oil, p. s. y..... | Lb. | 18 1/2 @ | 19 |
| Menhaden Oil, crude (southern)..... | Gal. | — @ | — |
| Neat's-foot Oil, 20°..... | Gal. | 2.25 @ | 2.30 |
| Paraffin, crude, 118 to 120 m. p..... | Lb. | 8 @ | 8 1/2 |
| Paraffin Oil, high viscosity..... | Gal. | 29 1/2 @ | 30 |
| Rosin, "F" Grade, 280 lbs..... | Bbl. | 6.80 @ | 7.00 |
| Rosin Oil, first run..... | Gal. | 42 @ | 43 |
| Shellac, T. N..... | Lb. | 48 @ | 49 |
| Spermaceti, cake..... | Lb. | 25 @ | |
| Sperm Oil, bleached, winter, 38°..... | Gal. | 1.70 @ | 1.72 |
| Spindle Oil, No. 200..... | Gal. | 24 @ | 25 |
| Stearic Acid, double-pressed..... | Lb. | 23 @ | 24 |
| Tallow, acidless..... | Gal. | 1.55 @ | 1.60 |
| Tar Oil, distilled..... | Gal. | 31 @ | 33 |
| Turpentine, spirits of..... | Gal. | 49 1/2 @ | 50 |

METALS

| | | | |
|----------------------------------|----------|----------|-------|
| Aluminum, No. 1, ingots..... | Lb. | 36 @ | 37 |
| Antimony, ordinary..... | Lb. | 13 1/2 @ | 14 |
| Bismuth, N. Y..... | Lb. | 2.85 @ | 2.90 |
| Copper, electrolytic..... | Lb. | 23 1/2 @ | — |
| Copper, lake..... | Lb. | 23 1/2 @ | — |
| Lead, N. Y..... | Lb. | 6 1/2 @ | 6 1/4 |
| Nickel, electrolytic..... | Lb. | 55 @ | 56 |
| Platinum, refined, soft..... | Oz. | 105.00 @ | |
| Silver..... | Oz. | 85 3/4 @ | 86 |
| Tin, Straits..... | Lb. | 72 @ | 73 |
| Tungsten (WO ₃)..... | Per Unit | 24.00 @ | 26.00 |
| Zinc, N. Y..... | Lb. | 8 @ | 8 1/4 |

FERTILIZER MATERIALS

| | | | |
|--|-----------------|----------|--------|
| Ammonium Sulfate..... | 100 Lbs. | 7.00 @ | — |
| Blood, dried, f. o. b. Chicago..... | Unit | 6.10 @ | 6.15 |
| Bone, 3 and 50, ground, raw..... | Ton | 32.00 @ | 35.00 |
| Calcium Cyanamid..... | Unit of Ammonia | nominal | |
| Calcium Nitrate, Norwegian..... | 100 Lbs. | — @ | |
| Castor Meal..... | Unit | — @ | |
| Fish Scrap, domestic, dried, f. o. b. works..... | Unit | 6.65 @ | 10 |
| Phosphate, acid, 16 per cent..... | Ton | 16.00 @ | 18.00 |
| Phosphate rock, f. o. b. mine: | | | |
| Florida land pebble, 68 per cent..... | Ton | 3.15 @ | 3.25 |
| Tennessee, 78-80 per cent..... | Ton | 5.50 @ | 6.00 |
| Potassium "muriate," basis 80 per cent..... | Ton | 330.00 @ | 350.00 |
| Pyrites, furnace size, imported..... | Unit | nominal | |
| Tankage, high-grade, f. o. b. Chicago..... | Unit | 5.90 @ | 10 |